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(24) This type of hemiacetal structure has ample precedent in the literature; e.g., 1,2,4,5-benzenetetracarboxaldehyde exists as the bishemiacetal, from which the tetraaldehyde can be obtained by heating: M. Kerfanto and N. Soyer, *C. R. Acad. Sci., Ser. C*, **264**, 1072 (1967).
(25) O. Isler, H. Gutmann, M. Montavon, R. Rüegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta*, **40**, 1242 (1957).
(26) See P. J. Garratt and K. Grohmann in Houben-Weyl, "Methoden der Organischen Chemie", Vol. V, Part 1d, Georg Thieme Verlag, Stuttgart, 1972, pp 533–535.
(27) R. T. Weavers and F. Sondheimer, *Angew. Chem.*, **86**, 165 (1974).
(28) I. C. Calder, Y. Gaoni, P. J. Garratt, and F. Sondheimer, *J. Am. Chem. Soc.*, **90**, 4954 (1968).
(29) F. Sondheimer and D. A. Ben-Efraim, *J. Am. Chem. Soc.*, **85**, 52 (1963).
(30) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).
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Solvolysis of Deuterium-Labeled β-(*syn*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonates. Multiple Cation Automerizations in Tight Ion Pairs[1]

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Abstract: The brosylates of α,α-$^2H_2$-, β,β-$^2H_2$-, and α,α,β,β-$^2H_4$-β-(*syn*-7-norbornenyl)ethanol have been prepared and solvolyzed at 25 °C in buffered acetic acid, in buffered formic acid, and in buffered 90% acetone–water. The deuterated *exo*-2-brendyl and *exo*-4-brexyl derivatives produced in each case after a single hydrogen or deuterium shift have been converted to deuterated brendan-2-one and brexan-4-one mixtures and the position of the deuterium labels in each ketone determined mass spectrometrically. Comparison of the deuterium content of the brexan-4-one both before and after base-catalyzed exchange with protium permits analysis of the fractions of solvolysis product derived from each recognizably discrete rearranged cation. From these results it is clear that some hydrogen or deuterium migration occurs from each methylenic carbon of the starting brosylate and that 10–19% of those migrations are preceded by at least one Wagner–Meerwein automerization. A similar analysis of the products from the formolysis of internally returned $^2H_2$-*exo*-2-brendyl brosylate, isolated originally from the acetolysis of α,α-$^2H_2$-β-(*syn*-7-norbornenyl)ethyl brosylate, confirms that the hydrogen or deuterium shift that converts an initial 2-brexyl cation into a product-producing, rearranged cation is irreversible under solvolysis conditions and implies that all carbon and/or hydrogen or deuterium shifts occur within the initially formed ion pair. It is suggested that the observed effect of the different solvents on the product distribution is due in part to ion pairing which affects the rate of transformations that change the net charge separation in the initial intermediate. The possible structure of the 2-brexyl cation is considered, and it is demonstrated by means of equivalent kinetic models that a choice between the classical (C_2) and nonclassical (C_s) structures cannot be made on the basis of our deuterium scrambling analysis since it does not discriminate between 8,8- and 9,9-dideuterated brexyl derivatives.

The acetolysis of β-(*syn*-7-norbornenyl)ethyl *p*-bromobenzenesulfonate (**1**-OBs) is accelerated by π-electron participation[2] and yields, in addition to some deltacyclane (**2**), a 1.1 to 1.0 mixture of *exo*-2-brendyl and *exo*-4-brexyl acetates, **3**- and **4**-OAc, respectively.[2,3] No 2-brexyl acetate (**5**-OAc) can be detected. The acetolysis is accompanied by extensive ion pair return to *exo*-2-brendyl brosylate (**3**-OBs) and probably to the kinetically undetectable[2,4] *exo*-4-brexyl isomer (**4**-OBs) as well. The less reactive[4] 2-brexyl brosylate (**5**-OBs) has not been detected. When solvolyzed separately both **3**- and **4**-OBs produce mixtures of **2**, **3**-OAc, and **4**-OAc which are similar to the ultimate acetolysis mixture from **1**-OBs.[2,4]

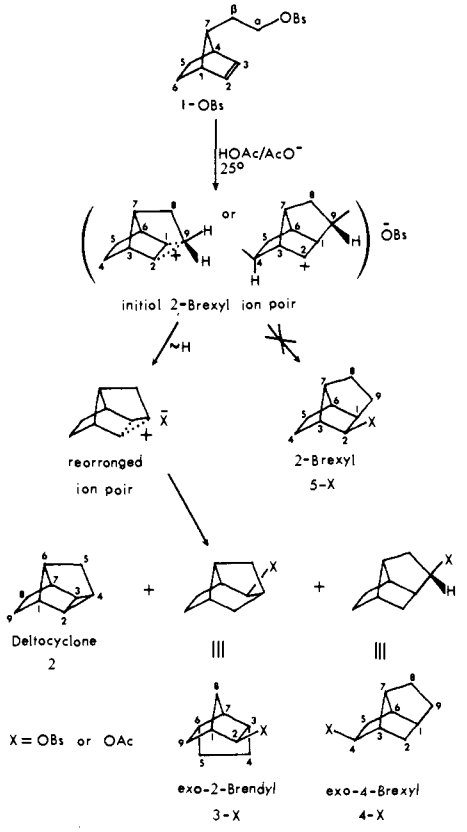
The most concise interpretation clearly consistent with these data is that of an initially formed 2-brexyl ion pair, R^+OBs^-, being converted by a hydrogen shift directly to the product-forming intermediate, a rearranged cation or ion pair[5] (Scheme I).

The actual situation, however, may be much more complex for studies utilizing only nonlabeled starting material leave important questions unanswered. Is the initial 2-brexyl cation, R^+, charge delocalized? Does this potentially 20-fold degenerate cation[7] undergo one or more Wagner–Meerwein automerizations prior to hydrogen migration? What is the provenance of the migrating hydrogen? Is the hydrogen migration reversible? And finally, how important is ion pairing in the overall solvolytic process?

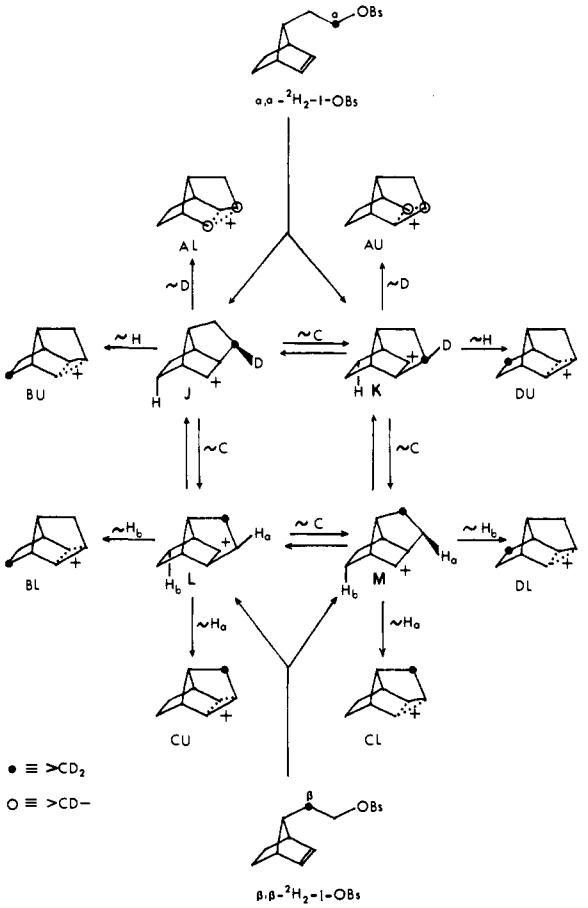
The use of specifically labeled starting material would permit these aspects of the solvolysis to be investigated. By analogy with its unlabeled counterpart, a β-(*syn*-7-norbornenyl)ethyl brosylate (**1**-OBs) having a *gem*-dideuterio label at C-α, C-β, C-5, or C-6 will generate one or more of the four possible classical (C_2) or nonclassical (C_s) 2-brexyl cations shown in Schemes II and III, respectively. The shift of one or the other of two symmetrically situated hydrogens and/or deuteriums will convert each of these "initial" cations into one or two of the four isotopically diastereomeric "rearranged" (4-brexyl) cations depited in Scheme IV.[9] Nucleophilic solvent attack on each of these "rearranged" cations will produce a single pair of specifically deuterated *exo*-2-brendyl ($^2H_2$-**3**-OS) and *exo*-4-brexyl ($^2H_2$-**4**-OS) isomers; cf. Scheme IV. The analogous possibilities in the case of a vicinal, bis-gem-dideuterated starting material are outlined in Schemes V–VII.

Obviously a knowledge of the product mixtures resulting from the solvolyses of α,α-$^2H_2$-, β,β-$^2H_2$-, and α,α,β,β-$^2H_4$-β-(*syn*-7-norbornenyl)ethyl brosylates would permit us to answer some of the questions which we had previously been unable to consider. In this paper we report the preparation,

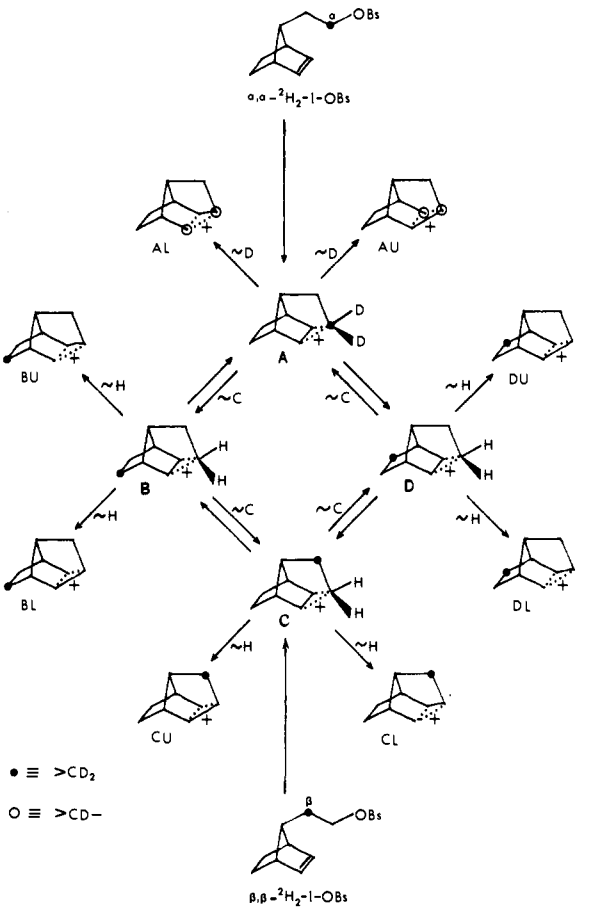
Scheme I. Acetolysis of Nonlabeled β-(*syn*-7-Norbornenyl)ethyl Brosylate[5,6]



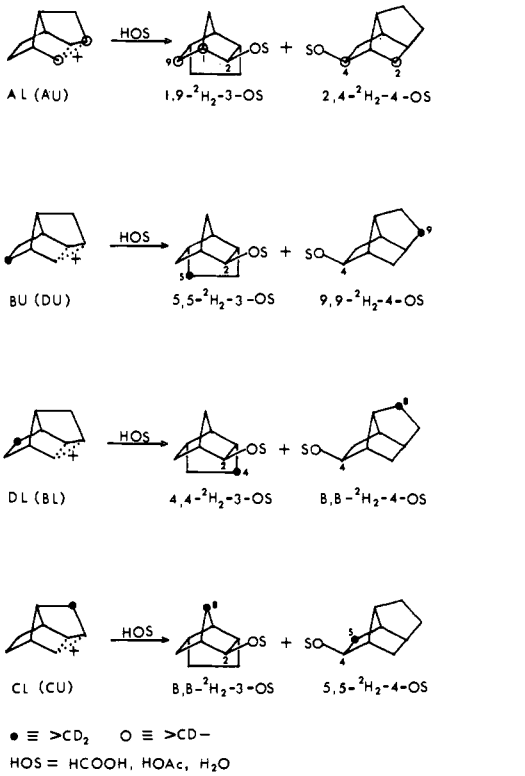
Scheme II. Possible Classical (C_2) 2-Brexyl Cations from the Solvolysis of *gem*-Dideuterio-β-(*syn*-7-norbornenyl)ethyl Brosylates[5]



