Molecular Rearrangements. XXIV. A Mechanistic Analysis of Available Isotopic Data for Solvolyses of 2-*exo*-Norbornyl and 2-(Δ^3-Cyclopentenyl)ethyl Esters[1]

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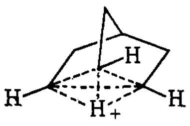
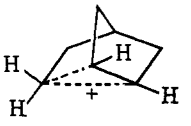
Abstract: Standard mechanistic and mathematical procedures were applied to available isotopic data for the solvolyses of 2-*exo*-norbornyl and 2-(Δ^3-cyclopentenyl)ethyl esters, and the ratios k_S/k_3 and k_S/k_6 (k_S, k_6, and k_3 are the specific reaction rate constants for cation–anion collapse, 6,2- and 3,2-hydride shift, respectively) are evaluated by means of programs written for the IBM 7090 computer. Only in the formolyses[4] of 2-*exo*-norbornyl-2,3-$^{14}C_2$ brosylate (Iab) and of 2-(Δ^3-cyclopentenyl)ethyl *p*-nitrobenzenesulfonate (III) does there appear to be definite evidence for the 3,2-hydride shift. In addition, the carbon-14 distribution in the product of π-route acetolysis of 2-(Δ^3-cyclopentenyl)ethyl-2-^{14}C *p*-nitrobenzenesulfonate (III) cannot be correlated in terms of nonclassical ions, but is compatible with equilibrating, classical norbornyl ions.

Since Wagner's explanation[2] of the isoborneol–camphene transformation, few structures of organic chemistry have received the intensive study devoted to derivatives of norbornane (bicyclo[2.2.1]heptane).[3] One of the most widely quoted[3] papers in this field is the isotopic tracer study of the acetolysis of norbornyl-2,3-$^{14}C_2$ brosylate (Iab) by Roberts, Lee, and Saunders,[4] in which the shift of hydrogen from the 6 to the 2 position of the norbornane skeleton was demonstrated.[5] The observations of Doering and Wolf,[5] Toivonen,[5] and Roberts, *et al.*,[4] posed the question of the mode of such shifts, Roberts[4] suggesting that the "face"-protonated nortricyclonium ion is responsible for the hydrogen migration, and pointing out that the carbon-14 distribution in the product of acetolysis of Iab is consistent with a mechanism in which 45% of the reaction proceeds through the nortricyclonium ion and 55% through the norbornyl bridged ion. An alternate possibility, namely that the reaction goes through bridged norbornyl ions which are interconvertible through hydride shifts, was proposed[6] and is still preferred[7] by Winstein.

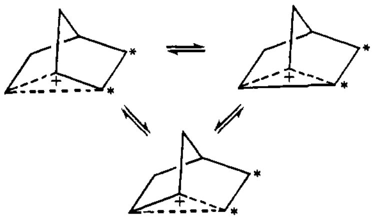


nortricyclonium ion

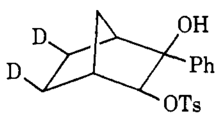


norbornyl bridged ion

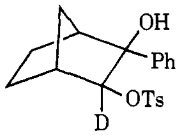
Recently we showed[8,9] that the substituted norbornyl tosylates IIa and IIb undergo hydrogen and deuterium migration, upon hydrolysis, in discrete, consecutive steps (6,1, 6,2, and 1,2 shifts), a result consistent with interconverting norbornyl bridged (or classical!) ions,[6,7] but unexplainable through substituted, "face-protonated" nortricyclonium ions.[4,10] Since the phenyl and hydroxyl groups in IIa and IIb destroy the threefold symmetry of the substituted nortricyclonium ion derived therefrom, it is possible to argue against projecting our results[8,9] to explain the solvolyses[4] of Iab.



norbornyl bridged ions which interconvert through hydride shifts



IIa



IIb

The recent tracer results of Lee and Lam on the acetolysis[11] and formolysis[12] of *exo*-norbornyl-2-*t* brosylate (Ic) and of 2-(Δ^3-cyclopentenyl)-2-^{14}C-ethyl *p*-nitrobenzenesulfonate[13,14] (III) seemed important with respect to the nature of norbornyl carbonium ion intermediates provided they could be related to one another and to the original data of Roberts.[4] We have long

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

[2] G. Wagner, *J. Russ. Phys. Chem. Soc.*, 31, 680 (1899).

[3] (a) J. A. Berson in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3, gives a comprehensive survey of the field through the first half of 1961. (b) W. Hückel, *Ann. Acad. Sci. Fennicae, Ser. A, II*, No. 134, 1 (1966), gives a penetrating discussion of the rearrangements which occur in bicyclo[2.2.1]heptyl derivatives with particular reference to the fenchane system.

[4] J. D. Roberts, C. C. Lee, and W. H. Saunders, *J. Am. Chem. Soc.*, **76**, 4501 (1954); J. D. Roberts and C. C. Lee, *ibid.*, **53**, 5009 (1951).

[5] Berson[3] credits Roberts, *et al.*,[4] and W. von E. Doering and A. P. Wolf, *Perfumery Essent. Oil Record*, **42**, 414 (1951), with the first "virtually simultaneous" demonstration of a 6,2 shift of hydrogen. N. J. Toivonen, *Suomen Kemistilehti*, **24B**, 62 (1951), also demonstrated that the fenchol $\rightleftharpoons$ isofenchol rearrangement proceeds through a 6,2-hydride shift.

[6] S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, 71, 2953 (1949); **74**, 1147, 1154 (1952).

[7] A. Colter, E. C. Friederich, N. J. Holness, and S. Winstein, *ibid.*, **87**, 378 (1965).

[8] B. M. Benjamin and C. J. Collins, *ibid.*, **88**, 1556, 1558 (1966); *Tetrahedron Letters*, **45**, 5477 (1966).

[9] C. J. Collins and B. M. Benjamin, *J. Am. Chem. Soc.*, **89**, 1652 (1967).

[10] (a) See also J. A. Berson and P. W. Grubb, *ibid.*, **87**, 4016 (1965); and (b) a series of papers by J. A. Berson, *et al.*, *ibid.*, **89**, 2561, 2563, 2569, 2573, 2581, 2590 (1967).

[11] C. C. Lee and L. K. M. Lam, *ibid.*, **88**, 2831 (1966).

[12] C. C. Lee and L. K. M. Lam, *ibid.*, **88**, 5355 (1966).

[13] C. C. Lee and L. K. M. Lam, *ibid.*, **88**, 2834 (1966).

