The Acetolysis of *exo-* and *endo*-2-*t*-2-Norbornyl Brosylates[1a]

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Abstract: The acetolysis of *exo-* and *endo*-2-*t*-2-norbornyl brosylates gave products in which the isotopic distributions may be explained by a combination of the processes of (1) complete equivalence of all carbons, (2) C-1 and C-2 equivalent, and (3) C-1, C-2, and C-6 equivalent. In the *endo* case, there is also some S_N2 contribution. The results confirm the earlier findings of Roberts and co-workers from their studies with ^{14}C labeling, but the contributions of the various processes are more clearly delineated by the present data. A small amount of 3,2 hydride shift is indicated and this together with Wagner–Meerwein 6,2, and 6,1 hydride shifts resulted in all carbons being equivalent. The present results also support a mechanism in which hydride shifts occur sequentially following, rather than competitively with, the formation of the Wagner–Meerwein intermediate. Acetolysis of the *exo* brosylate at 25 and and 45° indicated the formation of a lesser proportion of products from 6,2 and 6,1 hydride shifts at the higher temperature. This observation suggests that for the initially formed ion, as the temperature is raised, the rate of its reaction with solvent increases more rapidly than the rate of 6,2 and 6,1 hydride shifts. A possible implication of this finding in relation to the acetolysis of the *endo* brosylate carried out at reflux temperature is discussed.

From an investigation of the solvolyses of *exo-* and *endo*-2,3-$^{14}C_2$-2-norbornyl brosylates (*exo-* and *endo*-I-OBs-2,3-$^{14}C_2$), Roberts and co-workers[2] have demonstrated a net 6,2 hydride shift, besides the Wagner–Meerwein rearrangement, in the norbornyl cation. The observed isotope position rearrangements were interpreted in terms of nonclassical carbonium ions. In recent years, however, rapidly equilibrating classical ions have been suggested as an alternative to nonclassical ions and this matter still remains controversial.[3] In the work with *exo-* and *endo*-I-OBs-2,3-$^{14}C_2$, a direct observation of the 3,2 hydride shift is not possible, although a comparison of the ^{14}C activities at C-7 and at C-1 and C-4 of the product suggested that 3,2 hydride shift may be important in formolysis. A clear-cut choice also could not be made[4a] between the sequential or competitive occurrence of the 6,2 hydride shift and Wagner–Meerwein rearrangement. In the present work, acetolyses of *exo-* and *endo*-2-*t*-2-norbornyl brosylates (*exo-* and *endo*-I-OBs-2-*t*) were studied to provide data which should confirm the earlier results from ^{14}C labeling and also might yield further information regarding the various rearrangement processes that may take place with the norbornyl cation.

Results and Discussion

Reduction of 2-norbornanone (II) with $LiAlH_4$-*t* gave a mixture of about 90% *endo-* and 10% *exo*-2-*t*-2-norbornanols.[5] Conversion of the mixed alcohols to the brosylates followed by selective solvolysis in aqueous acetone[2] gave pure *endo*-I-OBs-2-*t*. Reaction of the *endo* brosylate with tetramethylammonium acetate in anhydrous acetone,[6] followed by reduction ($LiAlH_4$), gave *exo*-I-OH-2-*t* which was converted to pure *exo*-I-OBs-2-*t*. Oxidation of *exo*-I-OH-2-*t* to II[7] resulted in the recovery of 0 ± 0.5% of the original activity, indicating the location of essentially all of the label at C-2.

Acetolyses of *exo-* and *endo*-I-OBs-2-*t* were carried out in the presence of added acetate ions, reactions with the *exo* epimer being effected at 25 and at 45° for 24 hr and with the *endo* epimer at reflux temperature for 20 hr. In the analogous studies with the ^{14}C-labeled brosylates,[2] the *exo* epimer was acetolyzed at 45° for 20 min and the *endo* epimer at reflux temperature for 20 hr. The resulting *exo*-I-OAc-*t* was converted to *exo*-I-OH-*t* ($LiAlH_4$), part of which was oxidized to II[7] and the remainder degraded to *cis*-cyclopentane-1,3-dicarboxylic acid (III) to *cis*-cyclopentane-1,3-diamine to succinic acid (IV).[2] Determination of the specific activities of *exo*-I-OH-*t*, II (as the semicarbazone), III, and IV gave the tritium contents at C-2, C-3, C-1,4,7, and C-5,6. The results are summarized in Table I. When *exo*-I-OAc-2-*t* was stirred in HOAc–NaOAc at 25° for 24 hr, recovered, and degraded, some rearrangements were also observed and the results are included in Table I.