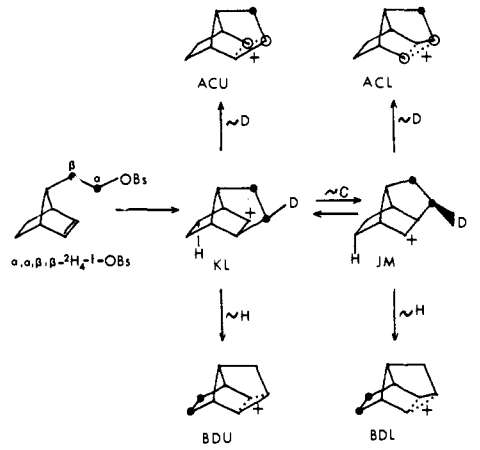
Scheme III. Possible Nonclassical (C_s) 2-Brexyl Cations from the Solvolysis of *gem*-Dideuterio-β-(*syn*-7-norbornenyl)ethyl Brosylates[5]



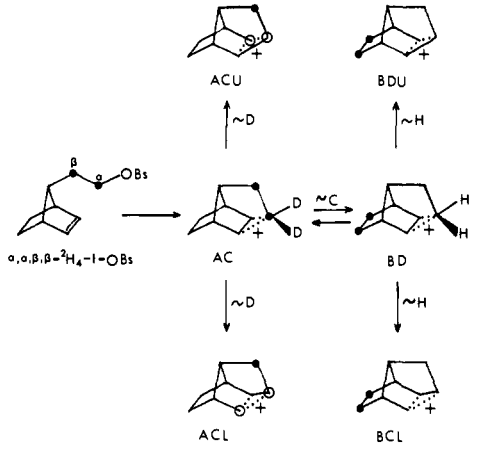
Scheme IV. Possible "Rearranged Cations" and Products from the Solvolysis of *gem*-Dideuterio-β-(*syn*-7-norbornenyl)ethyl Brosylates[5,6,9]



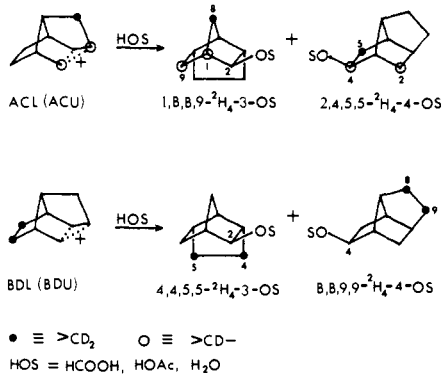
Scheme V. Possible Classical (C_2) 2-Brexyl Cations from the Solvolysis of a Vicinal, Bis-gem-dideuterated β-(*syn*-7-Norbornenyl)ethyl Brosylate[5]



Scheme VI. Possible Nonclassical (C_s) 2-Brexyl Cations from the Solvolysis of a Vicinal, Bis-gem-dideuterated β-(*syn*-7-Norbornenyl)-ethyl Brosylate[5]



Scheme VII. Possible "Rearranged Cations" and Products from the Solvolysis of Vicinal, Bis-*gem*-dideuterio-β-(*syn*-7-norbornenyl)ethyl Brosylates[5,6,9]



solvolysis, and partial product analysis of these specifically labeled brosylates.

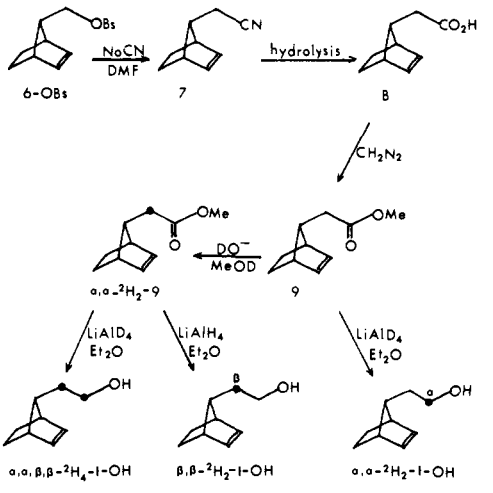
Methods and Results

Synthesis and Solvolysis. The labeled alcohols were prepared from the known *syn*-7-norbornenylcarbinyl brosylate (**6**-OBs).[10] A small portion of each alcohol was converted to the corresponding trimethylsilyl ether (**1**-OSiMe$_3$) for mass spectral assay of its deuterium content—the remainder was used to prepare the brosylate (**1**-OBs). Each brosylate was solvolyzed at 25 °C in dilute solutions of buffered formic acid, buffered acetic acid, and buffered aqueous acetone.

Table I. Observed Product Distributions and Origins from the Solvolysis of Di- and Tetradeuterated β-(*syn*-7-Norbornenyl)ethyl Brosylates

Starting material[a]	Solvent[b]	Percent of total products		
		AL and AU[c]	BL, BU, DL, and DU[d]	CL and CU[e]
α,α-$^2H_2$-**1**-OBs	HCOOH	45	36	19
	H_2O/Me_2CO	58	30	12
	HOAc[f]	66	23	11
β,β-$^2H_2$-**1**-OBs	HCOOH	10	34	56
	H_2O/Me_2CO	10	24	66
	HOAc[g]	8	21	71
		ACL and ACU[h]	BDL and BDU[i]	
α,α,β,β-$^2H_4$-**1**-OBs	HCOOH	53	47	
	H_2O/Me_2CO	65	35	
	HOAc	70	30	

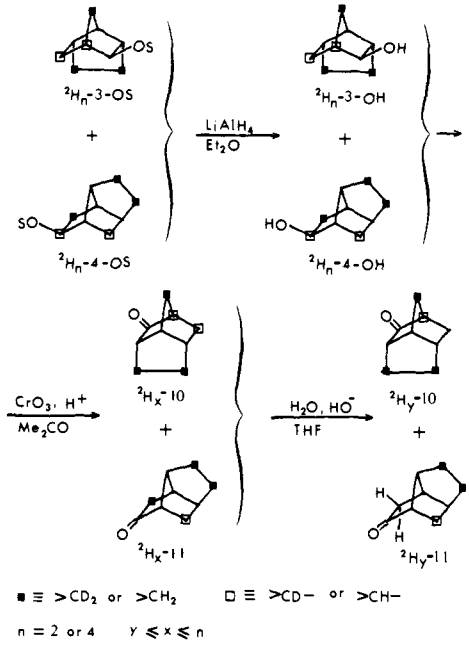
[a] For deuterium analyses of individual samples see Table III. [b] Buffered, 25 °C, >10 half-lives. [c] (% d_2 in the starting material − % d_2 in **11** before exchange)/(% d_2 in the starting material); products consist predominantly of 1,9-$^2H_2$-**3**-OS and 2,4-$^2H_2$-**4**-OS. [d] (% d_2 of **11** after exchange)/(% d_2 of starting material); products consist predominantly of 4,4- and 5,5-$^2H_2$-**3**-OS as well as 8,8- and 9,9-$^2H_2$-**4**-OS. [e] (% d_2 of **11** before exchange − % d_2 of **11** after exchange)/(% d_2 of starting material); products consist predominantly of 8,8-$^2H_2$-**3**-OS and 5,5-$^2H_2$-**4**-OS. [f] Runs 8 and 9 only. [g] Run 18 only. [h] (% d_4 of starting material − % d_4 of **11**)/(% d_4 of starting material); products consist of 1,8,8,9-$^2H_4$-**3**-OS and 2,4,5,5-$^2H_4$-**4**-OS. [i] (% d_4 of **11**)/(% d_4 of starting material); products consist of 4,4,5,5-$^2H_4$-**3**-OS and 8,8,9,9-$^2H_4$-**4**-OS.



Product Analysis. The deuterium distribution in the solvolysis product mixtures was assayed as follows. The isotopically labeled *exo*-2-brendyl and *exo*-4-brexyl products from each solvolysis were separated gas chromatographically from solvent and deltacyclane,[11] reduced with hydride and/or oxidized with chromic acid. This procedure converts 2,4-$^2H_2$-**3**-OS to 4-$^2H_1$-brendan-2-one (4-$^2H_1$-**10**) but transforms all

the other dideuterated brendyl and brexyl products (Scheme IV) to the corresponding brendan-2-one ($^2H_2$-**10**) or brexan-4-one ($^2H_2$-**11**), respectively, without significant loss of deuterium; cf. Experimental Section. A portion of the resulting ketone mixture was separated gas chromatographically into isomerically deuterated mixtures of brendan-2-one: 1,9-; 4,4-; 5,5-; and 8,8-$^2H_2$-**10**, designated ^2H_x-**10** for convenience, and brexan-4-one: 2-$^2H_1$- and 5,5-; 8,8- and 9,9-$^2H_2$-**11**, designated ^2H_x-**11**. The deuterium content of the separated ketones, ^2H_x-**10** and ^2H_x-**11**, was determined mass spectrometrically.

The remainder of each ketone mixture (i.e., ^2H_x-**10** + ^2H_x-**11**) was equilibrated in excess basic, aqueous tetrahydrofuran at ~65 °C for ~4 days, a procedure sufficient to convert 5,5-$^2H_2$-**11** to 5,5-$^1H_2$-**11** without homoenolate exchange.[12] The resulting partially deuterated brexan-4-one



mixture: $^2H_0$-, 4-$^2H_1$-, 8,8-$^2H_2$-, and 9,9-$^2H_2$-**11** (^2H_y-**11** for short) was separated gas chromatographically from the isomerically deuterated brendanones, ^2H_y-**10**, and the deuterium content was determined as before; cf. Table III. The deuterium content of the tetradeuterated solvolysis products was determined in a similar manner except that the now superfluous final equilibration step was omitted. Unfortunately this method of deuterium assay does not permit a separate estimate of the amount of deuterium at the 8,8 or 9,9 position of **11** and hence of the relative amount of the two brexyl solvolysis products 8,8- and 9,9-$^2H_2$-**4**-OS.

To minimize possible interpretive problems posed by incomplete deuteration of the starting material, deltacyclane formation and cleavage, and/or incomplete exchange during equilibration (cf. Experimental Section), the rounded, normalized product distributions and origins (Table I) were computed exclusively from the % d_2 values (Table III).

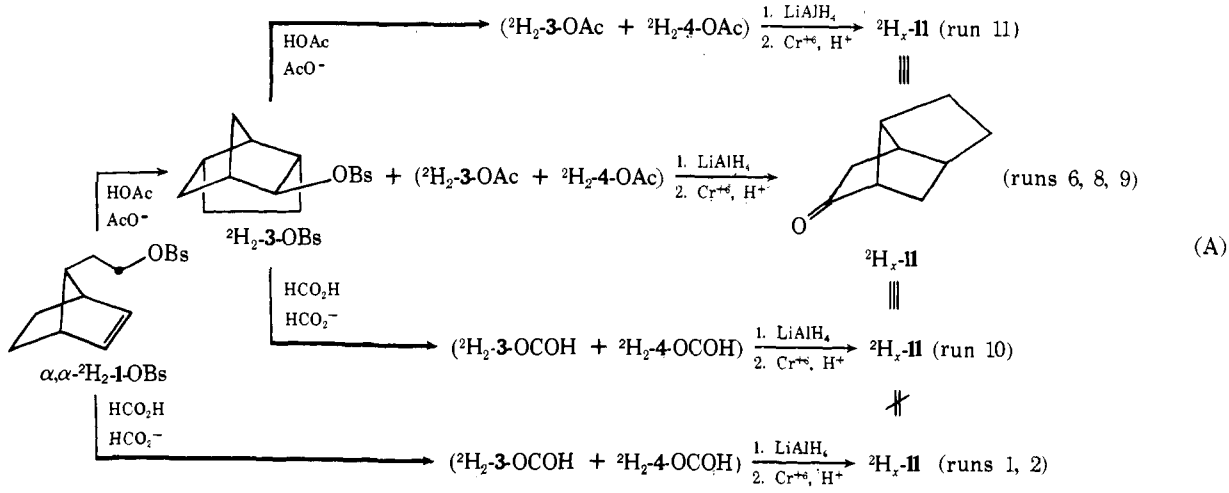
Formolysis of Returned Brosylate. To investigate the reversibility of the hydrogen (deuterium) shift, internally returned $^2H_2$-*exo*-2-brendyl brosylate ($^2H_2$-**3**-OBs) from the *acetolysis* of α,α-$^2H_2$-β-(*syn*-7-norbornenyl)ethyl brosylate (α,α-$^2H_2$-**1**-OBs) was isolated and subjected to *formolysis*. The nonexchanged brexan-4-one (^2H_x-**11**) derived from this *formolysis* has the same deuterium content as that from the acetolysis of both α,α-$^2H_2$-**1**-OBs and $^2H_2$-**3**-OBs (cf. Table III, runs 6 and 8–11). Brexan-4-one derived from the *formolysis* of α,α-$^2H_2$-**1**-OBs has a distinctly different deuterium content (Table III, runs 1–2). Had the initial 2-brexyl ion pool been regenerated by retrohydrogen or deuterium shifts (Scheme II or III) during the formolysis, the nonexchanged brexanone derived from run 10 (Table III) would have contained more d_2 and less d_1 than that from run 11.[13] See reaction scheme in eq A.