[14] See also K. Humski, S. Borcic, and D. Sunko, *Croat. Chem. Acta*, **37**, 3 (1965).

been concerned[15-24] with the use of multiple-labeling techniques in studying carbonium ions for it is possible thereby to recognize many separate isotope position isomers from differently labeled species of the same reactant. This fact was never more obvious than it now becomes when we consider the recognizable intermediates possible from 2-*exo*-norbornyl brosylate labeled with carbon-14 in the 2 (Ia)[4] or in the 3 position (Ib)[4] or with tritium on position 2 (Ic).[11,12] If we neglect stereochemical differences and ignore, for the moment, 3,2-hydride shift,[12] then the mechanisms for the acetolyses of Iab and Ic can be represented[8,9] as shown in Charts I and II, respectively. The intermediates from Iab are A and B, and the moles of the three isotope position isomers produced are designated m_1, m_2, and m_3 (Chart I). For 2-*exo*-norbornyl-2-*t* brosylate (Ic) the intermediates are A′ and B′, and the mole fractions of each product are m_1', m_2', and m_3' (Chart II). The primary isotope effect of tritium does not concern us here, for tritium migration leads to a structure indistinguishable isotopically from its parent (B′). If we overlook secondary isotope effects of tritium, then k_6 and k_S, respectively, are the specific reaction rate constants for hydride shift and cation–anion collapse (Charts I and II). It can easily be shown (see Appendix) that

$$m_1/m_3 = (k_S/k_6) + 1 \tag{1}$$

and

$$m_1'/m_3' = (k_S/k_6) + {}^1/_2 \tag{2a}$$

If we make a reasonable assumption[25] about the secondary (tritium) isotope effect, then the specific reaction rate constant for B′ → A′ becomes $0.75k_6$, and eq 2a becomes (2b). These equations are also valid (see

$$m_1'/m_3' = (k_S/k_6) + {}^3/_8 \tag{2b}$$

Appendix) if internal return[6] takes place. Thus the distribution of carbon-14 in the product from Iab (Chart I) is predictably different than the distribution of tritium in the product from Ic (Chart II). Provided, therefore, that the carbon-14 and tritium distributions can be measured with sufficient accuracy we should be able to distinguish between the mechanism of Charts I and II and that involving the nortricyclonium ion,[4] for the latter implies that $m_1 = m_1'$, $m_2 = m_2'$, and $m_3 = m_3'$.

Chart I

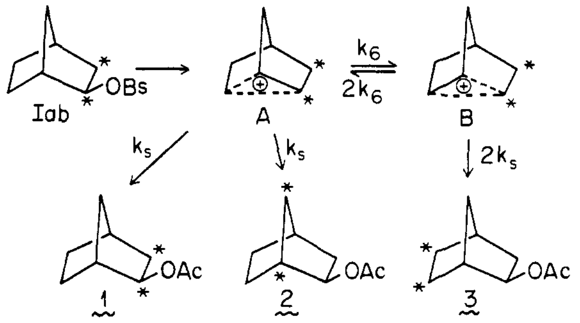
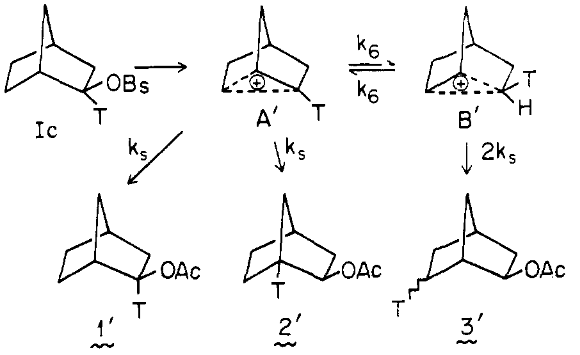


Chart II



Berson and co-workers[10b] in paper V of their recent series derived equations similar to 1, 2a, and 2b to describe the same[4,12] isotopic data, and used their equations to calculate the relative rates of hydride shift and solvent attack. Our equations differ from Berson's[10b] in that we have combined those isotope position isomers which differ stereochemically and have written single structures for them. In addition, we point out the important fact that the *primary* isotope effect of tritium cannot be measured during the solvolyses of Ic, a conclusion implied but not emphasized in the discussion of Lee and Lam [11] (see Appendix B).

The recent report[12] that 3,2-hydride shift occurs in the formolysis of Ic with the indication that a measurable 3,2 shift is also possible in acetolysis complicates the simple schemes shown in Chart I and II and multiplies the number of recognizable intermediates. It has the advantage, however, of providing an explanation for Roberts' observation[4] that the 2-*exo*-norbornyl acetate obtained on acetolysis of Iab apparently contains more carbon-14 in the 1, 4, and 7 positions (45%) than in the 2 and 3 positions (40%).[26]

We have now undertaken an analysis of the solvolyses of Iab and Ic in which we consider *both* 6,2- and 3,2-hydride shifts. This was done primarily because of our interest in demonstrating the potential elegance and power of the isotopic tracer method, which we do not believe has yet been used in so sophisticated a manner as we now hope to indicate is possible. Secondly, it seemed important to obtain whatever additional information could be gleaned about the mechanism of the solvolysis of 2-*exo*-norbornyl brosylate (I) from already existing[4,11,12] tracer data.

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[15] C. J. Collins and W. A. Bonner, *J. Am. Chem. Soc.*, 77, 92, 6725 (1955); 77, 99 (1955).

[16] C. J. Collins, *ibid.*, 77, 5517 (1955).

[17] B. M. Benjamin and C. J. Collins, *ibid.*, 78, 4329 (1956).

[18] V. F. Raaen and C. J. Collins, *ibid.*, 80, 1409 (9158).

[19] B. M. Benjamin, L. W. Kendrick, Jr., and C. J. Collins, *ibid.*, 80, 4057 (1958).

[20] C. J. Collins, W. T. Rainey, W. B. Smith, and I. A. Kaye, *ibid.*, 81, 460 (1959).

[21] C. J. Collins, W. A. Bonner, and W. T. Lester, *ibid.*, 81, 466 (1959).

[22] C. J. Collins, J. B. Christie, and V. F. Raaen, *ibid.*, 83, 4267 (1961).

[23] C. J. Collins and B. M. Benjamin, *ibid.*, **85**, 2519 (1963).

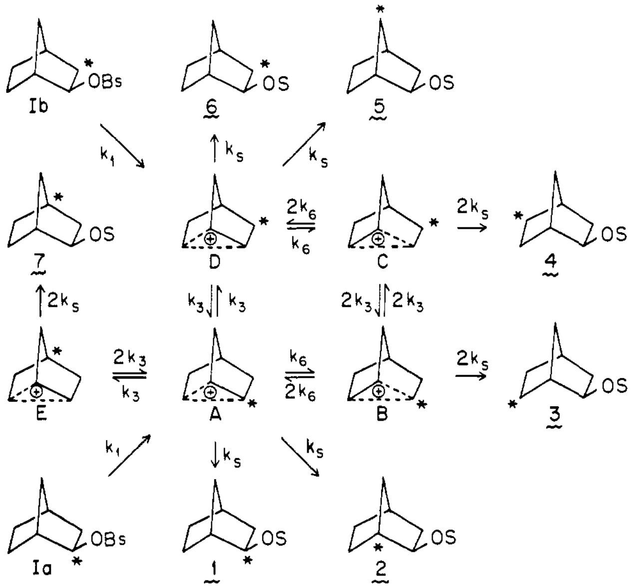
[24] C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *ibid.*, **86**, 4913 (1964).