Data in Table I show that a small portion of the rearrangements could have taken place subsequent to the formation of *exo*-I-OAc-*t*. The activities detected at C-3 indicated small amounts of a net 3,2 hydride shift,[8] most, if not all, of which could have resulted from subsequent ionization of *exo*-I-OAc-*t*. The occurrence of 3,2 hydride shift, together with Wagner–Meerwein and 6,2-hydride shifts, would give a complete equilibration of the *t* label over all seven carbon positions.

The rearrangements arising from the acetolyses shown in Table I can be dissected into three processes: (1) complete equivalence of all seven carbons, (2) C-1 and

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[1] (a) Supported by a grant from the National Research Council of Canada; (b) holder of a Canadian Industries Limited Fellowship, 1964–1966.

[2] J. D. Roberts and C. C. Lee, *J. Am. Chem. Soc.*, **73**, 5009 (1951); J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *ibid.*, **76**, 4501 (1954).

[3] For leading references, see (a) H. C. Brown and M.-H. Rei, *ibid.*, **86**, 5008 (1964); (b) S. Winstein, *ibid.*, **87**, 381 (1965).

[4] J. A. Berson in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963: (a) pp 145–148; (b) pp 179, 180.

[5] (a) C. C. Lee and E. W. C. Wong, *Can. J. Chem.*, **43**, 2254 (1965); (b) R. Howe, E. C. Friedrich, and S. Winstein, *J. Am. Chem. Soc.*, **87**, 379 (1965).

[6] C. C. Lee and E. W. C. Wong, *ibid.*, **86**, 2752 (1964).

[7] A. Nickon and J. H. Hammons, *ibid.*, **86**, 3322 (1964).

[8] J. A. Berson, R. G. Bergman, J. H. Hammons, and A. W. McRowe, *ibid.*, **87**, 3246 (1965); J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Ramanick, and D. Houston, *ibid.*, **87**, 3248 (1965).

Table I. Tritium Distributions

	Tritium content, %[a]							
	C-2		C-3		C-1,4,7		C-5,6	
Reaction	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
exo-I-OAc-2-*t* in HOAc -NaOAc, 25°, 24 hr	96.0	96.5	1.0	1.1	2.2	1.7	0.8	0.7
Acetolysis, *exo*-I-OBs-2-*t*, 25°, 24 hr	34.3	35.6	1.8	2.1	37.3	35.7	26.6	26.6
Acetolysis, *exo*-I-OBs-2-*t*, 45°, 24 hr	38.3	38.0	1.3	1.3	40.1	40.0	20.2	20.7
Acetolysis, *endo*-I-OBs-2-*t*, reflux, 20 hr	37.8	37.6	0.8	0.8	36.3	35.4	25.1	26.1

[a] Activities measured by a liquid scintillation counter. In various runs, 100% corresponded to specific activities ranging from about 120,000 to 390,000 counts/min/mmole. In some experiments, the specific activity of the starting brosylate was shown to be the same as that of the resulting *exo*-I-OH-*t*, indicating no loss of tritium during acetolysis.

Table II. Calculated Tritium Distributions for Acetolyses of *exo*- and *endo*-I-OBs-2-*t*

	% contribution			Calcd % *t*, *exo*								Calcd % *t*, *endo*			
	exo		*endo* at reflux	C-2		C-3		C-1,4,7		C-5,6					
Process	25°	45°		25°	45°	25°	45°	25°	45°	25°	45°	C-2	C-3	C-1,4,7	C-5,6
S_N2	0	0	5									5.0			
Complete equivalence	10	7	5	0.9	0.6	1.8	1.3	3.6	2.6	3.6	2.6	0.5	0.9	1.8	1.8
C-1, C-2 equivalent	45	55	43	22.5	27.5			22.5	27.5			21.5		21.5	
C-1, C-2, C-6 equivalent	45	38	47	11.3	9.5			11.3	9.5	22.5	19.0	11.8		11.8	23.5
Calcd *t* content				34.7	37.6	1.8	1.3	37.4	39.6	26.1	21.6	38.8	0.9	35.1	25.3