Discussion

With the aid of the product distribution data in Table I which do not depend upon an a priori assumption about the classical or nonclassical nature of the initial 2-brexyl cations, it is now possible to answer some of the questions originally left unanswered by our earlier studies with nonlabeled β-(*syn*-7-norbornenyl)ethyl brosylate.[2]

"Does the initial 2-brexyl cation, R^+, undergo one or more Wagner–Meerwein automerizations prior to hydrogen (deuterium) migration"? Clearly it does. As detailed in Scheme II, at least one carbon shift is required to produce either CL or CU from a classical (C_2) 2-brexyl cation when the starting brosylate is α,α-$^2H_2$-**1**-OBs or AL and AU when β,β-$^2H_2$-**1**-OBs is the starting material. Alternately, a minimum of two carbon shifts would be required if the 2-brexyl cations are charge delocalized (Scheme III). The "concise interpretation" of Scheme I is thus inadequate.[2]

"What is the provenance of the migrating hydrogen (deuterium)"? The formation of all four possible isotopically discrete rearranged cations[5,15] (Scheme IV) during the solvolysis of an α- or β-gem-dideuterated brosylate requires that hydrogen (deuterium) migration occur from each of the methylenic carbons of the starting material, viz. C-α, C-β, C-5, and C-6.[6] In terms of the initial intermediate, this means that migration occurs at some point in the reaction from *each* carbon



(A)

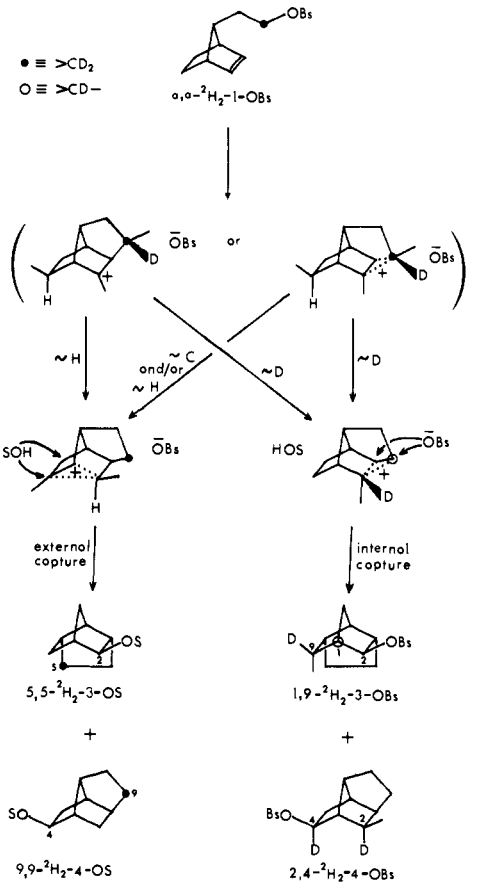
in *both* ethano bridges, i.e., from C-4, C-5, C-8, and C-9,[6] of the "C_2" or "C_s" 2-brexyl cations (Schemes II and III, respectively).[16]

"Is the hydrogen (deuterium) migration reversible"? Our studies with returned brosylate demonstrate that under formolysis conditions, it is not.[17] Presumably, this is true for hydrolysis and acetolysis as well[18] and reflects the greater thermodynamic stability of the rearranged cation(s).[4,19]

"How important is ion pairing in the overall solvolytic process"? In considering this question it will be helpful to examine some further aspects of the solvolysis mechanism which our data reveal. Because the hydrogen or deuterium shift is effectively irreversible, the label distribution in the products is a function of its importance vis-a-vis Wagner–Meerwein automerization. Our results with the isomerically dideuterated starting materials α,α- and β,β-$^2H_2$-**1**-OBs (Table I) make it clear that the relative importance of these competing processes is influenced by the position of the deuterium label in the starting brosylate and by the nature of the solvent. The fraction of products formed after one (C_2) or two (C_s) carbon shifts is greater when the shift(s) can be followed by hydrogen rather than deuterium migration. About 19% of the formolysis products of α,α-$^2H_2$-**1**-OBs result from a hydrogen shift following Wagner–Meerwein rearrangement(s), while only 10% of the formates from β,β-$^2H_2$-**1**-OBs result from a deuterium shift following Wagner–Meerwein(s). The difference is less striking, though still apparent, in hydrolysis and acetolysis as well. It is the expected consequence of the primary deuterium isotope effect which renders deuterium shifts less facile than hydrogen.[20] In each dideuterated case the fraction of products produced after at least one automerization is greatest in formic acid and least in acetic. Thus, the ability of a Wagner–Meerwein rearrangement to compete with a hydrogen or deuterium migration reflects the dissociating (solvolyzing) power of the solvent, viz: HCOOH ($Y = 2.054$,[21] $D = 58$[22]) > 90% acetone-water ($Y = -1.856$,[21] $D = 25$[23]) ≥ AcOH ($Y = -1.639$,[21] $D = 6.2$[22]). So, in fact, does the importance of ion pair dissociation relative to ion pair return.[18] No *exo*-2-brendyl brosylate (**3**-OBs) can be detected in the formolysis of **1**-OBs and only traces are observed spectroscopically in hydrolysis (90% acetone-water) mixtures, but as much as 40% of the starting material is converted to this brosylate during acetolysis.[2] Clearly, ion pair intermediates play a major role in the solvolyses of β-(*syn*-7-norbornenyl)ethyl brosylates.[18b]

Some years ago Winstein and Robinson speculated that, in principle, ". . .the [initially formed] first intimate ion pair . . . could rearrange to a still intimate ion pair, but with the anion near some other portion of the cation, thus, leaving the reactive spot on the cation exposed to solvent".[24] The present system would appear a priori to present a nearly ideal situation for the observation of such an effect: a single Wagner–Meerwein and/or hydrogen shift would convert the initially formed "C_s" or "C_2" 2-brexyl ion pair into a new rearranged ion pair expected to be more accessible to attack by solvent than to return by brosylate counterion. Thus, returned 2-brendyl brosylate ($^2H_2$-**3**-OBs) isolated from the acetolysis of α,α-$^2H_2$-**1**-OBs could be enriched in 1,9-$^2H_2$ relative to 5,5-$^2H_2$, while 4-brexyl acetate ($^2H_2$-**4**-OAc) isolated from the same reaction mixture ought then to contain relatively more 9,9-$^2H_2$ and less 2,4-$^2H_2$. Since retrohydrogen (deuterium) migration to regenerate a C_s or C_2 cation does not occur under these conditions, a separate acetolysis of the isolated, returned *exo*-2-brendyl brosylate ($^2H_2$-**3**-OBs) would thus be expected to yield *exo*-4-brexyl acetate ($^2H_2$-**4**-OAc) enriched with deuterium at the 2,4 positions relative to the 8,8. Brexan-4-one (^2H_x-**11**) derived from the reacetolysis of returned brosylate ($^2H_2$-**3**-OBs) isolated originally from the acetolysis of α,α-$^2H_2$-**1**-OBs should show less d_2 and more d_1 than brexan-4-one derived from 4-brexyl acetate produced in the initial acetolysis. This does not appear to be the case; cf. Table III, runs 6–9 and 11. Thus, our earlier supposition is incorrect:[2] *gegenion reorientation and return competes quite effectively with ion pair dissociation and/or attack by solvent during acetolysis.*[18b,25] The implication of this result is that in acetic acid both *the Wagner–Meerwein rearrangement(s) and the product-determining hydrogen (deuterium) shift occur exclusively at the same ion pair stage.* The ion pairs involved are probably tight ion pairs though solvent separated species cannot be rigorously excluded on the basis of our present data.[29]

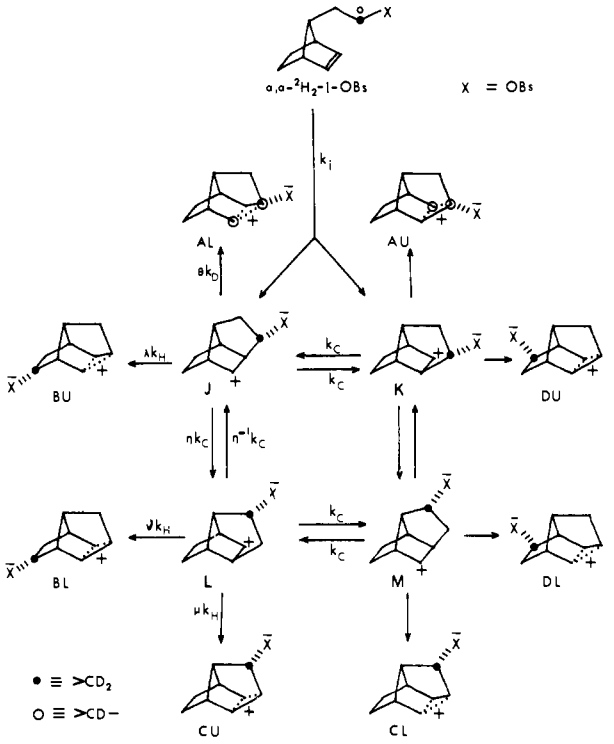
Scheme VIII. Possible Internal vs. External Cation Capture in the Solvolysis of α,α-$^2H_2$-β-(*syn*-7-Norbornenyl)ethyl Brosylate[5,6]



Most of the products in each solvolysis come from "rearranged cations" formed by a hydrogen or deuterium shift from the ethano bridge adjacent to the brosylate anion in the initial ion pair. This "memory effect" [30] is most apparent in the tetradeuterio derivative where, in spite of the unfavorable primary isotope effect,[20] deuterium migrates more often than hydrogen, i.e., more products result from ACL and ACU than from BDL and BDU (Scheme VII). The "spread" between near-side deuterium and far-side hydrogen migration in the tetradeuterio brosylate is 6% in formolysis, 30% in hydrolysis, and 40% in acetolysis. Similar trends are evident in the two dideuterio cases as well (Table I). We attribute these "memory" or proximity effects to the counterion of the initial 2-brexyl intermediate, R^+BsO^-, which retards the rate of a rearrangement (such as the first Wagner–Meerwein or a far-side hydrogen migration, Scheme III) that increases the effective charge separation and enhances the rate of any process (a second Wagner–Meerwein or a near-side shift) that decreases the net charge separation in the ion pair.[31,32]

The conclusions which we have drawn to this point do not depend upon any a priori assumptions about the electronic structure of the initial 2-brexyl cation. Bearing this in mind we now ask "Is a distinction between the C_s and C_2 formulations possible and if so do our data permit such a distinction

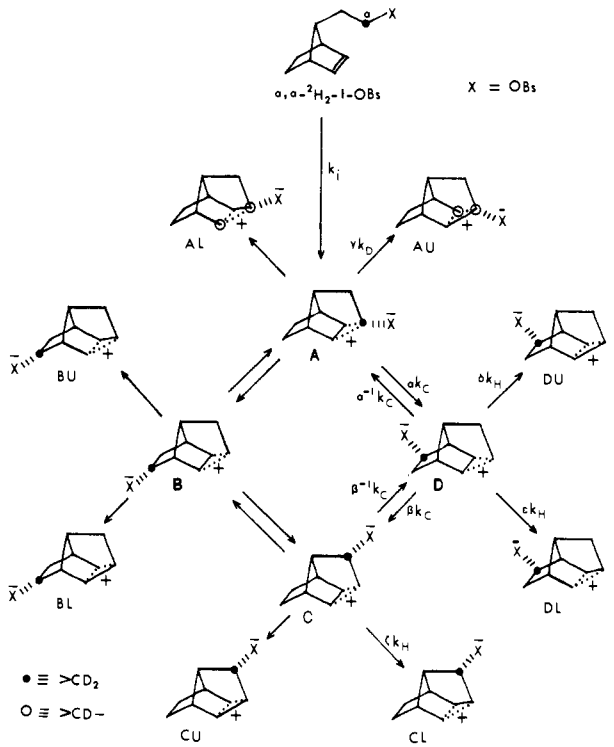
Scheme IX. Classical (C_2) 2-Brexyl Cation Model for the Solvolysis of α,α-$^2H_2$-β-(*syn*-7-Norbornenyl)ethyl Brosylate



$$d[J]/dt = -(k_C + \eta k_C + \lambda k_H + \theta k_D)[J] + k_C[K] + \eta^{-1}k_C[L] + 0.5\,k_i S_0 e^{-k_i t}$$
$$d[K]/dt = k_C[J] - (k_C + \eta k_C + \lambda k_H + \theta k_D)[K] + \eta^{-1}k_C[M] + 0.5\,k_i S_0 e^{-k_i t}$$
$$d[L]/dt = \eta k_C[J] - (k_C + \eta^{-1}k_C + \mu k_H + \nu k_H)[L] + k_C[M]$$
$$d[M]/dt = \eta k_C[K] + k_C[L] - (k_C + \eta^{-1}k_C + \mu k_H + \nu k_H)[M]$$