[25] See, for example, the comprehensive review on secondary isotope effects of deuterium by P. Laszlo and Z. Welvart, *Bull. Soc. Chim. France*, 2412 (1966).

[26] Because of the possibility of an accumulation of errors owing to primary isotope effects during the degradation procedures, it is conceivable that this result[4] could be a consequence of experimental error. Berson (ref 3a, p 145) quotes calculations made by C. E. Dills (Dissertation, Harvard University, 1955) using the data of Roberts, Lee, and Saunders[4] for the carbon-14 distribution in the product of formolysis, at reflux, of a mixture of *exo*- (Iab) and *endo*-2-norbornyl-2,3-$^{14}C_2$ brosylate. Since the sum of per cents of carbon-14 at positions 1, 4, and 7 (40.6%) is so much greater than that at positions 2 and 3 (28.1%), Berson concludes that 3,2 shift, in this case, seems to be established.

Although expansion of the mechanism of Chart I to include 3,2-hydride shift results in an extremely complicated scheme, the problems presented by two carbon-14 labels (C_2 and C_3 in Iab) can be simplified by treating each label separately. Given in Chart III

Chart III



is a mechanism for the solvolysis of Ia (or Ib). Once again we ignored stereochemical differences between the carbonium ions generated; if two stereochemically different structures cannot be differentiated isotopically, they are considered identical for the purpose of Chart III. The 2-labeled reactant Ia leads initially to ion A which can then proceed to the isotope position isomers **1**–**7** through the ions B–E by the processes shown. *exo*-Norbornyl brosylate labeled in the 3 position (Ib) leads initially to ion D in the scheme of Chart III. Equations 3–7 exactly

$$m_3\left(\frac{k_6}{k_S}+\frac{k_3}{k_S}+1\right)=m_1\frac{k_6}{k_S}+m_4\frac{k_3}{k_S}\tag{3}$$

$$m_4\left(\frac{k_6}{k_S}+\frac{k_3}{k_S}+1\right)=m_3\frac{k_3}{k_S}+m_5\frac{k_6}{k_S}\tag{4}$$

$$m_5\left(\frac{k_6}{k_S}+\frac{k_3}{k_S}+2\right)=m_4\frac{k_6}{k_S}+m_1\frac{k_3}{k_S}\tag{5}$$

$$m_7\left(\frac{k_3}{k_S}+1\right)=m_1\frac{k_3}{k_S}\tag{6}$$

$$2m_1+m_3+m_4+2m_5+m_7=1\tag{7}$$

describe the mechanism of Chart III when Ia is the reactant. The specific reaction rate constants k_3, k_6, and k_S, respectively, stand for 3,2- (and 7,1-) hydride shift, 6,1- (and 6,2-, 1,2-, etc.) hydride shift, and irreversible cation–anion collapse to product. The symbols m_1–m_7 represent the mole fractions of each respective isotope position isomer of the product. Since $m_1 = m_2$ and $m_5 = m_6$, m_2 and m_6 have been eliminated from the equations.

Similarly for reactant Ib, which leads to ion D of Chart III, we derived a new set of equations which differ from those pertaining to Ib only in that eq 8 is substituted for eq 5.

$$m_1\left(\frac{2k_3}{k_S}+\frac{k_6}{k_S}+2\right)=m_7\frac{k_3}{k_S}+m_5\frac{k_3}{k_S}+m_3\frac{k_6}{k_S}\tag{8}$$

If we knew the distribution of carbon-14 in each of the seven carbons of 2-*exo*-norbornyl ester formed upon acetolysis or formolysis[4] of Ia or of Ib, we could solve the appropriate equations uniquely for the ratios k_3/k_S and k_6/k_S. Since we know only the sums of carbon-14 percentages in $C_2 + C_3$, $C_1 + C_4$, $C_5 + C$—C_7 is the only position independently determined—it was easier to try arbitrary values of k_3, k_6, and k_S, solve for all mole fractions of product from Ia and, separately, Ib, then average each mole fraction for both cases. In other words, the final value of m_1, for example, is an average of that calculated for an initial 50:50 mixture of reactants Ia and Ib. From these results we obtained the carbon-14 distributions in the form reported by Roberts.[4] The foregoing was accomplished very easily with a program written for the IBM 7090 computer. Several solutions for acetolysis of Iab are given in Table I. From Lee's data[11] it appears possible that during acetolysis there could be as much as 1% of the label originally at carbon 2 transferred to carbon 3. The last column of Table I shows how much of the label of Ia is calculated to transfer to the 3 position of acetolysis product for the given values of k_3, k_6, and k_S. The best fit for acetolysis (calculation 2) requires that 1% of the label of Ia find its way to the 3 position of product. Such a result implies the ratio of 6,2- to 3,2-hydride shift (k_6/k_3) is only 10. A transfer of more than 1% radioactivity from $C_2 \rightarrow C_3$ requires that k_3/k_6 be correspondingly smaller. From calculations 4 and 6 we can make an estimate of the error in our calculation of the ratio k_S/k_6 by assuming arbitrarily that the value[4] for the per cent carbon-14 in $C_{5,6}$ of the acetolysis product is 15 ± 2.5%. Thus, $k_S/k_6 \cong 1.9 \pm 0.6$. A further decrease in k_3 has only an insignificant effect on the ratio k_S/k_6 and the carbon-14 distribution calculated therefrom; as k_3 approaches zero, eq 3–8 collapse to the very simple eq 1. (From eq 1, in which 3,2-hydride shift is neglected, k_S/k_6 = 1.7.)

Table I. A Comparison of the Data of Roberts, *et al.*,[4] for the Acetolysis, at 45°, of Iab with the Data Calculated Using Eq 3–8

Calculation no.	k_S/k_3	k_S/k_6	Acetolysis, % ^{14}C at positions $C_{2,3}$	$C_{1,4}$	C_7	$C_{5,6}$	C
			Obsd[4] values				
			40	23	22	15	<1[a]
1	50	1.79	42.2	21.4	21.2	15.4	0.4[b]
2	18.7	1.87	42.1	21.9	21.3	14.7	1.0[b]
3	3.3	1.65	40.2	23.9	20.8	15.1	4.2[b]
4	20	2.5	43.3	22.4	21.9	12.4	0.96[b]
5	5	2.38	42.1	23.8	21.7	12.4	3.2[b]
6	20	1.34	40.8	21.1	20.6	17.5	0.9[b]
7	2.5	1.25	38.7	23.9	20.1	17.3	5.0
	Best values		$k_S/k_3 \geqq 19$; $k_S/k_6 = 1.9 \pm 0.6$				

[a] Estimated per cent of the carbon-14 of Ia transferred to carbon 3 from data of Lee and Lam.[11] [b] Calculated per cent of the carbon-14 of Ia transferred to carbon 3.