Table III. ^{14}C Distributions for Acetolyses of *exo*-I-OBs-2,3-$^{14}C_2$ at 45° and of *endo*-I-OBs-2,3-$^{14}C_2$ at Reflux Temperature

	exo, % ^{14}C				*endo*, % ^{14}C,
	C-2,3	C-1,4	C-7	C-5,6	C-2,3
Calculated	42.2	22.1	21.1	14.7	43.6
Observed[a]	40	23	22	15	43.7, 44.2

[a] From ref 2.

C-2 equivalent, (3) C-1, C-2, and C-6 equivalent. In addition, for the *endo* case, some S_N2 displacement also occurred. Table II shows the estimated contribution of each of these processes and the calculated tritium distributions. The calculated values are in good agreement with the observed results given in Table I.

In the earlier work,[2] the acetolysis of *exo*-I-OBs-2,3-$^{14}C_2$ gave results suggesting that the reaction proceeded 55% by way of a process with C-1 and C-2 equivalent and 45% with C-1, C-2, and C-6 equivalent. No 3,2 hydride shifts were detectable since the ^{14}C contents at C-1,4 and at C-7 were considered to be the same within the experimental precisions; however, they did actually differ by 1% which suggested 1% activity at C-4 arising from complete equilibration occurring to the extent of 7% of the total reaction. Table III shows the ^{14}C distributions recalculated using the same processes employed for the calculation of the tritium contents (Table II). Again good agreements were obtained between the calculated and observed values. The present results thus fully confirm the earlier data from ^{14}C labeling, but with the contributions from the various processes more clearly delineated.

There is considerable current interest in the opposing theories of nonclassical *vs.* rapidly equilibrating classical ions as intermediates in solvolyses of norbornyl derivatives,[3] but a differentiation between these theories cannot be made on the basis of isotopic rearrangements.[9] More recent communications,[10] however, tend to favor the interpretation involving nonclassical ions. The present results will be discussed in terms of nonclassical structures, although it should be noted that the isotopic distribution arising from a nonclassical ion could be equally well attributed to a pair of equilibrating classical ions.

Roberts and co-workers[2] have explained the equivalence of C-1 and C-2 and of C-1, C-2, and C-6, respectively, by the intervention of the norbornonium ion (V) and the nortricyclonium ion (VI). Recently, Berson and Grubb[11] have reported evidence for the exclusively *endo–endo* 6,2 hydride shift in a related norbornyl system and such stereochemistry is not consistent with ion VI. An alternative to VI is the equilibration of Va with Vb and Vc.[12] For the acetolysis of *exo*-I-OBs-2-*t*, leaving aside the minor process of 3,2 hydride shift, the observed isotopic distributions in the product can be explained by Chart I.[13] The initially formed ion Va may either give rise to products with the label located at C-1 and at C-2 or undergo 6,2 and the analogous 6,1 hydride shifts to Vb and Vc, respectively. The process of Vb ⇆ Va ⇆ Vc would result in products with C-1, C-2, and C-6 equivalent. The mechanism suggests that 6,2 and 6,1 hydride shifts take place sequentially following formation of Va. No C–T bond rupture occurs in a slow step and this is consistent

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[9] N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1964).