where S_0 is the initial concentration of α,α-$^2H_2$-1-OBs

Scheme X. Nonclassical (C_s) 2-Brexyl Cation Model for the Solvolysis of α,α-$^2H_2$-β-(*syn*-7-Norbornenyl)ethyl Brosylate



$$d[A]/dt = -(2\alpha k_C + 2\gamma k_D)[A] + \alpha^{-1}k_C[B] + \alpha^{-1}k_C[D] + k_i S_0 e^{-k_i t}$$
$$d[B]/dt = \alpha k_C[A] - (\alpha^{-1}k_C + \beta k_C + \delta k_H + \epsilon k_H)[B] + \beta^{-1}k_C[C]$$
$$d[C]/dt = \beta k_C[B] - (2\beta^{-1}k_C + 2\zeta k_H)[C] + \beta k_C[D]$$
$$d[D]/dt = \alpha k_C[A] + \beta^{-1}k_C[C] - (\alpha^{-1}k_C + \beta k_C + \delta k_H + \epsilon k_H)[D]$$

where S_0 is the initial concentration of α,α-$^2H_2$-1-OBs

to be made"? We have attempted to answer these related questions by developing equivalent kinetic formulations for the two alternatives from which product distributions can be predicted, tested against and possibly reconciled with the observed values reported in Table I. Because of their independence, use can be made of our previous conclusions to simplify the kinetic treatments. Thus, in formulating the models we consider that all four possible isotopically discrete, diastereomeric C_2 or C_s 2-brexyl ion pairs are involved, that all product-determining rearrangements occur in the ion pair[33] and are rapid relative to gegenion reorientation, that all hydrogen and deuterium shifts are irreversible, that hydrogen shifts are more facile than deuterium, and that all shifts which increase effective charge separation in the ion pair are retarded relative to those which decrease net charge separation.[31] Using the solvolysis of α,α-$^2H_2$-**1**-OBs as an example, the alternate C_2 and C_s interpretations are illustrated in Schemes IX and X. The Greek letters included in the models reflect the effect on the rate of the particular change in charge separation associated with a specific carbon, hydrogen, or deuterium shift. As detailed in the Kinetic Appendix,[34] the fraction of discretely labeled brexyl (and brendyl) products derived from each of the isomeric C_2 or C_s ion pairs can be computed as a function of a single solvent parameter, Q (to which with appropriate geometric assumptions the solvent counterion perturbation factors $\eta - \nu$ or $\alpha - \zeta$ can be related) and the "unperturbed" carbon to hydrogen and hydrogen to deuterium shift ratios, r and l, respectively. Similar equations utilizing identical parameter values may be used to predict product compositions from the solvolysis of β,β-$^2H_2$- and $\alpha,\alpha,\beta,\beta$-$^2H_4$-**1**-OBs.

Utilizing a computer-programmed, minimization routine which separately adjusts the three parameters, Q, r, and l, to achieve the best overall match of predicted and measured product distributions for the formolysis, the hydrolysis, and the acetolysis of the di- and tetradeuterio-β-(*syn*-7-norbornenyl)ethyl brosylates we have tested the ability of both the C_2 and the C_s models to reproduce the observed product distributions (Table II).

It is apparent that our product distribution data from the solvolyses of the di- and tetradeuterated starting materials *do not* permit us to distinguish between the alternate classical and nonclassical models depicted in Schemes IX and X, respectively. Although the classical cation (C_2) model predicts distinctly different amounts of the 8,8- and 9,9-$^2H_2$-4-brexyl derivatives while the nonclassical (C_s) model suggests that these isomers would be present in essentially identical amounts, similar *total* amounts of both are expected in either case. Unfortunately, our method of deuterium analysis reveals only the amount of 8,8- *plus* 9,9-$^2H_2$-**4**-OS present in the solvolysis mixtures, and a distinction on this basis is not possible.

Although our data *do not* permit a distinction between the classical and nonclassical ion pair formulations outlined in Schemes IX and X, the kinetic models themselves imply that a clear choice would be possible if C-8 and C-9 labeled brexyl (or C-4 and C-5 labeled brendyl) derivatives could be uniquely distinguished.[35] In the following paper we report the use of ^{13}C labeling for this purpose.[14]

Experimental Section[36]

***syn*-7-Norbornenylacetonitrile** (7).[37] A mixture of 13.9 g (0.0405 mol) of *syn*-7-norbornenylcarbinyl *p*-bromobenzenesulfonate (**6**-OBs),[10] 10 g (0.20 mol) of sodium cyanide, and 200 ml of dimethylformamide (DMF) was heated with stirring under reflux for 12 h, cooled to room temperature, poured into 500 ml of water, and extracted with four 100-ml portions of pentane. The combined extract was washed with 100 ml of water and dried over anhydrous sodium

Table II. Calculated and Observed Product Distributions for the Solvolysis of Di- and Tetradeuterio β-*syn*-7-Norbornenyl)ethyl Brosylates at 25 °C

Solvent	Deuterium label position: Starting material (1-OBs)	Deuterium label position: Brexyl product (4-OS)	Calculated %: C_2 model	Calculated %: C_s model	Obsd %
HCOOH	α,α	2,4	41.6	41.7	45
		5,5	17.8	17.9	19
		8,8 + 9,9	40.6	40.5	36
		8,8	8.4	20.1	
		9,9	32.2	20.4	
	β,β	2,4	10.0	9.7	10
		5,5	56.7	56.8	56
		8,8 + 9,9	33.3	33.5	34
		8,8	25.0	16.9	
		9,9	8.3	16.6	
	α,α,β,β	2,4,5,5	56.0	56.0	53
		8,8,9,9	44.0	44.0	47
	Solvent parameter, Q		10.95	10.98	
	$k_C/k_H = r$		0.909	2.81	
	$k_H/k_D = l$		1.75	1.73	
	Mean deviation of fit (%)		2.1	2.1	
	Maximum deviation (%)		4.6	4.4	
	Standard deviation (%)		1.6	1.6	
90% acetone-water	α,α	2,4	56.2	56.2	58
		5,5	12.3	12.3	12
		8,8 + 9,9	31.6	31.5	30
		8,8	4.3	15.6	
		9,9	27.3	15.9	
	β,β	2,4	7.9	7.7	10
		5,5	66.7	66.7	66
		8,8 + 9,8	25.4	25.7	24
		8,8	21.2	13.0	
		9,9	4.2	12.7	
	α,α,β,β	2,4,5,5	67.0	66.9	65
		8,8,9,9	33.0	33.1	35
	Solvent parameter, Q		15.34	14.51	
	$k_C/k_H = r$		0.543	1.68	
	$k_H/k_D = l$		1.53	1.51	
	Mean deviation of fit (%)		1.5	1.5	
	Maximum deviation (%)		2.1	2.3	
	Standard deviation (%)		0.7	0.7	
HOAc	α,α	2,4	63.6	63.5	66
		5,5	10.1	10.2	11
		8,8 + 9,9	26.4	26.2	23
		8,8	3.0	12.9	
		9,9	23.4	13.3	
	β,β	2,4	7.0	6.8	8
		5,5	71.5	71.6	71
		8,8 + 9,9	21.5	21.5	21
		8,8	18.6	10.9	
		9,9	2.9	10.6	
	α,α,β,β	2,4,5,5	72.8	72.7	70
		8,8,9,9	27.2	27.3	30
	Solvent parameter, Q		18.04	17.89	
	$k_C/k_H = r$		0.453	1.48	
	$k_H/k_D = l$		1.42	1.41	
	Mean deviation of fit (%)		1.8	1.8	
	Maximum deviation (%)		3.4	3.2	
	Standard deviation (%)		1.2	1.1	

sulfate. The pentane was removed at atmospheric pressure. Distillation of the residue gave 5.10 g (95%) of **7**: bp 76–78 °C (5 mm); IR (CCl_4) 3070, 1580, 720 (-CH=CH-, cis), 2260 cm^{-1} (C≡N); ^1H NMR (CCl_4) δ 5.92 (perturbed triplet, 2 =CH-), 2.81 (broad, poorly resolved multiplet, 2 >CH, bridgehead), 2.32–~1.9 (AB_2 multiplet, $>CHCH_2- + >CHCH_2-$) partly overlapping a multiplet at ~1.9–0.8 (4 H, ethano bridge).

Anal. ($C_9H_{11}N$) C, H.

***syn*-7-Norbornenylacetic Acid (8).**[37] A solution of 5.01 g (0.0376 mol) of **7** and 5.0 g (0.13 mol) of sodium hydroxide in 60 ml of 70% aqueous ethanol was heated under reflux for 20 h, cooled, poured into 500 ml of water, and washed with three 50-ml portions of ether. The aqueous phase was acidified with 1.5 M HCl and extracted with four 50-ml portions of ether. The ether extract was washed with 50-ml of saturated sodium chloride and dried (Na_2SO_4). The ether was removed at atmospheric pressure, and the residue was distilled to give 5.48 g (95.8%) of the acid **11**: bp 90–93 °C (0.5 mm); IR (CCl_4) 3530 (OH, nonbonded), ~3400–2500, broad (OH, bonded) overlapping with sharp bands at 3060, 2960, 2940, 2910, 2875 (=C-H), 1715 (C=O), 1580 (C=C), 720 cm^{-1} (-HC=CH-, cis); ^1H NMR (CCl_4) δ 11.98 (singlet, $-CO_2H$), 5.88 (perturbed triplet, 2 =CH-), 2.76 (broad, poorly resolved multiplet, 2 >CH, bridgehead), 2.38–~2.0 (AB_2 multiplet, $>CHCH_2- + >CHCH_2-$), partly overlapping a multiplet at ~1.9–0.8 (4 H, ethano bridge).

Anal. ($C_9H_{12}O_2$) C, H.

Methyl *syn*-7-Norbornenylacetate (9). The acid **8** (5.48 g, 0.0360 mol) was slowly combined with an excess of ethereal diazomethane.[38] The solution was dried ($MgSO_4$) and the ether removed at atmospheric pressure. Distillation of the residue gave 5.40 g (90.2%) of **9**: bp 77–80 °C (5.5 mm); IR (CCl_4) 3060, 1585, 720 (-CH=CH-, cis), 1750 (C=O), 1162 cm^{-1} (C-O, methyl ester); ^1H NMR (CCl_4) δ 5.85 (triplet, 2 =CH-), 3.60 (singlet, $-OCH_3$), 2.71 (broad, poorly resolved multiplet, 2 >CH, bridgehead), 2.30–~2.0 (AB_2 multiplet, $>CHCH_2-$ + $>CHCH_2-$), partly overlapping a multiplet at ~1.9–0.85 (4 H, ethano bridge).

Anal. ($C_{10}H_{14}O$) C, H.

α,α-$^2H_2$-β-(*syn*-7-Norbornenyl)ethanol (α,α-$^2H_2$-1-OH). An ethereal solution containing 5.68 g (34.2 mmol) of **9** was added dropwise to a stirred ethereal slurry of 1.50 g (35.8 mmol) of lithium aluminum deuteride.[39] The mixture was stirred for 3 h at room temperature, and the organic product was isolated in the usual manner.[40] Distillation under vacuum gave 4.65 g (97.1%) of a colorless oil: ^1H NMR (CCl_4) δ 5.78 (perturbed triplet, 2 =CH-), 2.64 (broad, poorly resolved multiplet, 2 >CH, bridgehead), 2.24 (singlet, -OH), and 1.85–0.78 (complex multiplet, 7 H). The 2-hydrogen triplet, J = 6.5 Hz, at δ 3.45, present in the spectrum of the nondeuterated β-(*syn*-7-norbornenyl)ethanol, **1**-OH,[2] and attributed to $-CH_2-CH_2-O-$, is missing in the spectrum of this material.

α,α-$^2H_2$-β-(*syn*-7-Norbornenyl)ethyl Trimethylsilyl Ether (α,α-$^2H_2$-1-OSiMe$_3$). A solution of 50 mg of α,α-$^2H_2$-**1**-OH and 0.25 ml of *N,O*-bis(trimethylsilyl)acetamide (BSA)[41] in 1 ml of anhydrous pyridine was allowed to stand at room temperature overnight, poured into 5 ml of 10% HCl, and quickly extracted with two 3-ml portions of pentane. The pentane extract was washed with 5 ml of saturated sodium bicarbonate and 5 ml of water and dried (Na_2SO_4). Most of the pentane was removed at atmospheric pressure and the product isolated by GLC on the DEGS column (retention time relative to the starting alcohol is 0.16). The product, α,α-$^2H_2$-**1**-OSiMe$_3$, was shown by mass spectral analysis to contain 97.1% d_2, 3.9% d_1, and 0.0% d_0.[42]

Similar determinations on other batches of α,α-$^2H_2$-**1**-OsiMe$_3$ showed 96.6% d_2, 3.4% d_1, 0.0% d_0, and 96.3% d_2, 3.7% d_1, 0.0% d_0; cf. Table III. These data serve to establish the deuterium content of the α-dideuterated alcohol, α,α-$^2H_2$-**1**-OH, and, hence, of the starting brosylate, α,α-$^2H_2$-**1**-OBs.