The results of our analysis of Roberts'[4,5,26] data for formolysis of a mixture of *endo*- and *exo*-Iab are given in Table II. Here we were forced to assume that both components of the mixture solvolyze through the same

Table II. A Comparison of the Data of Roberts, *et al.*,[4] for the Formolysis, at Reflux, of a Mixture of *exo*- and *endo*-Iab with the Data Calculated Using eq 3–8

Calculation no.	k_S/k_3	k_S/k_6	Formolysis, % ^{14}C at positions $C_{2,3}$	$C_{1,4}$	C_7	$C_{5,6}$	C_3
			Obsd[4] values				
			31.3	22.1	18.5	28.1	
1	1.5	0.167	32.8	22.1	17.0	28.1	6.8[a]
2	0.5	0.125	31.1	25.1	16.1	27.7	10.2[a]
3	2.5	0.25	34.0	21.1	17.6	27.2	5.0[a]
4	3.0	0.33	34.6	20.9	17.8	26.6	4.5[a]
5	0.77	0.1	31.4	23.7	16.3	28.6	9.0[a]
6	0.5	0.05	30.5	24.6	15.7	29.1	15.7[a]
Best values			$k_S/k_3 = 1.5 \pm 1$; $k_S/k_6 = 0.17 \pm 0.1$				

[a] Per cent carbon-14 originally in 2 position of Ia calculated to transfer to 3 position.

intermediates; k_6/k_3 is equal to about 10 but k_S/k_3 decreases to about 1.5. Thus formolysis of singly labeled Ia should result in a transfer of at least 5% of the original carbon-14 to the 3 position of the product.

We next turned our attention to the acetolysis[11] and formolysis of 2-*exo*-norbornyl-2-*t* brosylate (Ic).

Chart IV

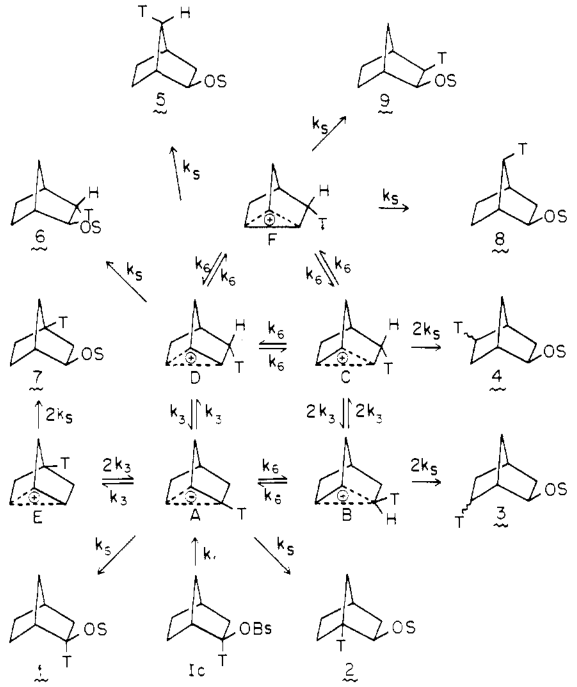


Chart IV shows all of the isotopically distinguishable intermediate carbonium ions resulting from 6,2- and 3,2-hydride shift and the products to which they lead. Fortunately the primary isotope effect for tritium migration can be ignored, for whenever tritium shifts to an adjacent carbon it forms a new cation isotopically indistinguishable from (although enantiomeric with) the old one. Following are the equations applicable to Chart IV.

$$m_3\left(\frac{3k_6}{8k_S} + \frac{k_3}{k_S} + 1\right) = m_1\frac{k_6}{k_S} + m_4\frac{k_3}{k_S} \tag{9}$$

$$m_4\left(\frac{k_6}{k_S} + \frac{k_3}{k_S} + 1\right) = m_3\frac{k_3}{k_S} + m_5\frac{k_6}{k_S} + m_8\frac{k_6}{k_S} \tag{10}$$

$$m_5\left(\frac{2k_6}{k_S} + \frac{3k_3}{4k_S} + 2\right) = m_1\frac{k_3}{k_S} + m_4\frac{k_6}{2k_S} + m_8\frac{k_6}{k_S} \tag{11}$$

$$m_7\left(\frac{k_3}{k_S} + 1\right) = m_1\frac{k_3}{k_S} \tag{12}$$

$$m_8\left(\frac{2k_6}{k_S} + 2\right) = m_4\frac{k_6}{2k_S} + m_5\frac{k_6}{k_S} \tag{13}$$

$$2m_1 + m_3 + m_4 + 2m_5 + m_7 + 2m_8 = 1 \tag{14}$$

The secondary isotope effect is easily allowed for by making two small changes in the transformations B → A and D → A. If we assume that hydrogen attached to C–T shifts at three-fourths the rate of hydrogen attached to C–H,[25] then the specific reaction rate constants for B → A and D → A, respectively, become $0.75k_6$ and $0.75k_3$, requiring only minor changes in eq 9 and 11.[27] From Table III it is clear that for acetolysis of Ic at 45°, $k_S/k_6 = 1.55 \pm 0.35$ (although individual calculations are not recorded, for acetolysis[11] of Ic at 25°, $k_S/k_6 = 1 \pm 0.25$).

Table III. A Comparison of the Data of Lee and Lam[11] for the Acetolysis, at 45°, of Ic with the Data Calculated Using Eq 9–14

k_S/k_3	k_S/k_6	Acetolysis, % ^{14}C at positions $C_{2,3}$	$C_{1,4,7}$	$C_{5,6}$	C_3
		Obsd[11,a] values			
		39.45	40.05	20.45	*Ca.* 0.2[b]
200	2	41.2	41.4	17.4	0.1
155	1.55	39.6	39.9	20.5	0.1
130	1.3	38.4	38.7	22.9	0.16
120	1.2	37.9	38.2	23.9	0.17
20	1.54	39.0	40.9	20.1	0.9
20	1.82	40.0	41.9	18.0	0.9
12	1.5	38.5	41.3	20.1	1.3
Best values		$k_S/k_3 \geqq 120$; $k_S/k_6 = 1.55 \pm 0.35$			

[a] Average values of two runs.[11] [b] Not significant, since the blank (1.05%) is the same as the observed value (1.3%) within experimental error.