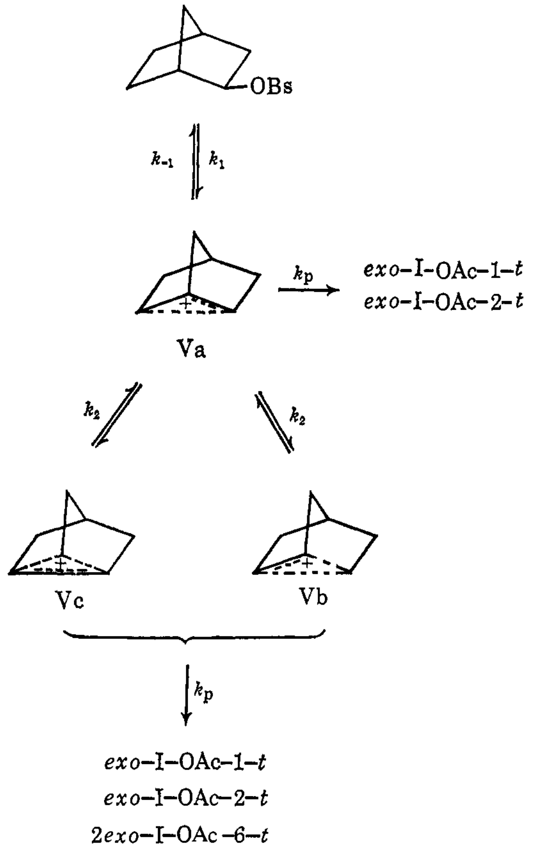
[10] J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *J. Am. Chem. Soc.*, **87**, 3248 (1965); W. J. Le Noble and B. L. Yates, *ibid.*, **87**, 3515 (1965); H. L. Goering and C. B. Schewene, *ibid.*, **87**, 3516 (1965); P. G. Gassman and J. L. Marshall, *ibid.*, **87**, 4648 (1965).

[11] J. A. Berson and P. W. Grubb, *ibid.*, **87**, 4016 (1965).

[12] S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952).

[13] For simplicity, the tritium label is not shown in the structural formulas in Chart I.

Chart I



with the observation of only a minor secondary kinetic isotope effect in the acetolysis of *exo*-I-OBs-2-*d*.[6] The equilibration of ions Va, Vb, and Vc also agrees with the low-temperature nmr spectrum of the norbornyl cation, which showed relative peak areas of 1:4:6.[14]

It is of interest to note that acetolysis of *exo*-I-OBs-2-*t* at 25 and 45° gave different isotopic distributions (Tables I and II). Since the reproducibility of the experimental results in duplicate runs are good, the differences in activities, especially at C-5,6, apparently are significant. The results indicate that as the temperature is raised from 25 to 45°, the net proportion of 6,2 (and 6,1) hydride shift is decreased. Referring to Chart I, this finding suggests that k_p, the rate of product formation, has a higher temperature dependence than k_2, the rate of 6,2 and 6,1 hydride shifts.

In the acetolysis of *endo*-I-OBs-2-*t*, the observed rearrangements could be accommodated by assuming "leakage" of the initially formed classical norbornyl cation to nonclassical intermediates.[3b] However, it has been pointed out[15] that it is not yet known whether a rearrangement of *endo* to *exo* sulfonate precedes solvolysis. This could result, for example, from internal return, although the migration of the returning sulfonate group from the *endo* to the *exo* side might compete poorly with the formation of solvolysis product.[4b] The possibility, however, should still be considered that part, if not all, of the isotopic rearrangements observed in the *endo* case may have been derived from acetolysis of the *exo* brosylate, formed by internal return, but is solvolyzed rapidly under the reaction conditions. Such an interpretation appears not to be consistent with expectation if the temperature effect observed in the acetolysis of *exo*-I-OBs-2-*t* were taken into account. The acetolysis of *exo*-I-OBs-2-*t* at a higher temperature gave a lesser amount of rearrangement to C-5,6. The acetolysis of *endo*-I-OBs-2-*t* was effected at reflux temperature, but the activity found at C-5,6 of the product was nearly the same as that found for the acetolysis of *exo*-I-OBs-2-*t* at 25°. Such results suggest that the isotopic rearrangements observed in the *endo* case apparently did not arise from a path involving conversion of the *endo* brosylate to the *exo* brosylate before solvolysis; acetolysis of the *exo* brosylate at reflux temperature would be expected to result in a lesser amount of activity at C-5,6. Further experimentation is needed to confirm or deny this tentative conclusion.

