rity was present (about 7% by v.p.c.). The v.p.c. also showed that no more than 1% of the *exo* isomer was still present.

Method of Deuterium Analysis. Combustion.—A standard type combustion train was assembled which was large enough to handle samples up to 125 mg. The main combustion tube was packed according to the directions outlined by Niederl[30] for combustion of compounds containing carbon, hydrogen, sulfur, and halogen. The water was collected in a modified U-tube immersed in a Dry Ice–acetone bath. After the combustion was completed the tubes were cut from the system with a torch so that the water was completely sealed from any atmospheric moisture.

Dilution of Samples.—If the deuterium content was estimated to be higher than three atom per cent, the sample was diluted with distilled, demineralized water. This was done by transferring the sample by means of micropipet to a pear shaped container of about 1 cc. volume. The dilution was done by weight on an analytical balance. After dilution, the sample was stoppered with a clean, dry rubber serum stopper and rotated for at least 20 hr. to ensure proper mixing.

Calibration Curve for Infrared.—The calibration standards were made up gravimetrically from deuterium oxide and water carefully distilled and demineralized; the maximum range represented was $0.0 \rightarrow 3.3$ atom % deuterium oxide. If more than 1 week lapsed between determinations, a new calibration curve was made; otherwise, at least one point was checked each day.

Determination of Deuterium Oxide Content.—The relative atom per cent of D_2O and H_2O contained in the water mixture after combustion was determined by use of infrared analysis as described by Trenner and co-workers.[31] A single beam Beckman Model IR 2A was used with a specially thermostated Perkin–Elmer microcell, 127–xx18.[32] The temperature was held constant within $\pm 0.1°$. The temperature control is necessary owing to the large temperature coefficient of the absorbance of the O–D

(30) B. Niederl and J. B. Niederl, "Micromethods of Quantitative Organic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1942.

(31) (a) *Perkin–Elmer Instrumental News*, **4**, No. 1 (1952); (b) N. R. Trenner, B. H. Arison, and R. W. Walker, *Appl. Spectry.*, **7**, No. 4 (1953); (c) N. R. Trenner, B. H. Arison, and R. W. Walker, *Anal. Chem.*, **28**, 530 (1956).

(32) "Instruction Manual, Perkin–Elmer Infrared Equipment," Vol. 2, The Perkin–Elmer Corp., Norwalk, Conn., 1952, pp. 5–6.

band at 3.98 μ. The spectrophotometrical measurement of the O–D band is made possible by the magnitude of the shift in wave length of the stretching frequency (2.8 to 3.98 μ). This shift accompanies the substitution of a deuterium atom for one of the hydrogen atoms of water.

The technique employed in the determination was essentially the same as that described by Trenner.[31] The cell was filled by applying gentle suction by means of a standard hypodermic syringe. The cell was placed in the thermostated cell holder and allowed to come to temperature for about 10 min. Good (averaged) I-values were then obtained for the sample (I_x) and standard (I_0); these values were measured on the recorder paper with reference to the dark line. The relative absorbance is simply log I_0/I_x. From these values the per cent D_2O in the sample was determined, reference being made to the calibration curve previously described.

TABLE II

DATA OBTAINED FROM THE ANALYSIS FOR DEUTERIUM CONTENT

	Theoretical[a] atom % D	Corrected atom % D[b]	Found atom % D[c]	Deuterium lost, %
Polar addition				
Norbornyl bromide	9.09		8.24	
Norbornene	10.0	9.06	4.90	46
Cyclopentanedicarboxylic acid	10.0	9.06	4.60	49
Free radical addition				
Norbornyl bromide	9.09		6.28	
Norbornene	10.0	6.91	2.67	61.4
Cyclopentaneedicarboxylic acid	10.0	6.91	0.00	100

[a] Calculated on the basis that one atom of deuterium existed in place of one atom of hydrogen in each compound. [b] Since only 8.24 atom % deuterium (90.6% of the theoretical) had been introduced during the addition to form norbornyl bromide, the corresponding theoretical values for the degradation products required appropriate corrections. [c] Found experimentally by the infrared method described elsewhere in this Experimental section.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE, NEWARK, DEL.]

Deuterium Tracer Studies on the Elimination Reactions of Norbornyl Tosylate and Bromide. XI

BY H. KWART, T. TAKESHITA,[1] AND J. L. NYCE

RECEIVED DECEMBER 11, 1963

The elimination reaction of *exo*-norbornyl tosylate with strong base in tertiary alcohol solvent proceeds with indications of considerable E1 character, yielding only about 18% *cis* elimination product. The same reaction in hydrocarbon solvent medium occurs with a "pure" E2 mechanism and results in about 65% *cis* elimination. Norbornyl bromide appears to undergo *cis* elimination nearly exclusively (98%) *via* a concerted E2 process even in the tertiary alcohol medium, when appropriate correction is made for a deuterium isotope effect. These results are discussed in the light of *cis* and *trans* elimination (E2) requirements recently formulated by DePuy and co-workers. The most attractive interpretation of the E1 elimination pattern, in consonance with recent studies in acyclic systems, appears to justify the assumption of an intimate ion pair intermediate.[29,30]

Introduction

Our present knowledge of the elimination reaction recognizes a spectrum of possibilities lying between the extremes of mechanism. We approach at one end the carbanion (E1CB) mechanism which finds the β-proton bond completely ruptured in the transition state. On the other is located the fully formed carbonium ion (E1) mechanism. The most usual expressions of the E2 mechanism[2] calls for concerted action in which

(1) Fulbright Fellow, 1959–1962, at the University of Delaware.