The results of our application of eq 9–14 to the formolysis[12] of Ic (at 25°) are shown in Table IV, from which it is evident that the results of Lee and Lam[12] (excepting the tritium content in the 3 position of the formolysis product) are consistent with $k_S/k_6 \cong 1.25 \pm 0.25$, very little different from the situation in acetolysis. In connection with the anomalous percentage of tritium (5–6%) in carbon 3, it is instructive to see how the tritium contents of $C_{2,3}$ and $C_{1,4,7}$ vary as a function of 3,2-hydride shift (k_3). Given in Figure 1 is such a

Table IV. A Comparison of the Data of Lee and Lam[12] for the Formolysis, at 25°, of Ic with the Data Calculated Using Eq 9–14

k_S/k_3	k_S/k_6	Formolysis, % ^{14}C at positions $C_{2,3}$	$C_{1,4,7}$	$C_{5,6}$	C_3
		Obsd[11] values			
		37.25	39.15	23.55	*Ca.* 6
300	1	36.6	36.7	26.6	0.1
125	1.25	38.1	38.5	23.4	0.15
100	1.25	38.1	38.5	23.3	0.14
30	1.25	37.9	39.1	23.1	0.46
15	1.5	38.7	41.0	20.2	0.9
Best values		$k_S/k_3 \geqq 30$; $k_S/k_6 = 1.25 \pm 0.25$			

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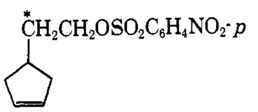
[27] These changes are shown in the foregoing equations. Since the secondary isotope effect does not greatly alter the results only the latter data (with the isotope effect) are recorded in Table II.

plot in which k_6/k_3 increases from 1 to 20 while k_6/k_S remains constant at unity. A C_3 tritium content of 5% (Figure 1) requires that $k_S/k_3 = 1.6$, and that $C_{2,3}$ and $C_{1,4,7}$ are 33.8 and 43.3%, respectively, or a difference of nearly 10%. The tritium content of C_3 is dependent almost wholly on the ratio k_3/k_S, and is relatively insensitive to changes in k_6. This means that the 5–6% tritium content in C_3 observed in the formolysis product of Ic is incompatible with the tritium contents of $C_{2,3}$ (37.25%) and $C_{1,4,7}$ (39.15%) reported by Lee and Lam. Even if we assume C_3 contains only 3% of the tritium, the difference in tritium content between $C_{1,4,7}$ and $C_{2,3}$ is about 8% (see also Berson, *et al.*,[10b] p 2585).

Our final calculations related to the π-route solvolyses[13] of 2-(Δ³-cyclopentenyl)-2-¹⁴C-ethyl *p*-nitrobenzenesulfonate (III). Since III is directly converted to ion C (Chart III), eq 3 and eq 5–8 are applicable to the solvolyses of III. The results for formolysis at 60° are shown in Table V. The data for acetolysis are incompatible with the bridged-ion mechanism of Chart III, but can be correlated with a mechanism including only equilibrating classical ions, as discussed later in this paper.



$\overset{*}{C}H_2CH_2OSO_2C_6H_4NO_2\text{-}p$

III

Table V. A Comparison of the Data of Lee and Lam[13] for the Formolysis, at 60°, of III with the Data Calculated Using Eq 3 and 5–8

		Formolysis, % ¹⁴C at positions			
		$C_{2,3}$	$C_{1,4}$	C_7	$C_{5,6}$
		Obsd[13] values			
k_S/k_3	k_S/k_6	31.45	3.4	26.45	38.7
4.0	0.25	29.2	4.7	25.2	40.9
5.0	0.135	30.4	3.9	27.0	38.7
5.9	0.131	30.5	3.4	27.5	38.6
5.9	0.079	31.5	3.4	28.6	36.5
Best values		$k_S/k_3 = 5 \pm 1$; $k_S/k_6 = 0.13 \pm 0.08$			

Discussion

In Table VI we summarize the values calculated for k_S/k_3 and k_S/k_6 for the various solvolyses of Iab, Ic, and III. Only in the formolyses[4] of Iab and of III is there any evidence for 3,2 shift of hydrogen *during solvolysis.* The 5–6% of tritium observed[12] in the 3 position of the solvolysis product of Ic must be a consequence of some additional process[28] not included in Charts III and IV. This conclusion rests on the fact that 3,2 shift (k_3) in conjunction with 6,2 shift (k_6) of hydrogen causes tritium from Ic (or the carbon-14 from Iab) to be distributed among all seven positions of the solvolysis product, requiring the fraction of radioactivity in the 1, 4, and 7 positions to be predictably greater (see Figure 1) than the fraction in positions 2 and 3. In the formolysis[4] product from Iab the amount of carbon-14 in $C_{1,4,7}$ exceeds that in $C_{2,3}$ by 10% of the total carbon-14 content; this corresponds to a k_S/k_3 ratio of about 1.5–2, and means that k_6/k_3 is about 10,[29] and $k_S/k_3 \cong 1.5$.

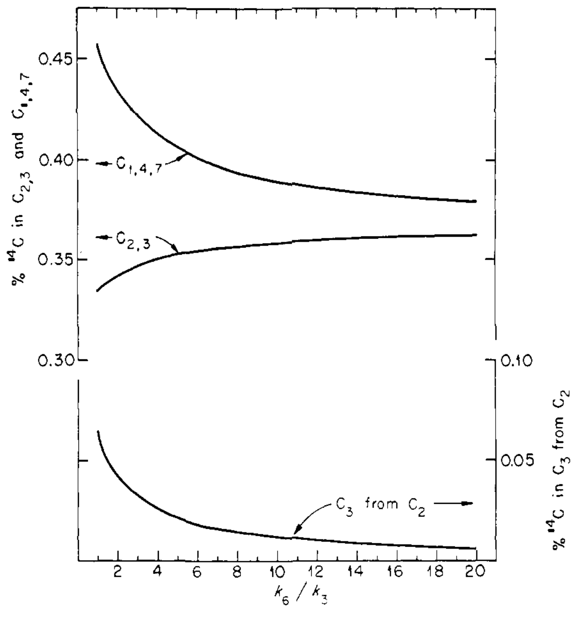
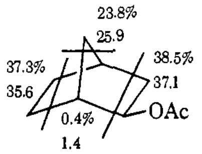


Figure 1. A plot of the variation of the carbon-14 contents of $C_{1,4,7}$ and $C_{2,3}$ in the solvolysis product of Ic as a function of k_6/k_3.

A comparison of the ratios k_S/k_6 in Table VI seems to indicate that at 25° the nucleophilicity of formic acid *for the norbornyl cation* is nearly identical with that of acetic acid (k_S/k_6 = 1–1.5). At higher temperatures, however, the values are considerably less, and this is reflected both in the σ-route (Iab) and π-route (Ic) formolyses.[30]

Perhaps the most interesting data analyzed in the present paper are those of Lee and Lam[13] for π-route acetolysis of III. The results of two separate runs are as follows.



The per cent of carbon-14 in positions 1 and 4 is barely on the threshold of significance, so the complicating factor of 3,2 shift can be ignored. The considerably greater amount of carbon-14 in the 2 and 3 positions *vs.* that in position 7 is well beyond any conceivable experimental error, but is completely unexplainable through nonclassical norbornyl carbonium ion intermediates alone. Thus, if III solvolyzes through the nonclassical ions C and D (Chart V), the mole fraction of **6** can never be greater than the mole

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(28) There is some evidence[11,12] that the solvolysis products themselves undergo isotope position isomerization. If this results from partial reversibility our calculated ratios k_6/k_S and k_3/k_S would be too large.