Methyl α,α-$^2H_2$-α-(*syn*-7-Norbornenyl)acetate (α,α-$^2H_2$-9). A sealed tube containing 4.10 g (24.7 mmol) of **9** dissolved in a solution prepared from the reaction of 0.3 g (13 mg-atom) of sodium and 37 g of anhydrous CH_3OD[44] was heated at 60 °C for 2 days. The reaction mixture was poured into 30 ml of D_2O, saturated with sodium chloride, and extracted with three 50-ml portions of pentane. The combined pentane layer was dried (Na_2SO_4), and the pentane was removed by distillation at atmospheric pressure. Distillation of the residue in vacuo gave 3.49 g (84%) of α,α-$^2H_2$-**9** shown by mass spectrometric analysis to contain 89.0% d_2, 10.9% d_1, 0.1% d_0.[45] An additional equilibration gave 3.11 g (75% overall) of α,α-$^2H_2$-**9** containing 97.9% d_2, 2.1% d_1, and 0.0% d_0;[45] ^1H NMR (CCl_4) δ 5.81 (slightly, perturbed triplet, J ~ 2 Hz, 2 =CH-), 3.56 (singlet, $-OCH_3$), 2.69 (broad, poorly resolved septet, 2 >CH, bridgehead), 1.91 (broad, slightly perturbed singlet, >CH-), overlapping a complex multiplet at ~1.9–0.74 (4 H, ethano bridge). Note that the low field portion of the AB_2 multiplet which appears at δ ~2.30–2.0 in the spectrum of the nondeuterated ester, **9**, is missing in the spectrum of the dideuterated derivative.

A similar deuterium exchange on another sample of the starting ester, **9**, gave material containing 86.6% d_2, 10.4% d_1, and 1.0% d_0[45] after the first equilibration; 97.5% d_2, 2.5% d_1, and 0.0% d_0[45] after the second.

β,β-$^2H_2$-β-(*syn*-7-Norbornenyl)ethanol (β,β-$^2H_2$-1-OH). This material was prepared by reduction of α,α-$^2H_2$-**9** with lithium aluminum hydride in the usual manner;[40] ^1H NMR (CCl_4) δ 5.81 (slightly perturbed triplet, J ~ 2 Hz, 2 =CH-), 3.68 (broad singlet, -OH), overlapping a sharp singlet at 3.40 ($-CH_2-O-$), 2.64 (broad, poorly resolved multiplet, 2 >CH, bridgehead), 1.85–0.8 (broad, complex multiplet, 5 H, >CH-, and 4 H, ethano bridge). Note that the resonance of the two magnetically equivalent α-hydrogens at δ 3.45, which, due to coupling with the two magnetically equivalent adjacent hydrogens, appear as a triplet, J ~ 6.5 Hz, in the spectrum of the nondeuterated alcohol **1**-OH[2] collapses to a singlet in the β-dideuterated material.

Mass spectral analyses of trimethylsilyl ethers prepared as described previously, vide supra, from separate batches of alcohol β,β-$^2H_2$-**1**-OH derived from the dideuterated acetate samples referred to above showed deuterium contents of 98.2% d_2, 1.8% d_1, 0.0% d_0 and 98.3% d_2, 1.7% d_1, 0.0% d_0, respectively.[42,46] These determinations serve to establish the deuterium content of the β-dideuterated alcohol β,β-$^2H_2$-**1**-OH and hence of the corresponding brosylate, β,β-$^2H_2$-**1**-OBs.

$\alpha,\alpha,\beta,\beta$-$^2H_4$-$\beta$-(*syn*-7-Norbornenyl)ethanol ($\alpha,\alpha,\beta,\beta$-$^2H_4$-1-OH). This material was prepared in 93% yield by reduction of methyl α,α-$^2H_2$-α-(*syn*-7-norbornenyl)acetate, α,α-$^2H_2$-**9** (97.4% d_2, 2.6% d_1, 0.0% d_0),[45] with lithium aluminum deuteride[39] in the manner described previously. Mass spectral analysis of the trimethylsilyl ether, vide supra,[42] reveals a deuterium content of 94.1% d_4, 5.9% d_3, and 0.0% d_2, d_1, and d_0.[47] This analysis establishes the actual deuterium content of the tetradeuterio alcohol and the corresponding brosylate, $\alpha,\alpha,\beta,\beta$-$^2H_4$-**1**-OBs.

Preparation of the Deuterated Brosylates (α,α-$^2H_2$-, β,β-$^2H_2$-, and $\alpha,\alpha,\beta,\beta$-$^2H_4$-1-OBs). The brosylates were prepared as described previously in the case of the nondeuterated brosylate **1**-OBs,[2] from samples of α,α-$^2H_2$-, β,β-$^2H_2$-, and $\alpha,\alpha,\beta,\beta$-$^2H_4$-**1**-OH whose deuterium content had been previously determined by mass spectrometric analysis of the corresponding trimethylsilyl ether.

α,α-$^2H_2$-β-(*syn*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonate (α,α-$^2H_2$-1-OBs). ^1H NMR (CS_2 containing a trace of pyridine) δ 7.57 (singlet, 4 =CH-, aromatic), 5.64 (perturbed triplet, J ~ 2 Hz, 2 =CH-), 2.41 (broad, perturbed singlet, 2 >CH, bridgehead), 1.48–0.56 (complex multiplet, 7 H). Note that the triplet at δ 3.91 (J ~ 6.2 Hz) in the spectrum of the nondeuterated brosylate,[2] **1**-OBs, due to the $-CH_2-CH_2-O-$ moiety is absent in the spectrum of α,α-$^2H_2$-**1**-OBs.

β,β-$^2H_2$-β-(*syn*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonate (β,β-$^2H_2$-1-OBs). ^1H NMR (CS_2 containing trace of pyridine) δ 7.61 (singlet, 4 =CH-, aromatic), 5.71 (triplet, J ~ 2 Hz, 2 =CH-), 3.83 (singlet, $-CH_2-O-$), 2.51 (broad, perturbed singlet, 2 >CH, bridgehead), 1.78–0.71 (complex multiplet, 5 H). Note that the triplet at δ 3.91 (J ~ 6.2 Hz) in the spectrum of the nondeuterated brosylate, **1**-OBs,[2] due to the $-CH_2-CH_2-O-$ moiety appears as a singlet ($-CD_2-CH_2-O-$) in the spectrum of β,β-$^2H_2$-**1**-OBs.

Solvolysis of the β-(*syn*-7-Norbornenyl)ethyl Brosylate (1-OBs). For purposes of product analysis the nondeuterated brosylate, **1**-OBs,[2] was solvolyzed at 25 °C in (1) anhydrous acetic acid buffered with excess sodium acetate containing 1% acetic anhydride,[48] (2) aqueous 90% acetone[49] buffered with a 20–30% molar excess of sodium carbonate,[50] and (3) anhydrous formic acid[51a] buffered with sodium formate.[51b] In each solvent duplicate 15–30 ml samples were used which were 0.020 M in brosylate and 0.023–0.05 M in the appropriate buffer. The acetolysis was allowed to proceed for 2 h,[52] the hydrolysis for 15 h,[55] and the formolysis for 15 min.[59]

The **acetolysis** and **formolysis** mixtures were treated as follows: each sample was poured into approximately twice its volume of ice-water and extracted with pentane. The pentane extracts were washed sequentially with saturated solutions of sodium chloride and sodium bicarbonate, dried (Na_2SO_4), and concentrated to ~1 ml by distillation of most of the pentane at atmospheric pressure.

The composition of the volatile reaction products was determined by GLC analysis on the DEGS column.[36] Samples of the pentane concentrates were coinjected with small amounts of pyridine.[2] As reported previously,[2] the **acetolysis** mixture contains the acetates **3**-OAc and **4**-OAc in the approximate ratio of 54 to 46 plus some deltacyclane (**2**). The **formolysis** mixture was found to contain two products in an approximate ratio of 59 to 41 having retention times at 150 °C of 14.4 and 15.8 min, respectively.[11]

In order to detect the presence of any unreacted starting material and/or brosylate formed by internal return, a rough proton magnetic resonance analysis at 60 MHz was performed on each of the concentrated pentane solutions of solvolysis products. In agreement with our previous findings,[2] the **acetolysis** mixture, while showing no signals in the olefinic hydrogen region, exhibits a fairly strong signal at δ ~7.7 due to the aromatic hydrogen resonances of *exo*-2-brendyl brosylate (**3**-OBs). The pentane concentrate was therefore cooled to −20 °C and the precipitated brosylate removed by filtration. The filtrate was combined with ~50 μl of pyridine, and the acetates were separated (as a mixture of isomers) from any remaining brosylate by collection from the DEGS column at 175 °C. No internally returned brosylate was detected in the **formolysis** product mixture as evidenced by the

absence of resonances in the δ 5.8–6.0 and 7.5–8.5 regions in the ^{1}H NMR spectrum of the pentane concentrate.

The stability of the **acetolysis** and **formolysis** products was tested by separating (GLC) a small sample of each component and subjecting it to the solvolysis and isolation conditions. Within the limits of our experimental accuracy, all were recovered unchanged.

The **acetate** and **formate** mixtures were usually converted to mixtures of the known ketones **10** and **11**[3] without prior separation of the isomeric components, although control experiments in each case demonstrated that the **3**-OS and **4**-OS could be separated and individually converted to brendan-2-one (**10**) and brexan-4-one (**11**), respectively.

The **hydrolysis** mixture was first concentrated to 2–3 ml by distillation of the acetone at atmospheric pressure; the residue was diluted with 100 ml of water and extracted with four 50-ml portions of pentane. The combined pentane extract was washed with 50 ml of saturated aqueous sodium chloride solution, dried over anhydrous sodium sulfate, filtered, and concentrated to ~1 ml by distillation of the pentane at atmospheric pressure. A 60-MHz proton magnetic resonance spectrum of the concentrate exhibited a weak resonance at δ ~7.7 due to the 2-brendyl brosylate **3**-OBs,[2] but since no precipitate formed when the pentane concentrate was cooled to −20 °C no further fractionation of brosylate and alcohol(s) was attempted. The volatile hydrolysis products could not be analyzed at this stage by GLC because 4-brexanol (**4**-OH) is isomerized to the more stable 2-brendanol (**3**-OH) under the conditions of the analysis.

Pure samples of alcohols **3**- and **4**-OH were obtained by GLC separation of the corresponding acetates (from acetolysis of **1**-OBs), followed by reduction of each with lithium aluminum hydride.[2] Each of the alcohols (from acetolysis of **1**-OBs) was treated with buffered aqueous acetone under conditions of the brosylate hydrolysis. After workup each of the samples was oxidized to the corresponding ketone, vide infra, and analyzed by GLC. A single ketone was obtained in each case demonstrating that no isomerization had occurred in the solvolysis medium.

Conversion of the Solvolysis Products of β-(*syn*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonate (1-OBs) into Mixtures of Brendan-2-one (10) and Brexan-4-one (11). The product ester mixtures obtained from the **acetolysis** and **formolysis**, respectively, were collected gas chromatographically and reduced with lithium aluminum hydride in the manner described previously.[2] Each of the ethanol solutions of 2-brendyl and 4-brexyl alcohols (**3**- and **4**-OH) thus obtained as well as the pentane extract of the alcohol mixture from the **hydrolysis** of **1**-OBs was combined with 5 ml of "Spectral Grade" acetone and concentrated to 2 ml by distillation of the solvent at atmospheric pressure through a 1-ft, wire spiral-packed column. The concentrated alcohol-containing acetone solution was in each case cooled in ice and "titrated" with an acidic solution of chromium trioxide in water[60] until an orange color persisted in the solution. After the reaction mixture had been stirred for an additional 5 min, the excess oxidizing agent was decomposed with a few drops of methanol. Each mixture was decanted into a separatory funnel containing 5 ml of pentane and 5 ml of saturated, aqueous sodium chloride. The ketonic products were extracted into pentane, and the aqueous layer was washed with an additional 5-ml portion of pentane. The combined pentane extract of each reaction mixture was washed again with saturated, aqueous sodium chloride, concentrated to ~0.5 ml, and analyzed by GLC on the DEGS column at 150 °C. The products collected for spectral analysis were found in each case to be identical with authentic samples of brendan-2-one (**10**) and brexan-4-one (**11**).[2-4]

The relative amounts of these two ketones obtained from the **acetolysis** and **formolysis** products were identical in each case with those of the corresponding esters prior to reduction and oxidation. The **hydrolysis** mixture, which could not be analyzed at the alcohol stage due to isomerization on the column, gave **10** and **11** in an approximate ratio of 45 to 55.