(2) The terms E1CB, E2, and E1 are defined by C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter 8.

abstraction of the β-proton and separation of the leaving group occur simultaneously. Recent studies, however, have disputed the generality of this picture and indicate that these two steps do not necessarily take place synchronously. Bunnett and co-workers[3] have presented the case of "E2 leaning toward E1."

Investigations seeking to establish the existence of the E1CB mechanism can be grouped in two categories: (1) cases studied in which the *trans* coplanar stereochemical requirement of the E2 mechanism cannot be satisfied,[4–9] and (2) cases studied in which the β-proton

(3) J. F. Bunnett, G. T. Davis, and H. Tanida, *J. Am. Chem. Soc.*, **84**, 1606 (1962).

is one of relatively high acidity,[10-17] such as in β-phenylethyl derivatives. Some correlation of the incidence of *cis* elimination with "carbanion" mechanism has been sought and this has culminated in the recent suggestion by DePuy and co-workers[18] that the maximum elimination rates are observed when the eliminated groups are disposed at the dihedral angles of 0 or 180°; *i.e.*, both *cis and trans coplanar elimination geometry favor the E2 mechanism and not the E1CB* even in cases where the acidity of the β-proton is considerable. A very recent article by LeBel and co-workers[9] discloses that data obtained in studies of E2 elimination in bicyclic (vicinal) dihalides appear to be in agreement with this proposal.

These ideas can now be scrutinized in the light of our results with monosubstituted norbornane derivatives undergoing elimination, where we are not required to consider the influence of a second (β) electronegative center on the course of reaction, as in LeBel's case.[9] Here, again, the important[18] dihedral angle between the eliminated groups is known even in the transition state, a condition imposed by the rigid norbornane ring, and where, furthermore, unusual acidity of the β-proton is not a factor. The particular substances selected for study were 2-*exo-p*-toluenesulfoxy-3-*endo-d*-norbornane (I)[19] and 2-*exo*-bromo-3-*exo-d*-norbornane (II).[19] The elimination of X–Y was accomplished by heating with potassium 3-methyl-3-pentoxide in 3-methyl-3-pentanol (polar) or *p*-cymene(nonpolar) solvent.

I, X = CH₃—$\bigcirc$—SO₃⁻

Y₁ = H, Y₂ = D

IIA, X = Br, Y₁ = D, Y₂ = H, Z = H

IIB, X = Br, Y₁ = H, Y₂ = H, Z = D
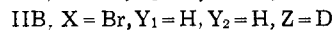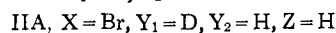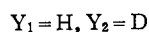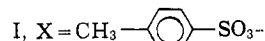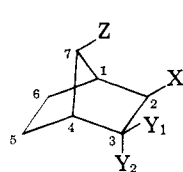
Results

The elimination was carried out by means of a bulky base in order to enforce a preference for *exo*-proton abstraction, the *exo* representing the sterically favored direction along which an external reagent will ordinarily approach[20] the bicyclic nucleus. The norbornene (III) elimination product was examined by means of KMnO₄ oxidation to the *cis*-1,3-cyclopentanedicarboxylic acid (IV). The relative amounts of deuterium in each (I or II and III and IV) were determined by combus-

(4) S. J. Cristol, *J. Am. Chem. Soc.*, **69**, 338 (1947).

(5) S. J. Cristol, N. L. Hause, and J. S. Meek, *ibid.*, **73**, 674 (1951); see also ref. 24.

(6) S. J. Cristol and D. D. Fix, *ibid.*, **75**, 2647 (1953).

(7) S. J. Cristol and E. F. Hoegger, *ibid.*, **79**, 3438 (1957).

(8) (a) F. G. Bordwell and R. J. Kern, *ibid.*, **77**, 1141 (1955); (b) J. Weinstock, R. G. Pearson, and F. G. Bordwell, *ibid.*, **78**, 3468 (1956).

(9) N. A. LeBel, P. D. Beirne, E. R. Karger, J. C. Powers, and P. M. Subramanian, *ibid.*, **85**, 3199 (1963).

(10) P. S. Kell and C. R. Hauser, *ibid.*, **67**, 1661 (1945).

(11) D. G. Hill, B. Stewart, S. W. Kantor, W. A. Judge, and C. R. Hauser, *ibid.*, **76**, 5129 (1954).

(12) E. M. Hodnett and J. J. Flynn, Jr., *ibid.*, **79**, 2300 (1957).