(29) The value $k_6/k_3 \cong 10$ is in marked contrast to the value $k_6/k_3 \geqq 10^9$ estimated by M. Saunders, P. von R. Schleyer, and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 5680 (1964), for the norbornyl cation in SbF_5–SO_2–SO_2F_2 over a wide range of temperature. See also J. A. Berson, R. G. Bergmann, J. H. Hammons, and A. W. McRowe, *ibid.*, **87**, 3246 (1965), who estimated that k_S/k_3 in the 3-*endo*-methyl-2-norbornyl cation formed upon acetolysis of the appropriate brosylate is at least 119, and J. A. Berson, *et al.*, *ibid.*, **89**, 2589 (1967), who discuss the results of Lee and Lam.[11,12]

(30) The nucleophilicity scale measured on this basis depends on the tenuous assumption (see later discussion) that 6,2-hydrogen migration (k_6) remains constant with temperature and changes in solvent.

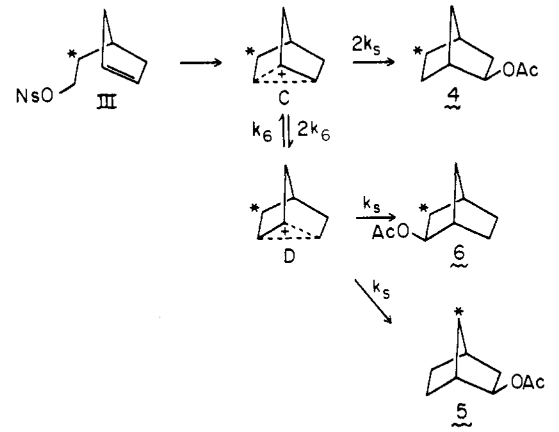
Table VI. Summary of Values Calculated for k_S/k_3 and k_S/k_6 from Isotopic Distribution in Products of Solvolysis of Iab, Ic, and III

Reactant	Solvent	Temp, °C	k_S/k_3	k_S/k_6	k_S/k_c[a]
Ic[11]	Acetic acid–sodium acetate	25	>120	1 ± 0.25	...
Ic[11]	Acetic acid–sodium acetate	45	>20	1.55 ± 0.35	...
Iab[4]	Acetic acid–sodium acetate	45	>20	1.9 ± 0.6	...
Ic[12]	Formic acid–sodium formate	25	>30	1.25 ± 0.25	...
Iab[4]	Formic acid–sodium formate	Reflux	1.5 ± 1	0.17 ± 0.1	...
III[13]	Formic acid	60	5 ± 1	0.125 ± 0.025	...
III[13]	Acetic acid	60		0.02	0.33

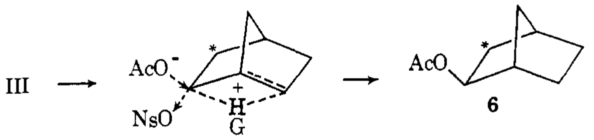
[a] k_c is the specific reaction rate constant for interconversion of the presumed classical ions of Chart VI.

fraction of **5**. Lee and Lam[13] suggest that the nonclassical ions C and D compete with a concerted mechanism involving a transition state similar to G

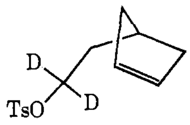
Chart V



which would, of course, allow the radioactivity in $C_{2,3}$ to exceed that in $C_{1,4,7}$. The π-route acetolysis



of IIIa, carried out by Humski, Borcic, and Sunko,[14]

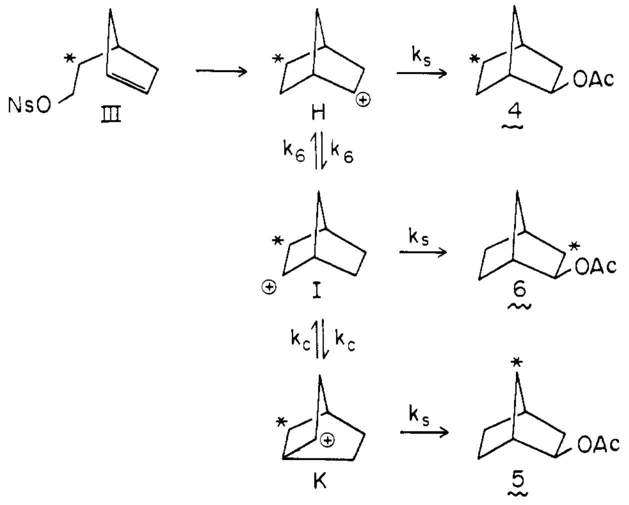


IIIa

however, does not indicate concerted hydrogen migration (transition state G) during the rate-determining step, since the isotope effect (at 44.6° $k_H/k_D = 1.13$) is too small.

There is, however, a simple and easy way out of the dilemma posed by the radioactivity distribution in the product of acetolysis of III, and that is the classical carbonium ion mechanism portrayed in Chart VI. As in all of our previous schemes (Charts I–V) we distinguish only isotopically different species. It is clear that if the rate I → K or K → I (k_c) is not fast with respect to solvent attack (k_S), then, as observed,[13] the mole fraction of **6** will be greater than that of **5**. We wish to make it clear that at this time we take no particular stand in favor of the scheme shown in Chart VI. We merely point out that it is consistent with the tracer results of Lee and Lam,[13] whereas the mechanism (Chart V) in which we have written nonclassical intermediates is not.

Chart VI



Equations 15 and 16 apply to the mechanism of

$$m_6/m_5 = (k_S/k_c) + 1 \tag{15}$$

$$m_6\left(\frac{k_6}{k_S} + \frac{k_c}{k_S} + 1\right) = m_4\frac{k_6}{k_S} + m_5\frac{k_c}{k_S} \tag{16}$$

Chart VI. From these equations we can calculate that when $k_S/k_c = {}^1/_3$ and $k_S/k_6 = 0.022$, then $m_4(C_{5,6}) = 37.25$, $m_5(C_{1,4,7}) = 26.89$, and $m(C_{2,3}) = 35.85$, within experimental error the same as the distribution observed[13] by Lee and Lam. As pointed out by Bartlett,[31] the norbornyl cation generated through the π route is situated quite differently with respect to the leaving anion than corresponding cations generated by solvolyses of 2-*exo*-norbornyl derivatives, and this is reflected by the lack of internal return during π-route solvolyses. Whereas acetolysis of 2-*exo*-norbornyl brosylate (I) results in internal return[6] and shielding against solvent attack by the leaving group, π-route acetolysis of III generates a norbornyl cation in which there should be no shielding by the leaving group, and solvent attack should be favored. Unfortunately, the label in III (and H, Chart VI) tells us nothing about