Solvolysis of the Polydeuterated β-(*syn*-7-Norbornenyl)ethyl Brosylates (α,α-$^2H_2$-, β,β-$^2H_2$-, and $\alpha,\alpha,\beta,\beta$-$^2H_4$-1-OBs). Each of the polydeuterated brosylates was solvolyzed in aqueous acetone and in acetic and formic acids under conditions identical with those employed for the nondeuterated material **1**-OBs. In each case the solvolysis products were converted as described previously to mixtures of polydeuterated brendan-2-one (^2H_x-**10**) and brexan-4-one (^2H_x-**11**) which were separated by preparative GLC on the DEGS column.

We note that these low-melting (28–29 °C) brosylates do not always dissolve instantaneously in the solvolysis medium, but sometimes appear first to "melt" to a transitory two-phase system, minute droplets of brosylate frequently persisting for several seconds after mixing at 25 °C. This behavior, which probably reflects the low meltig point, limited solubility and probable high molal freezing point-depression constant of these bicyclic compounds, may permit some deltacyclane (**2**) formation and cleavage, vide infra, to occur in what is essentially an unbuffered and perhaps highly acidic (HOBs) melt.

Deuterium Analyses of Polydeuterated Brexan-4-ones and Brendan-2-ones from the Solvolysis of Polydeuterated β-(*syn*-7-Norbornenyl)ethyl Brosylates. The deuterium content of pure polydeuterated 2-brendanone (^2H_x-**10**) and 4-brexanone (^2H_x-**11**) prepared from each solvolysis mixture and isolated as described above was determined mass spectrometrically at an ionization potential of 12–15 eV[36] (conditions under which the nondeuterated ketones **10** and **11** show no P − 1 fragment) by comparison of $M^{\cdot+}$ = 138, 137, and 136 fragments in the case of the dideuterated starting materials α,α-$^2H_2$- and β,β-$^2H_2$-**1**-OBs or the $M^{\cdot+}$ = 140, 139, and 138 fragments in the case of the tetradeuterio starting material, $\alpha,\alpha,\beta,\beta$-$^2H_4$-**1**-OBs.[43]

That a significant amount of deuterium is not lost through exchange during the Jones oxidation of the deuterated 4-brexanols ($^2H_2$-**4**-OH) is evident from the observation that the d_2 content of the resulting brexan-4-one, ^2H_x-**10**, is experimentally identical whether the oxidation at room temperature is carried out with a slight excess of oxidizing agent for 5 min or with a substantial excess of oxidant for 45 min. When the oxidation of **4**-OH is carried out under comparable conditions with chromium trioxide in D_2SO_4/D_2O, mass spectral analysis reveals that deuterium is not incorporated in the resulting brexan-4-one (**11**).

The deuterium contents of the ketones ^2H_x-**10** and ^2H_x-**11**, together with that of the appropriate batch of starting material (assayed as the trimethylsilyl ether, vide supra) are summarized in Table III.

In the case of the deuterated 4-brexanone mixtures derived from α,α- or β,β-$^2H_2$-**1**-OBs, the deuterium present at C-5, i.e., on the methylene carbon adjacent to the carbonyl, was determined in the following manner. An ~0.10-g sample of the crude ketone mixture, ^2H_x-**10** and −**11**, from each oxidation was dissolved in 3 ml of tetrahydrofuran (THF), mixed with 15 ml of aqueous 1 M sodium carbonate, and heated at reflux for 4–9 days. The reaction mixture was allowed to cool and extracted with four 10-ml portions of ether, and the combined ethereal layer was washed with 10 ml of saturated aqueous sodium chloride and dried over anhydrous sodium sulfate. The ether was removed by distillation at atmospheric pressure, and the two ketones were separated by preparative GLC as before. The deuterium content of each of the deuterated brexan-4-one mixtures, ^2H_y-**11**, was determined mass spectrometrically as outlined previously; cf. Table III.

While a 4-day equilibration is sufficient to effect essentially complete exchange of the methylenic deuterium adjacent to the carbonyl in the 5,5-$^2H_2$-brexan-4-one from α,α-$^2H_2$-**1**-OBs without homoenolization,[12,61] cf. runs 1–9, Table III, a slightly longer equilibration is required for the brexan-4-one derived from the solvolyses of β,β-$^2H_2$-**1**-OBs. In these latter cases, the % d_2 is approximately constant after 4 days of equilibration, but an additional 2 days is required before the % d_1 becomes constant; cf. run 13. Apparently the additional equilibration time is required to completely remove the *endo*-deuterium at C-5 in the samples of brexan-4-one which are more extensively deuterated at this position.[62] Since our analysis of the exchange data (Table I) considers only the fraction of dideuterated brexan-4-ones present after equilibration, vide infra, it is not biased by the presence of *endo*-5-$^2H_1$-**11** resulting from incomplete exchange.

The equilibration procedure does not, within experimental error which we estimate to be from 1.0–1.5%, affect the deuterium content of the 2-brendanones (^2H_x-**11**) derived from these solvolysis mixtures; cf. Scheme IV and Table III, footnote *h*.

Calculation of Product Distributions from the Mass-Spectral Analyses. Brendan-2-one derived from a solvolysis product mixture formed as outlined in Scheme II or III should have the same deuterium content as the starting material. This is the case within experimental error (1.0–1.5%) for nonequilibrated brendan-2-ones (^2H_x-**10**) derived from the hydrolysis mixtures, runs 3–5, 14, and 15, confirming the internal consistency of the deuterium assay. The small *mono*-deuterium losses evident in the nonequilibrated brendan-2-ones (^2H_x-**10**) from formolysis and acetolysis that are accompanied by

Table III. Mass Spectral Deuterium Analyses for Starting Materials and Derived Ketones

					Before exchange		After exchange[a]
Run	Compound	Solvent	%	1-OSiMe$_3$	^2H_x-10	^2H_x-11	^2H_y-11
1	α,α-$^2H_2$-1-OBs	HCOOH	d_2	96.1	93.9	53.2	34.8
			d_1	3.9	6.1	44.7	44.0
			d_0	0.0	0.0	2.1	21.2
2			d_2	96.1	93.8	52.6	
			d_1	3.9	6.2	45.3	
			d_0	0.0	0.0	2.1	
3,4[b]		H_2O/Me_2CO	d_2	96.1	95.8	40.2	
			d_1	3.9	4.0	58.5	
			d_0	0.0	0.0	1.3	
5			d_2	96.1	95.5	41.7	28.7[c]
			d_1	3.9	4.5	57.1	56.3
			d_0	0.0	0.0	1.2	15.0
6,7		HOAc	d_2	96.6	92.4	31.8[d]	
			d_1	3.4	7.5	65.8	
			d_0	0.0	0.1	2.4	
8,9			d_2	96.1	94.5	32.7	22.1[c]
			d_1	3.9	5.5	65.9	64.4
			d_0	0.0	0.0	1.4	13.5
10	d_2-3-OBs[e]	HCOOH	d_2	96.3	93.6	33.3	
			d_1	3.7	6.4	64.8	
			d_0	0.0	0.0	1.9	
11		HOAC	d_2	96.3	93.3	32.2	
			d_1	3.7	6.7	66.0	
			d_0	0.0	0.0	1.8	
12[f]			d_2	96.3	86.9	38.9	
			d_1	3.7	12.8	53.5	
			d_0	0.0	0.2	7.6	
13	β,β-$^2H_2$-1-OBs	HCOOH	d_2	98.3	96.6	88.8	33.7[g,h]
			d_1	1.7	3.4	11.2	8.0
			d_0	0.0	0.0	0.0	58.3
14		H_2O/Me_2CO	d_2	98.2	98.0	88.5	23.7[i]
			d_1	1.8	2.0	11.3	8.3
			d_0	0.0	0.0	0.2	68.0
15			d_2	98.2	97.8	87.9	
			d_1	1.8	2.2	12.0	
			d_0	0.0	0.0	0.1	
16,17		HOAc	d_2	98.2	97.2	88.2	
			d_1	1.8	2.7	11.3	
			d_0	0.0	0.1	0.5	
18			d_2	98.3	97.0	90.0	20.7[j]
			d_1	1.7	3.0	9.5	6.8
			d_0	0.0	0.0	0.5	72.5
19	$\alpha,\alpha,\beta,\beta$-$^2H_4$-1-OBS	HCOOH	d_4	94.1	90.4	44.4	
			d_3	5.9	8.2	50.0	
			d_2	0.0	1.4	4.8	
			d_1	0.0	0.0	0.8	
			d_0	0.0	0.0	0.0	
20,21		H_2O/Me_2CO	d_4	94.1	92.6	33.2	
			d_3	5.9	7.4	62.7	
			d_2	0.0	0.0	4.1	
			d_1	0.0	0.0	0.0	
			d_0	0.0	0.0	0.0	
22,23		HOAc	d_4	94.1	91.2	28.3	
			d_3	5.9	8.6	65.5	
			d_2	0.0	0.2	6.1	
			d_1	0.0	0.0	0.1	
			d_0	0.0	0.0	0.0	

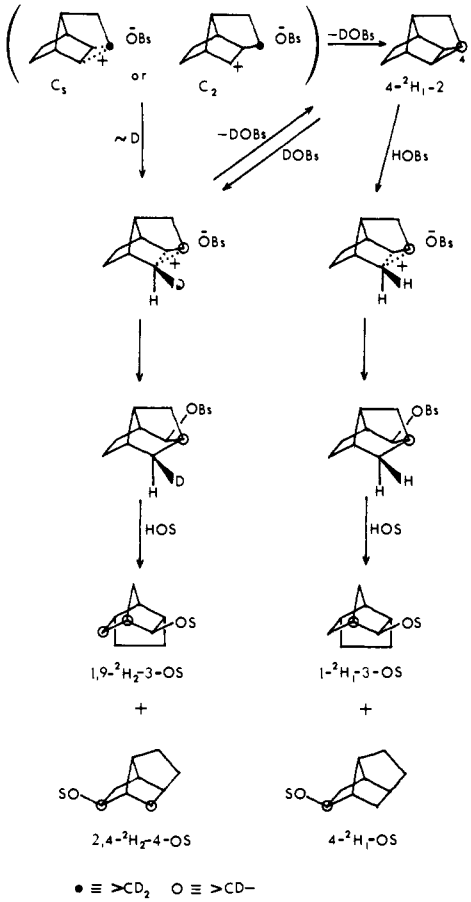
[a] Average of two successive 4-day equilibrations. [b] Buffered with 2,6-lutidine instead of sodium carbonate. [c] One 4-day equilibration. [d] Run 6 only. [e] Returned 3-OBs isolated from the acetolysis of α,α-$^2H_2$-1-OBs. [f] From the melt-phase rearrangement of α,α-$^2H_2$-1-OBs. [g] Equilibrated for 6 days; a second 6-day equilibration gave 33.2% d_2, 8.9% d_1, and 57.9% d_0. [h] Brendan-2-one isolated from the same mixture after a 6-day equilibration gave 97.1% d_2, 2.8% d_1, and 0.1% d_0. [i] After a 9-day equilibration; a 1-day equilibration gave 32.7% d_2, 48.3% d_1, and 19.0% d_0, an additional 4-day equilibration: 23.2% d_2, 11.2% d_1, and 65.6% d_0. [j] Equilibrated for 6 days.

enhanced dideuterium losses in the corresponding brexan-4-ones (^2H_x-11) are probably due to deltacyclane (2) formation and cleavage as outlined in Scheme XI. Since deltacyclane (2) is cleaved only in the presence of added strong acid,[4,21] deuterium loss by the process outlined in Scheme XI does not occur in the buffered solvolysis media. We presume that it occurs instead during the dissolution of the starting material; vide supra. That such a process could occur in the melt and lead to deuterium loss and scrambling was demonstrated by heating α,α-$^2H_2$-1-OBs at ~30 °C—the odor of deltacyclane was evident—until the melt had resolidified[2] and solvolyzing the resulting *exo*-2-

brendyl brosylate (^2H_n-3-OBs) in buffered acetic acid. The derived ketones (run 12, Table III) in this case exhibit more deuterium scrambling and loss than do those from the acetolysis of returned brosylate isolated in the usual manner (vide infra); cf. run 11. The smaller *mono*deuterium losses in the nonexchanged 2-brendanones (^2H_x-**10**) derived from hydrolysis mixtures could reflect the greater solubility of the starting brosylates in 90% acetone-water.