(13) T. J. Hauser, R. B. Bernstein, R. G. Miekka, and J. C. Argus, *ibid.*, **77**, 6201 (1955).

(14) S. I. Miller and W. G. Lee, *ibid.*, **81**, 6313 (1959).

(15) L. E. Erickson and R. A. Alberty, *J. Phys. Chem.*, **63**, 705 (1959).

(16) L. C. Leitch and H. J. Bernstein, *Can. J. Research*, **28B**, 35 (1950).

(17) C. H. DePuy and C. A. Bishop, *J. Am. Chem. Soc.*, **82**, 2532 (1960).

(18) C. H. DePuy, R. D. Thurn, and G. F. Morris, *ibid.*, **84**, 1314 (1962).

(19) (a) The preparations of these compounds are given elsewhere; see H. Kwart and J. L. Nyce, *ibid.*, **86**, 1601 (1964); (b) H. Kwart and T. Takeshita, *J. Org. Chem.*, **28**, 670 (1963).

(20) See L. Kaplan, H. Kwart, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **82**, 2341 (1960), for additional references and discussion of this point.

tion of the appropriate samples to water and analysis for deuterium content of the water by means of infrared measurements.

From Table I we deduce that in the tosylate elimination in the more polar alcoholic solvent more than half of the original deuterium went through to the terminal diacid product IV of the analytical series. No matter which mode of E2 elimination occurred (*cis* or *trans*) all residual deuterium on the vincinal position C-3 should have been lost on oxidation of the norbornene (III) to VI. We, therefore, conclude that some prior ionization of tosylate must have occurred, whereby the E2 mechanism has been modified by considerable E1 character even in the presence of the very strong alkoxide base employed. Apparently, however, the incursion of the E1 on the E2 mechanism occurs to only a very minor extent in the case of the norbornyl bromide under precisely the same reaction conditions.[21] The nature of the leaving group is clearly responsible for the difference noted.

TABLE I

ELIMINATION IN POLAR SOLVENT WITH *t*-HEXOXIDE BASE AT 130°

	Theoretical[a] atom % D	Corrected[b] theoretical atom % D	Atom % D found	% D retained
Tosylate series				
exo-Norbornyl tosylates (I)	5.56	..	4.88	..
Olefin III (norbornene)	10.0	8.78	5.87	66.9
Diacid IV (1,3-*cis*-cyclopentanedicarboxylic acid)	10.0	8.78	4.99	56.8[c]
Bromide series				
exo-Norbornyl bromide (*ca.* 0.5 IIa + 0.5 IIb)[d]				100
Olefin III	..	..	..	54
Diacid IV	..	..	..	51

[a] Based on 1 atom of deuterium per molecule. [b] Maximum % deuterium possible in degraded products based on per cent found in tosylate. [c] Correction for the 5% nortricyclene formed in the elimination reaction and lost in the oxidation gives a corrected value of 9% deuterium lost during oxidation. [d] The deuterated norbornyl bromide was prepared by polar addition of DBr to norbornene and was shown to be deuterated only in the 3- and 7-positions (corresponding to IIa and IIb); see ref. 19 for further analytical details. The 7-deuterionorbornene is deduced from oxidation of the norbornene to the diacid which retains deuterium. No proof is available to say that the label is *not* in the 1-, 4-, 5-, or 6-positions, but our results confirm that it is *not* in the 2- or 3-positions. Consequently, this product represents rearrangement.

In the effort to observe a "pure" E2 elimination result, the reaction was carried out in a nonpolar solvent to suppress transition state ionization as much as possible. The results obtained using the hydrocarbon *p*-cymene as the reaction medium are listed in Table II.

Discussion

E2 Elimination.—Since the principal part of the original C-3 deuterium in I is retained in the nor-

(21) If the addition reaction proceeded with the rearrangement course[19] and if similar rearrangement had occurred (consistent with a possible E1 reaction course), we could have anticipated that olefin III and diacid IV would have *ca.* 75% of the D retained *vs.* the *ca.* 50% observed. For further discussion of this point see considerations given in a later section of this article on the bridged ion pair V.

TABLE II

ELIMINATION IN NONPOLAR SOLVENT WITH t-HEXOXIDE BASE AT 130°

	D atom % theoretical[b]	D atom % found	Corrected[e] theoretical atom% D	%D retained
exo-Norbornyl tosylate[a]	5.56	2.13[c]	..	..
Olefin III	10.0	2.62[d]	3.83	68.5
Diacid IV	10.0	0.0	3.83	0.0

[a] Mixture containing 96.7% 2-exo-norbornyl tosylate and 3.3% 2-endo-norbornyl tosylate. [b] Based on one deuterium atom per molecule. [c] The original 2.2 atom % value has been corrected for 3% of the 7-tosylate which was formed during the preparation and contained the same percentage of deuterium as each of the other isomers. The correction was necessary since the 7-tosylate does not eliminate and yet is lost on dehydrotosylation {2.2 − (0.08 × 0.40 × 2.2)}. [d] The original 2.67 value has been corrected for the 5% of nortricyclene formed during the dehydrotosylation since it is lost in the following oxidation step [2.67 − (0.05 × 0.383 × 2.67)]. [e] This number is the theoretical value (2.13/5.56) × 10 that norbornene and the diacid would have if no deuterium had been lost.