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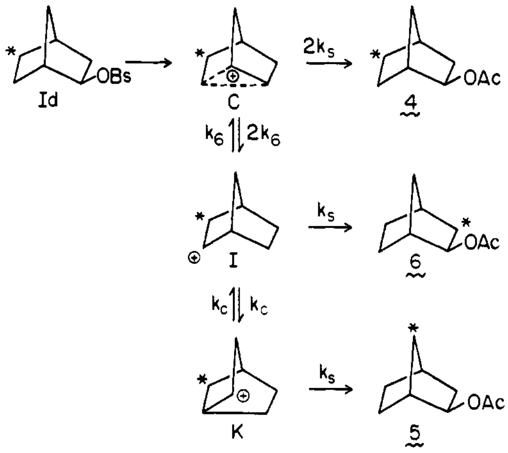
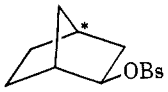
(31) P. D. Bartlett and G. D. Sargent, *J. Am. Chem. Soc.*, **87**, 1297 (1965); P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *ibid.*, **87**, 1288 (1965).

Wagner–Meerwein rearrangement *before* 6,1- or 6,2-hydride shift, for Wagner–Meerwein rearrangement of ion H produces the isotopically indistinguishable mirror image of H. It seems reasonable, however, that in the time sequence required for the processes III → H → I → K (Chart VI), there should also be no counterion available for ion-pair formation with I ⇌ K. Thus during π-route solvolyses both solvent attack (k_S) and hydride shift (k_H) might be expected to increase. Solvent attack should increase primarily because the leaving group is no longer in the way, and hydride shift should be faster because the counterion does not contribute to charge localization, as in σ-route solvolyses. If the ions of Charts I–V are really rapidly equilibrating classical carbonium ions then during σ-route solvolyses (Iab, Ic) it is possible that the leaving anion slows down k_S and k_6 so that the rate (k_c) of Wagner–Meerwein equilibration is fast enough to simulate a nonclassical ion. The position of the labels in Iab and Ic would prevent us from observing an accelerated solvent attack (k_S) or hydride shift (k_6) once ion A (Charts I, II, III, and IV) had been converted to ion B. After hydride shift has taken place in solvolysis of 2-*exo*-norbornyl brosylate (I), however, the norbornyl cation so generated should be without its counterion, and it might be possible then for solvent attack (k_S) to compete successfully with Wagner–Meerwein rearrangement (k_c, Chart VI). Thus a definitive experiment which immediately suggests itself is the solvolysis of Id, 2-*exo*-norbornyl-5-^{14}C brosylate (see Chart VII). Here the ion C (which for convenience is written in its nonclassical form) can react with solvent to give *only* the isotope position isomer **4**. Hydride shift, either 6,1 or 6,2, produces either classical ion I or the nonclassical ion corresponding to the equilibrating pair I ⇌ K. Since the counterion has departed from the other side of cation I, solvent attack might now compete successfully with Wagner–Meerwein rearrangement (k_c). Thus if the ions I ⇌ K are classical we might expect a significantly greater fraction of isomer **6** than of isomer **5** (Chart VII).

Chart VII



Two final points should be made. (1) The available isotopic data[4,11–13] for the solvolyses of I and III are not accurate enough to allow us to choose between a mechanism involving the nortricyclonium ion[4] and the intermediates of Charts I–V. (2) Although 3,2 shift of hydrogen seems established and k_6/k_3 can apparently be much smaller in formic and acetic acids than the value of 6 × 10^8 calculated by Saunders, Schleyer, and Olah[28] under vastly different conditions, more precise isotopic data will be required before the ratio k_6/k_3 can be calculated under all solvolytic conditions with confidence. We propose to study 3,2 shift with the isotope position isomer Ie, for only through 3,2 shift can carbon-14 escape the 4 position. The syntheses of both Id and Ie are now underway.



Ie

Appendix

A. Demonstration That Internal Return Does Not Affect the Final Product Ratio.[31a] Since the same uncomplicated method[17] was used to obtain each of eq 1–16, only a sample calculation will be given here. For the derivation of eq 1 (from Chart I)

$$\frac{\mathrm{d}[\mathbf{1}]}{\mathrm{d}t} = k_S[\mathrm{A}]$$

$$\frac{\mathrm{d}[\mathbf{3}]}{\mathrm{d}t} = 2k_S[\mathrm{B}]$$

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k_6[\mathrm{A}] - 2k_6[\mathrm{B}] - 2k_S[\mathrm{B}]$$

Integrate between 0 and ∞

$$m_1 = k_S\int_0^\infty [\mathrm{A}]\mathrm{d}t = \text{mole fraction of } \mathbf{1} \text{ produced}$$

$$m_3 = 2k_S\int_0^\infty [\mathrm{B}]\mathrm{d}t = \text{mole fraction of } \mathbf{3} \text{ produced}$$

$$k_6\int_0^\infty [\mathrm{A}]\mathrm{d}t - 2k_6\int_0^\infty [\mathrm{B}]\mathrm{d}t - 2k_S\int_0^\infty [\mathrm{B}]\mathrm{d}t = 0$$

Now replace the integrals $\int_0^\infty[\mathrm{A}]\mathrm{d}t$ and $\int_0^\infty[\mathrm{B}]\mathrm{d}t$ with the "integration areas"[17] S_A and S_B

$$S_A = m_1/k_S \qquad S_B = m_3/2k_S$$

$$k_6S_A = 2k_6S_B + 2k_SS_B$$

and after substituting for S_A and S_B we obtain

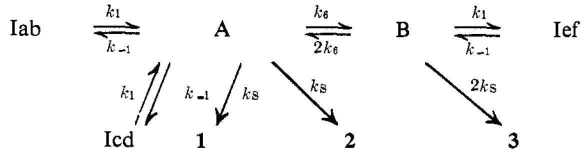
$$m_1/m_3 = (k_S/k_6) + 1 \tag{1}$$

since $m_1 + m_2 + m_3 = 1$ and $m_1 = m_2$.

To consider internal return, Chart I is modified as shown in Chart VIII.

(31a) NOTE ADDED IN PROOF. A referee has objected to our statement "internal return does not affect the final product ratio" on the grounds that internal return[6] implies ion-pair formation, and ion pairs are not included in our derivations. It is true that the inclusion of ion pairs complicates the mechanism, for, as pointed out elsewhere in this paper, k_3, k_6, and k_S need not necessarily be the same at the various ion-pair stages and in the separated carbonium ions. The term "internal return," however, applied to the isotope position isomers of I, implies recombination of carbonium ion and brosylate anion to generate (reversibly) unrearranged and rearranged 2-*exo*-norbornyl brosylate. Our point here is that whether or not there is reversible formation of norbornyl cation and brosylate anion, the final carbon-14 distribution in the product should be the same. Our only assumption is that the product itself is stable under the reaction conditions. Since the ratios k_6/k_S and k_3/k_S are average ratios for the processes represented at various ionic stages, we believe our statement that "internal return does not affect the final product ratio" is justified.