To the extent that deltacyclane formation and cleavage occur as outlined in Scheme XI with the concomitant loss of two deuteriums from the derived 4-brexanone prior to exchange (^2H_x-**11**), the reported isomer distributions (Table II) will be slightly altered. However, the validity of our analysis of the product origins is unaffected since both $^2H_1$- and $^2H_0$-**11** are formed from the same C_s or C_2 2-brexyl ion pair (Scheme XI).

Scheme XI. Deuterium Loss through Deltacyclane Formation and Cleavage[5,9b]



Isolation of Returned $^2H_2$-*exo*-2-Brendyl *p*-Bromobenzenesulfonate ($^2H_2$-3-OBs) from the Acetolysis of α,α-$^2H_2$-β-(*syn*-7-Norbornenyl)-ethyl *p*-Bromobenzenesulfonate (α,α-$^2H_2$-1-OBs).[2] A sample of freshly prepared brosylate, α,α-$^2H_2$-1-OBs, was solvolyzed as described previously in buffered, anhydrous acetic acid at room temperature. After 1.5 h[63] the reaction mixture was diluted with an ice-water mixture and extracted with five 50-ml portions of pentane. The extract was washed successively with saturated, aqueous sodium chloride and aqueous sodium bicarbonate and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was recrystallized from hexane. The recrystallized brosylate, mp 88–91 °C,[2] which exhibited a slight odor of acetate esters, was used in subsequent solvolyses without further purification.

Solvolysis of Returned $^2H_2$-*exo*-2-Brendyl *p*-Bromobenzenesulfonate ($^2H_2$-3-OBs) Isolated from the Acetolysis of α,α-$^2H_2$-β-(*syn*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonate (α,α-$^2H_2$-1-OBs). Samples of the returned brosylate isolated as described above were solvolyzed as described previously for >10 half-lives, respectively, in buffered acetic and formic acids at room temperature. The ester products were isolated, converted to ketones, and analyzed mass spectrometrically for deuterium as described earlier. The deuterium contents of the isolated, unequilibrated brexan-4-one mixtures (^2H_x-**11**) were: (HCOOH) 33.3% d_2, 64.8% d_1, 1.9% d_0; (HOAc) 32.2% d_2, 66.0% d_1, 1.8% d_0, Table III, runs 10 and 11, respectively. The figures should be compared with those (unnormalized) from similar samples of brexan-4-one (^2H_x-**11**) derived from the direct solvolysis of α,α-$^2H_2$-β-(*syn*-7-norbornenyl)ethyl *p*-bromobenzenesulfonate (α,α-$^2H_2$-**1**-OBs), viz.: (HCOOH) runs 1 and 2, (HOAc) runs 6–9, Table III.[13]

Preparation of $^2H_2$-*exo*-2-Brendyl *p*-Bromobenzenesulfonate ($^2H_2$-3-OBs) by Melt-Phase Rearrangement of α,α-$^2H_2$-β-*syn*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonate (α,α-$^2H_2$-1-OBs).[2] A 0.65-g (1.8 mmol) sample of α,α-$^2H_2$-1-OBs was warmed at 35 °C until it melted to a colorless oil. The liquid was cooled to room temperature and stirred until it crystallized (~5 min). The white solid, which had a distinct odor of deltacyclane (**2**), was recrystallized from hexane to give 0.48 g (1.3 mmol), (72%) of white crystals melting at 89–91 °C.

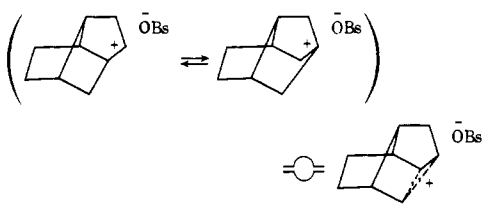
Acetolysis of $^2H_2$-*exo*-2-Brendyl *p*-Bromobenzenesulfonate ($^2H_2$-3-OBs) from the Melt-Phase Rearrangement of α,α-$^2H_2$-β-(*syn*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonate (α,α-$^2H_2$-1-OBs). A sample of $^2H_2$-3-OBs was solvolyzed as described previously for >10 half-lives in buffered acetic acid. The acetates were isolated, converted to ketones, and analyzed mass spectrometrically for deuterium as described earlier. The deuterium contents of the unequilibrated ketones are given in Table III, run 12.

Acknowledgment. Some of the initial computations described herein were carried out while the senior authors were on leave at the University of California, Berkeley. We appreciate the generous gift of computer time on the School of Chemistry's XDS 910 timeshare system and the hospitality of the Department of Chemistry and its faculty.

Supplementary Material Available: Details of the kinetic treatment of the solvolysis of α,α-$^2H_2$-1-OBs, including the method of assigning counterion parameters (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Portions of this work have been presented at (a) the 163d National Meeting of the American Chemical Society, Boston, Mass., April 1972, Abstract ORGN 3, and (b) the 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974, Abstract ORGN 29.
(2) R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail, *J. Am. Chem. Soc.*, **89**, 880 (1967).
(3) A. Nickon, H. Kawasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *J. Am. Chem. Soc.*, **87**, 1613, 1615 (1965).
(4) (a) Cf. T. D. Swartz, Ph.D. Dissertation, The Johns Hopkins University, 1966. (b) We thank Professor Nickon for communicating this information prior to its publication.
(5) It is convenient though not obligatory to depict the "*rearranged cations*" and *ion pairs* as charge delocalized. Our data can be interpreted quite adequately in terms of the equivalent pairs of rapidly equilibrating, charge-localized structures, viz.



(6) The numbering shown here is that appropriate to the approved chemical name rather than to the depicted structure per se, thus an individual atom may be assigned different numbers in the starting material, the intermediates, and the products.
(7) Leone, Barborak, and Schleyer have provided the generally accepted definition:[8a] "A degenerate carbonium ion is . . . a carbonium ion that can rearrange through a finite energy barrier . . . to regenerate the same gross structure . . . as that of the starting ion". Processes such as this which conserve both the molecular formula and structure of the starting material are frequently referred to as "automerizations".[8b] Within the framework of this definition, Schleyer et al. do not consider the preservation of enantiomeric purity a requirement for degeneracy and state that: "rearrangements whereby an optically active carbon is racemized or . . . an isotopic label dispersed by an automerization (are considered) to be examples of degeneracy".

(8) (a) R. E. Leone, J. C. Barborak, and P. v. R. Schleyer in "Carbonium Ions", Vol. IV, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1973, Chapter 33; (b) A. T. Balaban and D. Farcăslu, *J. Am. Chem. Soc.*, **89**, 1958 (1967).

(9) (a) Letters in parentheses designate the mirror image structure which is not shown. Since our starting materials are necessarily meso (have mirror-plane symmetry), *all* intermediates are either meso or racemic. Each of the discretely labeled ("isotopically diastereomeric" or "isotopically discrete") brexyl and brendyl products is therefore a racemic mixture of enantiomers. (b) The stereochemistry of the individual deuterium labels has not been determined but, where shown, is merely inferred from mechanistic considerations.

(10) R. K. Bly and R. S. Bly, *J. Org. Chem.*, **31**, 1577 (1966).

(11) We detect the presence of substantial but varying amounts of deltacyclane (**2**) in the acetolysis mixtures,[2] a trace in the hydrolysis products but none in the formolysis mixtures; cf. Experimental Section.

(12) A. Nickon, J. L. Lambert, J. E. Oliver, D. F. Covey, and J. Morgan, *J. Am. Chem. Soc.*, **98**, 2593 (1976).

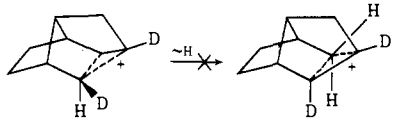
(13) Since neither of the brexan-4-one mixtures derived from the solvolysis of $^2H_2$-**3**-OBs (Table III, runs 10 and 11) was equilibrated to exchange deuterium at C-5, we do not know that the exact position of the label(s) within the individual molecules of these two ketone samples is identical with that of the $^2H_2$-11 derived from the direct acetolysis of α,α-$^2H_2$-1-OBs (runs 6, 8, and 9). As detailed in the following paper,[14] however, the fact that they are identical has been demonstrated through the use of ^{13}C labeling.

(14) R. S. Bly, R. K. Bly, J. B. Hamilton, J. N. C. Hsu, and P. K. Lillis, following paper in this issue. Note that structures and compounds common to this and the following paper are numbered similarly.

(15) Strictly speaking, because it does not differentiate between an 8,8- and a 9,9-$^2H_2$ label in the *exo*-4-brexyl derivatives, our method of product analysis does *not* demonstrate that *both* BU or BL *and* DU or DL are formed. As detailed in the following paper,[14] the formation of both B- and D-type rearranged ions *has* in fact been demonstrated through the use of ^{13}C labeling.

(16) The terminus of the migration is always the five-membered ring defined by carbons 1, 2, 3, 6, and 7 of the initial 2-brexyl intermediate (Scheme I, II, or III).

(17) These studies also demonstrate that hydrogen (deuterium) shifts do not take place in the "rearranged cation" or ion pair itself under these conditions, e.g.



for had they done so both the brendan-2-one (^2H_x-**10**) *and* the brexan-4-one (^2H_x-11) derived from the further solvolysis of returned 2-brendyl brosylate, $^2H_2$-**3**-OBs (cf Table III, runs 10 and 11), would have exhibited more *mono*deuterium loss than comparable ketones from the solvolyses of α,α-$^2H_2$-1-OBs (runs 6–9).

(18) (a) Rearrangement is normally more extensive during formolysis than in acetolysis or hydrolysis; cf. (b) S. Winstein, B. Appel, R. Baker, and A. Diaz in "Organic Reaction Mechanisms", *Chem. Soc., Spec. Publ.* **No. 19**, 109–130, (1965), and references cited therein.

(19) A. Nickon, G. D. Pandit, and R. O. Williams, *Tetrahedron Lett.*, 2885 (1967).

(20) (a) J. L. Fry and G. J. Karabatsos in "Carbonium Ions", Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1970, Chapter 14, and references cited therein; (b) C. J. Collins, *ibid.*, Vol. I, 1968, Chapter 9.

(21) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956).

(22) R. C. Weast, Ed., "Handbook of Chemistry and Physics", 49th ed, Chemical Rubber Co., Cleveland, Ohio, 1968, p E59.

(23) G. Akerlöf, *J. Am. Chem. Soc.*, **54**, 4125 (1932).

(24) S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, **80**, 169 (1958); cf. footnote 37.

(25) Internal return to a remote position has also been reported during the acetolysis of labeled *exo*-2-norbornenyl derivatives,[28] 7-chloro-*exo*-2-norbornyl tosylates,[27] 1,1-bishomocubyl methanesulfonate,[28] and β-(3-cyclopentenyl)ethyl thiocyanate.[27b]

(26) (a) S. J. Cristol and D. A. Beimborn, *J. Am. Chem. Soc.*, **95**, 3651 (1973); (b) C. C. Lee and E. C. F. Ko, Abstracts, 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974, ORGN 30.

(27) (a) H. L. Goering and M. J. Degani, *J. Am. Chem. Soc.*, **91**, 4506 (1969); (b) L. A. Spurlock and W. G. Cox, *ibid.*, **91**, 2961 (1969).

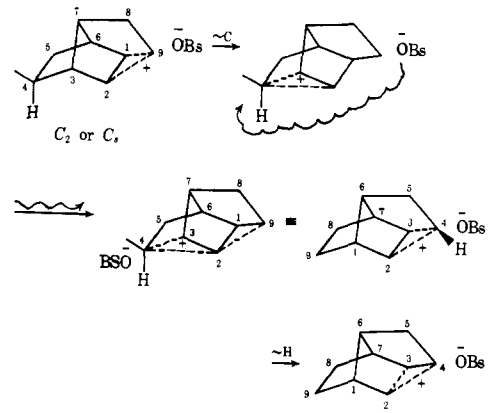
(28) W. G. Dauben and D. L. Whalen, *J. Am. Chem. Soc.*, **93**, 7244 (1971).

(29) (a) Cf. D. J. Raber, J. M. Harris, and P. v. R. Schleyer in "Ions and Ion Pairs in Organic Reactions", Vol. 2, M. Szwarc, Ed., Wiley-Interscience, New York, N.Y., 1974, Chapter 3, especially the footnote on p 256; (b) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 2538 (1970), footnote 8.

(30) (a) J. A. Berson, *Angew. Chem.*, **80**, 765 (1968); (b) C. J. Collins, *Rev. Chem. Soc.*, **4**, 251 (1975).

(31) (a) C. J. Collins, and M. H. Leitzke, *J. Am. Chem. Soc.*, **89**, 6565 (1967); (b) C. C. Lee and B.-S. Hahn, *ibid.*, **91**, 6420 (1969); (c) J. E. Nordlander, F. Y.-H. Wu, S. P. Jindal, and J. B. Hamilton, *ibid.*, **91**, 3962 (1969), and references cited therein.