bornene elimination product III and this label is totally lost on oxidation to the terminal diacid IV, we infer that E2 elimination (a presumably pure[3,4] mechanism when the hydrocarbon, p-cymene, medium is used) proceeds through the noncoplanar, *trans* mechanism to the minor extent. This relatively small predominance of the olefin product resulting from the coplanar, *cis* relationship of the eliminated groups in the transition state may be seen in the summary given in Chart A (where the data have been corrected for the presence of small amounts of *endo*-2 and *syn*-7 isomers known to contaminate our preparation of I).

CHART A

TOSYLATE E2 ELIMINATION SUMMARY
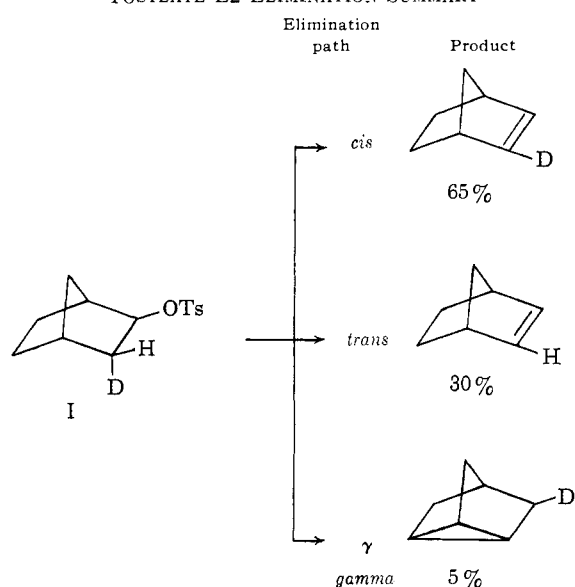
Normally[3] the E2 is regarded as a synchronous mechanism where the β-proton *trans* to the leaving group stretches concomitantly with the loosening of C–X. Even where rotation about C_α–C_β is possible, however, some kinetic evidence has been presented[17] to suggest that the extent of C–H and C–X bonds stretching in the transition state varies with both the leaving group and the base used. The impairment of the synchronous

process[3,4,22] has been advanced as an explanation in cases where *trans* coplanar alignment is not possible or where carbanion character can be stabilized by a β-substituent to an extent that fosters the occurrence of E1CB. These workers[21,22] believe that more than 20° departure from *trans* coplanarity introduces very considerable torsional energy in the elimination transition state. On this basis a prior deprotonation mechanism might be preferred in the 2,3-substituted norbornyl system we have studied (here), where the distortion from coplanarity can amount to 60°. However, in contradiction to this stands the recent work of DePuy[18] and LeBel[9] and their co-workers who have inferred a concerted bimolecular mechanism for such endocyclic olefin formation.

Though a decided preference for *trans* elimination is recognized in acyclic and alicyclic systems, in the rigid bicyclic system under study a number of considerations come to mind which lead us to anticipate in E2 a much greater predominance of *cis* elimination product than is actually observed for I (see Chart A). (1) The known kinetic isotope effect, $k_H/k_D = 8$, observed for t-alcoholate base elimination reactions in appropriately deuterated tosylates,[23a] when extrapolated according to the formula derived by Shiner,[23b] affords some quantitative understanding of the extent to which the *endo*-deuterium atom in I has biased the competition of *cis* and *trans* elimination mechanisms. Thus we have deduced that in I a deuterium isotope effect has increased the favor for *cis* elimination by a factor of about *3.5*.

(2) The requirement of a coplanar transition state has been most recently discussed by DePuy and co-workers[18] and attributed to the nature of the concerted bimolecular reaction. This requirement can be satisfied only in the case of *cis* elimination in I where the dihedral angle is (rigidly) zero. The relative ease of occurrence of *cis* and *trans* eliminations, where they are apparently controlled only by this mechanistic factor, can be evaluated by means of the data of Cristol and Hause[24] taken in the analogous case of 11,12-dichloro-9,10-ethanoanthracene. Consequently, we deduce the *cis* elimination reaction in I will take place *eight* times more readily than the *trans* due to the greater ease with which the transition state coplanar requirement may be fulfilled.

(3) Another rate-determining factor prevailing in the E2 t-alkoxide base elimination reactions of the bicyclo-[2.2.1]heptane system is the inherently greater facility for *exo* over *endo* deprotonation.[9,20] A crude indication of the magnitude of this rate factor may be gleaned by comparing the results of LeBel and co-workers[9] on dihalonorbornanes, where an *exo* preference is clearly operating, with those of Cristol and Hause[24] observed for the ethanoanthracene analogs where this factor does not exist (both sets of results extrapolated to our 130° reaction temperature). We can thus estimate that *cis* elimination is favored over the *trans* process which is handicapped by the necessity of *endo* proton abstraction by a factor of about *three*.