Chart VIII



Icd = 2-*exo*-norbornyl-1,7-$^{14}C_2$ brosylate
Ief = 2-*exo*-norbornyl-5,6-$^{14}C_2$ brosylate

As in the derivation of eq 1, the following expressions can be obtained.

$$k_1S_{\text{Iab}} - k_1S_\text{A} + k_1S_{\text{Icd}} - k_{-1}S_\text{A} - k_6S_\text{A} + 2k_6S_\text{B} - 2k_\text{S}S_\text{A} = 0$$

$$k_{-1}S_\text{A} - k_1S_{\text{Iab}} = -1 = -2m_1 - m_3$$

$$k_{-1}S_\text{A} - k_1S_{\text{Icd}} = 0$$

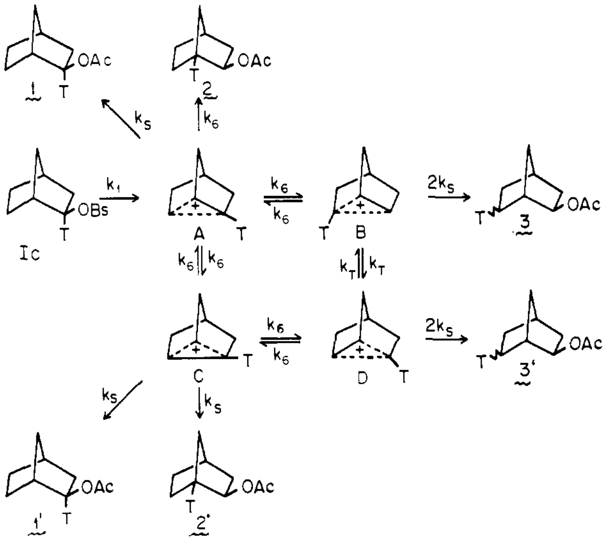
Add the foregoing three equations, substitute for S_A and S_B, and simplify, from which

$$m_1/m_3 = (k_\text{S}/k_6) + 1 \qquad (1)$$

Thus the same expression (eq 1) is obtained with or without considering internal return.

B. Demonstration That an Intramolecular Primary Isotope Effect Is Unobservable during Solvolysis of Ic. A primary *kinetic* isotope effect during solvolysis of Ic would be possible only if the tritium atom were somehow involved in the rate-determining ionization, but this event seems to be excluded by the experimental data of Lee and Wong.[32] The question still remains, however, whether a primary *intramolecular* isotope effect upon the product ratio can be observed.[33] It seems clear to us from inspection of Charts II and IV that when the tritium (in the intermediates derived on solvolysis of Ic) migrates, it always produces a structure indistinguishable from its parent. Thus, by inspection, we can say that the rates of intramolecular migration of tritium with respect to the rates of intramolecular migration of hydrogen have no effect upon the final product ratio. In other words, there is no observable intramolecular isotope effect. Chart IX shows the four intermediates used by Berson, *et al.*,[34] and treats tritium migration as a distinct process. We assigned the same specific reaction rate constants used in Charts I and II to the identical processes of Chart IX, plus the constant k_T, which is the rate of tritium migration between the ions B and D of Chart IX.[35]

Chart IX[a]



[a] Chart based on Scheme IV, ref 34.

At infinite time (when the reaction is over): m_1 is the mole fraction of **1**, m_1' is the mole fraction of **1'**, m_2 is the mole fraction of **2**, etc. Also, $m_1 = m_2$, $m_1' = m_2'$, and $\Sigma m_i = 1$.

In the same manner employed in Appendix A we can easily show

$$\frac{\text{d[B]}}{\text{d}t} = k_6[\text{A}] - k_6[\text{B}] - k_\text{T}[\text{B}] + k_\text{T}[\text{D}] - 2k_\text{S}[\text{B}]$$

and

$$k_6S_\text{A} + k_\text{T}S_\text{D} = S_\text{B}(k_6 + k_\text{T} + 2k_\text{S})$$

It is obvious that $S_\text{A} = m_1/k_\text{S}$, $S_\text{B} = m_3/2k_\text{S}$, $S_\text{C} = m_1'/k_\text{S}$, and $S_\text{D} = m_3'/2k_\text{S}$.

Making the appropriate substitutions we find

$$\frac{k_6}{k_\text{S}}m_1 + \frac{k_\text{T}}{2k_\text{S}}m_3' = m_3\left(\frac{k_6}{2k_\text{S}} + \frac{k_\text{T}}{2k_\text{S}} + 1\right) \qquad (17)$$

In like manner we can set up the equation for formation and destruction of ion D (Chart IX) and show

$$\frac{k_\text{T}}{2k_\text{S}}m_3 + \frac{k_6}{k_\text{S}}m_1' = m_3'\left(\frac{k_\text{T}}{2k_\text{S}} + \frac{k_6}{2k_\text{S}} + 1\right) \qquad (18)$$

If we now add eq 17 and 18

$$\frac{k_6}{k_\text{S}}m_1 + \frac{k_6}{k_\text{S}}m_1' + \frac{k_\text{T}}{2k_\text{S}}m_3 + \frac{k_\text{T}}{2k_\text{S}}m_3' = (m_3 + m_3')\left(\frac{k_\text{T}}{2k_\text{S}} + \frac{k_6}{2k_\text{S}} + 1\right)$$

Structures **1** and **1'** are identical as are structures **2** with **2'** and **3** with **3'**. Therefore let us state the identities

$$M_1 = m_1 + m_1' \qquad M_3 = m_3 + m_3'$$

and substitute

$$M_1\frac{k_6}{k_\text{S}} + M_3\frac{k_\text{T}}{2k_\text{S}} = M_3\frac{k_\text{T}}{2k_\text{S}} + M_3\frac{k_6}{2k_\text{S}} + M_3$$

upon which the functions $M_3k_\text{T}/2k_\text{S}$ cancel, leading to the equation

$$M_1/M_3 = (k_\text{S}/k_6) + {}^1/_2$$

The foregoing equation is identical with eq 2a, thus demonstrating that the primary intramolecular isotope effect during solvolysis of Ic should be unobservable.

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[32] C. C. Lee and E. W. C. Wong, *J. Am. Chem. Soc.*, **86**, 2752 (1964).

[33] For a discussion of the experimental complexities in such observations, see C. J. Collins, *Advan. Phys. Org. Chem.*, **2**, 60 (1964).

[34] J. A. Berson, *et al.*, *J. Am. Chem. Soc.*, **89**, 2588 (1967), Scheme IV.

[35] The rate constants k_6 and k_S of Chart IX are, in fact, one-half the values of k_6 and k_S in the other charts. Since the final eq 1 contains the simple ratio k_S/k_6, this constant factor of one-half cancels.