(32) An alternate though kinetically equivalent view is that ion pair reorganization is rapid with respect to a hydrogen or deuterium shift and that *all* such shifts occur from the side of the counterion in the reoriented C_2 or C_s ion pair, e.g.[5]



at a relative rate determined only by the deuterium isotope effect(s). Under such circumstances product partitioning would depend upon the relative rates of Wagner–Meerwein rearrangement, gegenion reorientation, and hydrogen or deuterium shift.

(33) This has actually been demonstrated only for acetolysis.

(34) See Supplementary Material Available paragraph.

(35) A referee has suggested that the kinetic models used here, Schemes IX and X, may be overcomplicated in that they assume a counterion effect which acts on all carbon, hydrogen, and deuterium shifts. He suggests that in setting up models for the classical and nonclassical cases, counterion effects need be considered only for the hydrogen or deuterium shifts that occur from the α position of the starting brosylate, i.e., that only θ (Scheme IX) or γ (Scheme X) have values other than 1.0. We will consider his suggestion in detail in the following paper.[14]

(36) Melting and boiling points are uncorrected. Microanalyses were performed by Bernhardt Mikroanalytisches Laboratorium, 5251 Elbach über Engelskirchen, West Germany. Spectra were determined on a Perkin-Elmer grating infrared spectrophotometer Model 337 using a polystyrene standard. Proton magnetic resonance spectra were recorded on a Varian A-60A spectrometer using tetramethylsilane (δ = 0.00) as a standard. Analytical gas chromatography was performed on F and M Model 500 or Varian Aerograph Model 1800 chromatographs using 14 ft × ¼ in. copper columns packed with 20% diethylene glycol succinate (DEGS) on 60/80 mesh Chromosorb W at helium flow rates of ~80 ml/min. No attempt was made to correct peak areas for differences in the thermal conductivities of the components. Preparative gas chromatography was carried out on an Aerograph Autoprep Model 700-A using a 20 ft × ⅜ in. aluminum column packed with 20% Carbowax 20M on 60/80 mesh Chromosorb W at helium flow rates of ~200 ml/min. Mass spectra were recorded on a Hitachi-Perkin-Elmer single focusing, RMU 6 spectrometer at ionization potentials of ~12–15 eV, unless otherwise specified. Each reported deuterium analysis represents an average of from four to eight scans.

(37) Adapted from an unpublished procedure kindly provided by Professor J. H. Richards, Department of Chemistry and Chemical Engineering, California Institute of Technology.

(38) J. A. Moore and D. E. Reed, *Org. Synth.*, **41**, 16 (1961).

(39) Ventron Corp., Beverly, Mass., 18.7% D.

(40) V. M. Micovic and M. L. Mihailovic, *J. Org. Chem.*, **18**, 1190 (1953).

(41) Pierce Chemical Company, Rockford, Ill.

(42) Calculated from the relative intensities of the $M\cdot^+$ fragments[43] at *m/e* 212, 211, and 210. The trimethylsilyl ether (1-$OSiMe_3$) of β-(*syn*-7-norbornenyl)ethanol (1-OH) exhibits no P − 1 or P − 2 fragments under these conditions.[36]

(43) Corrected for natural isotope abundances using the tables of R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N.Y., 1963. Control experiments on the nondeuterated compound verify the validity of the method and the corrections for natural isotope abundances.

(44) Diaprep Chemical Company, Atlanta, Ga., 99% minimum O-D.

(45) Calculated from the relative intensities of the $M\cdot^+$ fragments[43] at *m/e* 168, 167, and 166. The nondeuterated parent compound, methyl *syn*-7-norbornenylacetate (**9**) apparently exhibits a small P − 1 fragment under these conditions.[36]

(46) The deuterium content of the ether appears to be slightly greater than that of its deuterated acetate precursor because the small amount of P − 1 fragmentation that occurs during the mass spectral analysis of the ester causes its deuterium content to appear slightly too low.[42,45]

(47) Calculated from the relative intensities of the $M\cdot^+$ fragments[43] at *m/e* 214, 213, 212, 211, and 210.

(48) R. S. Bly and R. T. Swindell, *J. Org. Chem.*, **30**, 10 (1965).

(49) Prepared by mixing nine volumes of Reagent Grade acetone with one volume of distilled water.

(50) Similar results were obtained in the case of α,α-$^2H_2$-1-OBs when 2,6-lutidine was employed as a buffer; cf. Table III, runs 3 and 4.

(51) (a) Prepared by distilling Reagent Grade anhydrous formic acid, bp 99.2–99.8 °C (760 mm); cf. P. D. Bartlett, C. E. Dills, and H. G. Richey, *J. Am. Chem. Soc.*, **82**, 5414 (1960); P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *ibid*, **87**, 5169 (1965). (b) Dried at 120 °C for 4 h.

(52) Approximately 10 half-lives for α,α-$^1H_2$-derivatives, i.e., 1-OBs and β,β-$^2H_2$-1-OBs, and ~8.5 half-lives for the α,α-$^2H_2$ brosylates, α,α-$^2H_2$-1-OBs, and $\alpha,\alpha,\beta,\beta$-$^2H_4$-1-OBs.[53]

(53) The α,α-$^2H_2$-β,β-(*syn*-7-norbornenyl)ethyl brosylate is estimated to be ~0.9 times as reactive as the nondeuterated derivative, 1-OBs, from NMR measurements of the rate of disappearance of vinyl hydrogen.[2] This

compares favorably with the value of 0.871 for the relative acetolysis rates of α,α-$^2H_2$- and α,α-$^1H_2$-β-(3-cyclopentenyl)ethyl *p*-nitrobenzenesulfoates at 40 °C reported by Lee and Wong.[54]

(54) C. C. Lee and E. C. W. Wong, *J. Am. Chem. Soc.*, **86**, 2752 (1964).
(55) Approximately 30 half-lives for 1-OBs and β,β-$^2H_2$-1-OBs; 27 half-lives for α,α-$^2H_2$- and $\alpha,\alpha,\beta,\beta$-$^2H_4$-1-OBs.[56]
(56) Estimated from the Winstein–Grunwald *mY* relation[21,57] and the solvolysis constants of 1-OBs in anhydrous acetic acid (25 °C by ^{1}H NMR[2]), $k_1 = 9.1 \times 10^{-4}$ s^{-1}, and in 90/10 v/v dioxane/water (25 °C by UV[58]), $k_1 = 2.0 \times 10^{-4}$ s^{-1}.
(57) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).
(58) Unpublished data of S. P. Jindal.
(59) Greater than 10^6 half-lives.
(60) (a) L. F. and M. Fieser, "Reagents for Organic Synthesis", Wiley, New York, N.Y., 1968, p 142; (b) W. G. Dauben and G. H. Berezin, *J. Am. Chem. Soc.*, **85**, 468 (1963).
(61) Brexan-2-one and numerous ketonorbornanes are known to homoenolize under sufficiently vigorous conditions:[12] typically when treated with potassium *tert*-butoxide in anhydrous *tert*-butyl alcohol for several hours at 185–250 °C,[3] but such exchange is neither expected nor observed under the much milder conditions which we have employed; cf. (a) A. Nickon and J. L. Lambert, *J. Am. Chem. Soc.*, **84**, 4604 (1962); (b) A. Nickon, J. H. Hammons, J. L. Lambert, and R. O. Williams, *ibid.*, **85**, 3713 (1963); (c) R. Howe and S. Winstein, *ibid.*, **87**, 915 (1965); (d) T. Fukunaga, *ibid.*, **87**, 916 (1965); (e) A. Nickon and J. L. Lambert *ibid.*, **88**, 1905 (1966); (f) A. Nickon, J. L. Lambert and J. E. Oliver, *ibid.*, **88**, 2787 (1966); (g) A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstuik, *ibid.*, **88**, 3354 (1966); (h) D. H. Hunter, A. L. Johnson, J. B. Stothers, A. Nickon, J. L. Lambert, and D. F. Covey, *ibid.*, **94**, 8582 (1972).
(62) G. A. Abad, S. P. Jindal, and T. T. Tidwell, *J. Am. Chem. Soc.*, **95**, 6326 (1973), have demonstrated that the *exo*-hydrogen at C-3 in noncamphor undergoes base-catalyzed exchange about 680 times as rapidly as the *endo*.
(63) Approximately 6 half-lives for the starting brosylate α,α-$^2H_2$-1-OBs; approximately 0.1 half-life for the returned *exo*-2-brendyl brosylate, $^2H_2$-**3**-OBs.

Formolysis and Acetolysis of α-^{13}C-β-(*syn*-7-Norbornenyl)ethyl *p*-Bromobenzenesulfonate. π-Route Generated 2-Brexyl Cation, a Nonclassical Norbornyl Type[1]

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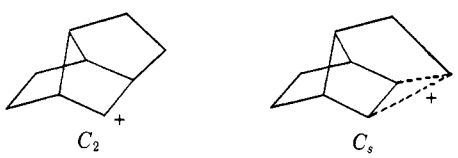
Abstract: The solvolysis of α-^{13}C-β-(*syn*-7-norbornenyl)ethyl brosylate in buffered solutions at 25 °C produces mixtures of *exo*-2-brendyl and *exo*-4-brexyl derivatives specifically labeled with carbon-13. Analysis by quantitative FT ^{13}C{H} NMR reveals the following carbon-13 distributions; 2-brendyl acetate: C-1 (79%), C-4 (6%), C-5 (8%), C-8 (7%); 4-brexyl acetate: C-4 (77%), C-5 (8%), C-8 (6%), C-9 (8%); 2-brendyl formate: C-1 (58%), C-4 (13%), C-5 (14%), C-8 (15%); 4-brexyl formate: C-4 (59%), C-5 (15%), C-8 (12%), C-9 (14%). Formolysis of returned, carbon-13 labeled *exo*-2-brendyl brosylate, isolated from the acetolysis of α-^{13}C-β-(*syn*-7-norbornenyl)ethyl brosylate, produces *exo*-2-brendyl and *exo*-4-brexyl formates specifically labeled with carbon-13 as follows: 2-brendyl: C-1 (77%), C-4 (6%), C-5 (9%), C-8 (8%); 4-brexyl: C-4 (79%), C-5 (7%), C-8 (6%), C-9 (8%). These results confirm previous conclusions based upon deuterium scrambling studies that π-route generated 2-brexyl cations undergo at least one Wagner–Meerwein automerization prior to an irreversible hydrogen shift, that these carbon and hydrogen shifts occur in the ion pair, and that they are influenced by the counterion. Kinetic models suggest that the π-route generated 2-brexyl cations may possess C_s symmetry and therefore be charge delocalized.

In the preceding paper[2a] we reported the use of deuterium labeling to demonstrate that the solvolysis of β-(*syn*-7-norbornenyl)ethyl brosylate (**1**-OBs) generates a 2-brexyl cation which can undergo at least one Wagner–Meerwein automerization prior to product formation. By the formolysis of returned 2-brendyl brosylate ($^2H_2$-**3**-OBs) isolated from the acetolysis of α,α-$^2H_2$-**1**-OBs we were further able to show that the product-forming hydrogen (deuterium) shifts are effectively irreversible and to infer that both they and the carbon shifts which precede them occur at the same ion pair stage. Finally, we were able to establish that the ratio of automerization to hydrogen (deuterium) shift is dependent upon the solvolysis medium, decreasing in the order: formic acid > 90% acetone–water > acetic acid. We were unable, however, to distinguish between alternate reaction paths involving 2-brexyl cations of C_2 or C_s symmetry; cf. Schemes IX and X, respectively, in the preceding paper.[2a] This distinction is important because, as illustrated, the local symmetry of the intermediates is expected to reflect the electronic nature of the ions themselves. Its significance transcends the present problem, for it is relevant to the structure of π-route generated norbornyl cation itself.[3]



C_2 C_s

Kinetic models,[2a,b] developed to approximate the observed deuterium distributions in the *exo*-4-brexyl products from the solvolyses of α,α-$^2H_2$-, β,β-$^2H_2$-, and $\alpha,\alpha,\beta,\beta$-$^2H_4$-**1**-OBs suggest that these alternate "classical" and "nonclassical" 2-brexyl cation reaction paths could be differentiated if *each* of the four methylenic carbons in the starting material could be uniquely recognized in the final products.[2a,c] Since our method of deuterium assay does not discriminate either between the C-4 and C-5 positions of the *exo*-2-brendyl or the C-8 and C-9 positions of the *exo*-4-brexyl products, we decided to reexamine the solvolyses using a carbon-13 label instead; cf. Schemes I and II. We report here the preparation of α-^{13}C-β-(*syn*-7-norbornenyl)ethyl brosylate (α-^{13}C-**1**-OBs) and the analysis of its C-13 labeled brendyl and brexyl solvolysis products by Fourier transform, ^{13}C nuclear magnetic resonance (FT ^{13}C NMR).