These considerations (above) suggest that, on the basis of prior studies[7,9,18,24] of HX elimination with

(22) (a) D. V. Banthorpe, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 4054 (1960); (b) E. D. Hughes and J. C. Maynard, *ibid.*, 4087 (1960).
(23) (a) W. H. Saunders and D. H. Edison, *J. Am. Chem. Soc.*, 82, 138 (1960); (b) V. J. Shiner, Jr., *ibid.*, 76, 1603 (1954).
(24) S. J. Cristol and N. L. Hause, *ibid.*, 74, 2193 (1952).

alkoxide base from bicyclic *vicinal* dihalides, a value of $k_{cis}/k_{trans} \cong 84$ for elimination in I could have been anticipated. We observe instead (Chart A) a value of $k_{cis}/k_{trans} \cong 2.3$ and must seek therefore to account for the unexpected *36-fold* increase in the facility for *trans* elimination here.

The extent of E2 *cis* elimination occurring in norbornyl bromide in polar solvent is considerably greater than for the norbornyl tosylate in the nonpolar medium. The results, corrected for the 7-deuterio content of the substrate,[19] are summarized below (see Chart B). Here the *exo*-deuterium atom in II is seen to improve the chances for occurrence of the *trans* elimination process. Thus, when the kinetic isotope correction[23] is applied

CHART B

BROMIDE E2 ELIMINATION SUMMARY
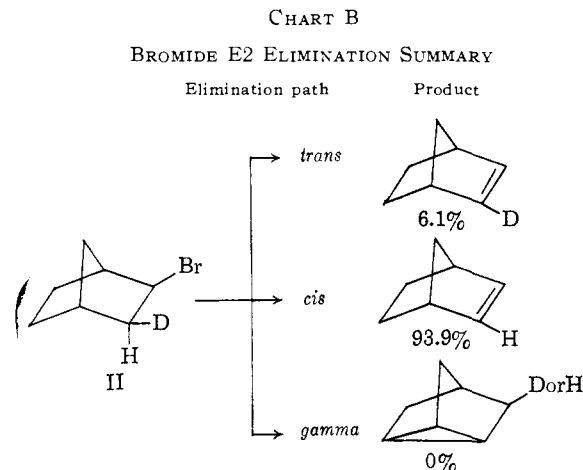
to the data in Chart B the preference for *cis* elimination is even greater, *ca.* 98%, and we may estimate the value $k_{cis}/k_{trans} \cong 49$. The enhancement of the *cis* elimination process accompanying the change of leaving group from tosylate to bromide is very evident.

This vast difference in preference for the *cis* elimination path demonstrated by corresponding bicyclic bromide and tosylate derivatives has a parallel in many previous studies[25,26] of elimination in acyclic and alicyclic substrates. In such cases it has been claimed[7,23a] that the nature of the transition state in E2 is extensively altered with a change in the leaving group and the reagent base. A number of proposals have been ventured to explain this variety of transition states. On the one hand DePuy and Bishop[17] have explained the differences as a matter of the timing of bond making and bond breaking steps and the consequent variation in the distribution of negative charge in the substrate between the β-carbon and the leaving group. In their view, the tosylate reaction possesses the less synchronous transition state and a great many observations of rate changes influenced by polar substituents[7] and deuterium isotope substitution[23a] seem to be in accord with this suggestion.

On the other hand, Brown and Wheeler[26] have identified steric shielding by the leaving group as the factor accounting for their observation that the formation of E2 elimination product occurs much less readily in the case of tosylate than of bromide. They have emphasized that the direction of elimination correlates with the steric requirements of the leaving group rather

than the charge character of the leaving group or charge distribution in the activated state.

In the rigid bicyclic system, by means of which we have here (again) compared tosylate and bromide in E2 elimination, the stereochemical factors are somewhat more easily perceived. As noted above, previous information and general knowledge of the salient rate-controlling features permitted us to anticipate a ratio of $k_{cis}/k_{trans} \cong 84$, attributing no particular role to the leaving group in controlling the rate or steric course of elimination in this system. We can now identify the bromide elimination as nearly normal and roughly in line ($k_{cis}/k_{trans} \cong 49$) with expectation based on these considerations[27] while the tosylate elimination ($k_{cis}/k_{trans} \cong 2.3$) develops the appearance of abnormality. Furthermore the tosylate manifests even greater departure from normalcy when we recall its enhanced proclivity for undergoing the E1 elimination in alcoholic media where bromide experiences E2 (see next section for further discussion of this point). Only when the ionization of the carbon–tosylate bond has been properly suppressed by use of a sufficiently low dielectric medium do we observe an E2 reaction pattern that can be compared to the bromide reaction in alcoholic media. It is possible that some of the observations of differences between corresponding bromides and tosylates in their response of polar rate influences in elimination may have been due to the unsuspected incursion of E1 character in the tosylate reaction.[7] Many demonstrations of this complicating factor in studies of the elimination reaction have been discussed in both the recent[4] and early literature.[3,21,22]

In the present instance we prefer to believe that, through appropriate variation in experimental conditions, E2 elimination has been achieved with tosylate and bromide derivatives, wherein we have realized comparable degrees of concertedness in their respective activated complexes. Thus it is possible to undertake a comparison of the stereochemical courses of these reactions without great concern for the influence of such factors as transition state charge distribution.[7] Under such circumstances we might expect that the removal of the 3-*exo* proton for *cis* elimination in the 2-norbornyl tosylate would be considerably more obstructed than in the corresponding bromide. A full exposition of this argument has been presented and justified by Brown and Wheeler[26] and requires no further elaboration. The logical test of this explanation for the diminished extent of *cis* elimination in the *exo*-norbornyl tosylate, namely by carrying out the analogous reaction in the *endo*-norbornyl case, is awaiting experimental study in these laboratories.

Furthermore, the occurrence of a small amount (*ca.* 5%) of nortricyclene in the E2 dehydrotosylation product, which is absent in the corresponding dehydrobromination product, might also be construed to support the steric shielding interpretation considered above. Thus, where the tosylate affords excessive interference with the preferred abstraction of the *cis-3-exo* proton,

(25) D. J. Cram, F. D. Greene, and C. H. DePuy, *J. Am. Chem. Soc.*, **78**, 790 (1956).

(26) H. C. Brown and H. Wheeler, *ibid.*, **78**, 2119 (1956).

(27) It will be noted that the ratio $k_{cis}/k_{trans} \cong 84$ for tosylate elimination was deduced as the total rate influence of three factors: a deuterium isotope effect in I possessing an *endo*-D atom and thereby favoring *cis-exo* elimination, and two other factors (*vide supra*). In the case of the bromide II a deuterium isotope effect due to the presence here of an *exo*-D will retard *cis-exo* elimination and our experimental value $k_{cis}/k_{trans} \cong 49$ has already been corrected for this factor. Consequently, the "deduced" ratio that applies for comparison with experimental in II is $k_{cis}/k_{trans} \cong 84/3.5 \cong 24$.

some competing γ-elimination takes place, such as is regularly observed in reactions where strong base is used.[28] The lack of a competing γ-elimination process in II can then be correlated with the fact that the approaching base encounters less interference from the cis-vic-bromine atom than from tosylate.

Further consideration of the possible origins of the observed cis elimination pattern will be given in the ensuing section of this report.

The E-1 Elimination.—The emergence of an E1 elimination mechanism when the tosylate I was subjected to strong base in alcoholic solvent was not entirely unexpected in view of the great ease of solvolysis of tosylate in hydroxylic media. The change from a cis to a trans course of elimination that accompanys the change from E2 → E1 is noteworthy. The E1 elimination results corrected for the presence of small amounts of isomers present in I are summarized in Chart C.

CHART C
TOSYLATE E1 ELIMINATION SUMMARY
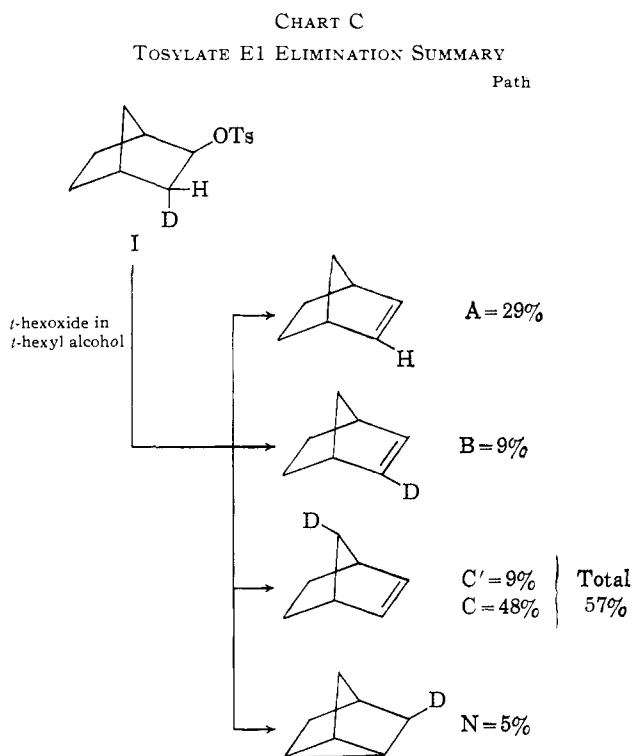
We deemed it unnecessary to correct these results for a kinetic isotope effect on the assumption that the proton abstraction in E1 does not enter into the rate-determining step. We assume, also, that under these circumstances the preference for exo-base attack disappears, since the energetic requirement is much smaller where the product-determining event does not occur in the transition state. The exo proton is less accessible, possibly owing to greater solvation of that side of the bridged carbonium ion intermediate (or its equivalent) and, consequently, we appear to observe even less cis elimination here than in E2 elimination.

A number of reports in the very recent literature have presented evidence indicating that the composition of the E1 product is strongly dependent on the nature of both the leaving group and the solvent. Cram and

Sahyun[29a] and Winstein and Cocivera[29b,c] have emphasized the intimate ion pair character of the intermediate in the E1 elimination reaction and the great importance of the nature of the counter ion and its possible assistance to the proton abstraction process that occurs in the product forming step. Skell and Hall[30] have stressed their deduction that the departing tosylate anion is still intimately associated with the same face of the original (reactant) 2-butyl ester at the instant of product formation. These authors have also urged that the occurrence of a cis elimination product is to be correlated with abstraction of the β-proton by the counter ion.

Our results on elimination in the bicyclic system also demonstrate that the product composition is dependent on the nature of both leaving group and solvent but in a way which is somewhat different from that which could have been expected on the basis of the proposals of Skell and Hall.[30] First we note that solvent can effect some discrimination as to reaction mechanism (E1 or E2) through its ability to ionize a leaving group; the greater ease of ionization (with hydroxylic solvent) of the tosylate creates E1 character for this substrate's reaction where the corresponding bromide gives evidence under these reaction conditions only of the concerted E2 mechanism. If the nearly exclusive cis elimination course observed for the bromide were due in any way to an E1 mechanism involving participation of the departing bromide in the proton abstraction step, as suggested,[29b,30] we could have expected that the symmetrical bridged ion pair intermediate V would have afforded an equivalent amount of cis $D^\ominus$ and $H^\oplus$ abstraction (as shown below).
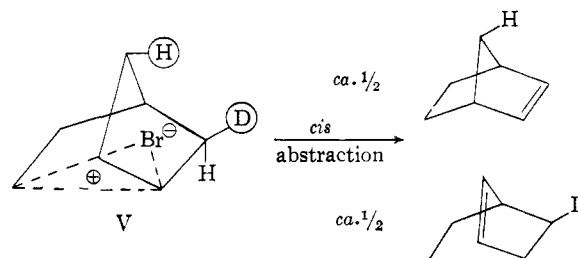
Since this expectation is obviously not consistent with our data, further confidence is engendered in the alternative E2 mechanism which does fit the observed course of the elimination reaction with exo-norbornyl bromide. On the other hand, the simplest and most attractive interpretation of our results for the same reaction of tosylate in hydroxylic media does appear to fall in line with an E1 elimination mechanism proceeding via a symmetrical bridged ion pair intermediate (VI). The cis elimination product can be readily

VI
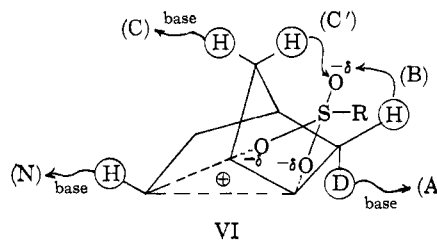
(28) (a) F. C. Whitmore, A. H. Popkin, H. I. Berstein, and J. P. Wilkins, J. Am. Chem. Soc., **63**, 124 (1941); (b) P. S. Skell and A. P. Kapacho, ibid., **83**, 754 (1961); (c) L. Friedman and J. G. Berger, ibid., **83**, 492 (1961); (d) P. W. Kirmse and W. von E. Doering. Tetrahedron, **1**, 266 (1960).

(29) (a) D. J. Cram and M. R. V. Sahyun, J. Am. Chem. Soc., **85**, 1257 (1963); (b) S. Winstein and M. Cocivera, ibid., **85**, 1702 (1963); (c) S. Winstein, et al., Chem. Ind. (London), 664 (1954); J. Am. Chem. Soc., **78**, 328 (1956).

(30) P. S. Skell and W. L. Hall, ibid., **85**, 2851 (1963).

visualized (in consonance with recent proposals[30]) to have taken place through proton abstraction by the tosylate counter ion and comprises (only) about 18% as the sum of the B and C' paths shown in VI. Although these paths are identical in the symmetrical ion pair, the presence of the deuterium label which distinguishes path (B) permits us therefore to assign the same weight to (C'), whose product is otherwise indistinguishable from (C).

trans-Proton abstraction by base is represented in VI by the competition of paths (C) and (A). Again, in the (truly) symmetrical ion pair these paths would be identical, but the deuterium isotope effect which results in somewhat greater difficulty for path A may be estimated to be less than a factor of *two* (roughly (C)/(A) = 48/29). Considering the relatively high temperature (130°) and the fact that this step is not rate determining, this small magnitude of the deuterium isotope effect seems to be very reasonable (see also reference 4).

It seems noteworthy, too, that path (N) in the E1 reaction produces an amount of nortricyclenic material identical with that formed in E2 dehydrotosylation, but is completely absent in the dehydrobromination. This would imply once again[29a] that differences in steric shielding, arising from structural features of the leaving group and (to a first approximation) apparently unrelated to electronic features of the elimination mechanism, can be of significance in the product-forming steps, presumably by exerting a regulatory influence over the access routes to proton abstraction. This conclusion, it must be pointed out, is at variance with expectation based on the classical picture of the E1 mechanism formulated by Hughes and Ingold.[31] In their original proposals these authors claimed that the departing group exerted little influence on the fate of the carbonium ion formed in the E1 transition state.

It would be very interesting to learn how much *cis*-E1 elimination occurs with *exo*-norbornyl tosylate in the absence of external base, which seems to be responsible for the competing product-forming paths (A), (C), and (N). Experiments devised to obtain this information are presently in progress in these laboratories.

Experimental

Method of Deuterium Analysis.—The procedures employed here, together with suitable references to the background literature, have been discussed in earlier articles.[19]

General Experimental Details Regarding Preparation and Elimination of Tosylate.—In a particular case, studying the elimination reaction in *p*-cymene solvent, a sample of norbornene oxide[19b] was reduced with lithium aluminum deuteride and the

(31) E. D. Hughes, C. K. Ingold, and U. G. Shapiro, *J. Chem. Soc.*, 1277 (1937); K. A. Cooper, E. D. Hughes, and C. K. Ingold, *ibid.*, 1280 (1937); E. D. Hughes and B. J. MacNulty, *ibid.*, 1283 (1937); K. S. Cooper, E. D. Hughes, C. K. Ingold, and B. J. MacNulty, *ibid.*, 2038 (1940).

resultant alcohol mixture converted to the tosylate. This product consisted of 16% 7-tosylate, 6% 2-*endo*-tosylate, and 78% 2-*exo*-tosylate.[19b] The total was diluted in half by nondeuterated 2-*exo*-tosylate so that the actual percentage of the 7- and 2-*endo*-tosylates became 8 and 3%, respectively. The 7-tosylate is lost completely on dehydrotosylation, so the experimental deuterium content must be corrected for as shown in Table II, footnote *c*.

During elimination about 5% of nortricyclene is formed, necessitating another correction, since the nortricyclene does not oxidize to the diacid (see footnote 4 in Table I). It is realized that these corrections are somewhat approximate, but owing to their small magnitude more elaborate calculations hardly seem justified.

Ignoring the presence of the *endo*-tosylate (3%), it is clear that the percentage of deuterated norbornene (68.5%) is actually a measure of the amount of *cis*-dehydrotosylation. The fact that all the deuterium is lost on oxidation to the diacid indicates that no rearrangement took place.

Since the *endo*-tosylate (3%) was ignored (and in light of the other corrections applied) a quite generous estimate of the error in the amount of *cis* elimination would be ±10%, giving a range in *cis/trans* elimination of 1.4 to 3.7. For the purposes of this paper this range is regarded as quite sufficient. Similar considerations were applied in the dehydrotosylation carried out in alcoholic solvent (Table I).

Dehydrotosylation of 2-*exo*-Norbornyl Tosylate-3-*endo*-d with Potassium 3-Methyl-3-pentoxide in 3-Methyl-3-pentanol.—The tosylate obtained was immediately used for the elimination reaction. To 150 g. of 3-methyl 3-pentanol in which 10 g. (0.25 g.-atom) of potassium was dissolved was added 25.5 g. (0.096 mole) of deuteriotosylate. The reaction immediately took place when heated to 130°, precipitating a voluminous quantity of the potassium *p*-toluenesulfonate. After heating 24 hr., the norbornene was distilled out of the reaction mixture together with some solvent. The portion boiling up to 120° was collected. After three distillations, the fraction from 90 to 100° amounted to 10.2 g. To remove the alcohol, this portion was repeatedly distilled over sodium. The solid norbornene fraction boiled at 85–92°, 4.8 g. (yield 53.3%). The middle cut was used for deuterium analysis. **Dehydrobromination of II** was carried out in a manner quite analogous to the above reaction and has been described in detail elsewhere.[19a]

Dehydrotosylation of 2-*exo*-Norbornyl Tosylate-3-*endo*-d with Potassium 3-Methyl-3-pentoxide in *p*-Cymene.—To 40 g. (0.38 mole) of 3-methyl 3-pentanol in 110 g. of *p*-cymene (distilled over potassium) was added 10 g. of potassium metal (0.25 g.-atom). The reaction mixture was heated to 130° while stirring until all the potassium dissolved to give a clear solution, which became jelly-like on cooling. To this mixture was added 26.5 g. (0.1 mole) of deuterated norbornyl tosylate (I) before heating and stirring at 130° was resumed. After heating at this temperature for 24 hr., the norbornene was distilled out of the reaction along with the solvent. The first distillation gave 117.2 g. of a fraction boiling from 105–115°. The distillate was redistilled and the portion coming over up to 120° was treated with metallic potassium to remove the alcohol, and distilled again to collect a major cut boiling from 87 to 92°. The yield was 5.5 g. (58.5%). The analytical sample was obtained after two more distillations over potassium.

Oxidation of norbornene (III) to diacid IV was carried out by a procedure developed by Birch, Oldham, and Johnson.[32] The analytical sample was recrystallized from water and vacuum sublimed.

(32) S. F. Birch, W. J. Oldham, and E. A. Johnson, *ibid.*, 818 (1947).