Experimental Section

***endo*-2-*t*-2-Norbornyl Brosylate (*endo*-I-OBs-2-*t*).** The preparation of *endo*-I-OBs-2-*t*, mp 62–63° (lit.[2] mp 62–63°), was effected by the procedures outlined for the analogous preparation of *endo*-I-OBs-2-*d*.[6a] It involved the reduction of norboranone with $LiAlH_4$-*t* (10 mcuries) to give a mixture of about 10% *exo*- and 90% *endo*-I-OH-2-*t* which was converted to the mixed brosylates followed by the removal of the *exo* brosylate by selective solvolysis in aqueous acetone.[2]

***exo*-2-*t*-2-Norbornyl Brosylate (*exo*-I-OBs-2-*t*).**[6] An aqueous solution of tetramethylammonium hydroxide was neutralized with HOAc, the water was removed under reduced pressure, and the resulting syrup was solidified on cooling. The solid tetramethylammonium acetate was digested in boiling anhydrous ether and then allowed to dry under vacuum in a desiccator over phosphorus pentoxide for 10 days.

In a 500-ml, round-bottomed flask were placed 48 g (0.36 mole) of the dry, pulverized tetramethylammonium acetate and a solution of 25.5 g (0.077 mole) of *endo*-I-OBs-2-*t* in 180 ml of dry acetone. The mixture was refluxed gently with stirring for 96 hr and then stirred at room temperature for an additional 24 hr. The acetone was removed by distillation at room temperature under reduced pressure. The residue was extracted successively four times, each time by refluxing with 80 ml of anhydrous ether following by decanting. The extract was washed with water, dried over anhydrous magnesium sulfate, and then fractionated to give 8.5 g (72%) of *exo*-I-OAc-2-*t*, bp 52–54° (2 mm). The acetate was converted in the usual manner[2] to *exo*-I-OH-2-*t* and then to *exo*-I-OBs-2-*t*, mp 59–60° (lit.[2] mp 60°).

Acetolysis of *exo*-I-OBs-2-*t*. A solution of 5.0 g (0.015 mole) of *exo*-I-OBs-2-*t* and 3.0 g (0.036 mole) of anhydrous NaOAc in 60 ml of HOAc was stirred at 25 or 45° for 24 hr. Water was then added and the product was extracted with ether. The extract was washed with 10% Na_2CO_3 solution until the washing remained basic. After a final washing with water and drying ($MgSO_4$), the ether solution of *exo*-I-OAc-*t* was directly reduced with $LiAlH_4$ to give *exo*-I-OH-*t*. The over-all yields were about 50–60%.

Acetolysis of *endo*-I-OBs-2-*t*. A solution of 3.3 g (0.010 mole) of *endo*-I-OBs-2-*t* and 1.0 g (0.012 mole) of anhydrous NaOAc in 25 ml of HOAc was heated under reflux for 20 hr and then worked up to give *exo*-I-OH-*t* as described in the acetolysis of the *exo* brosylate.

Treatment of *exo*-I-OAc-2-*t* in HOAc–NaOAc. A solution of 3.0 g (0.020 mole) of *exo*-I-OAc-2-*t* and 1.8 g (0.022 mole) of anhydrous NaOAc in 25 ml of HOAc was stirred at 25° for 24 hr. The acetate was then recovered and converted to *exo*-I-OH-*t* as in the acetolysis reactions.

Degradation of *exo*-I-OH-*t*. A part of each sample of *exo*-I-OH-*t* was oxidized[7] by CrO_3 in HOAc to norbornanone (II) which, in turn, was converted to its semicarbazone, mp 196–198° (lit.[16a] mp 196.5–197.5°). *Anal.* Calcd for $C_8H_{13}N_3O$: C, 57.49; H, 7.72. Found: C, 57.40; H, 7.80.

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[14] P. von R. Schleyer, W. E. Watts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 5679 (1964); M. Saunders, P. von R. Schleyer, and G. A. Olah, *ibid.*, **86**, 5680 (1964).

[15] E. J. Corey, J. Casanova, Jr., P. A. Vatakencherry, and R. Winter, *ibid.*, **85**, 169 (1963).

[16] "Dictionary of Organic Compounds," I. Heilbron and H. M. Bunbury, Ed., Eyre and Spottiswoode, London, 1953: (a) Vol. III, p 828; (b) Vol. IV, p 383.

Another portion of each sample of *exo*-I-OH-*t* was degraded by the procedures of Roberts and co-workers.[2] This involved oxidation first to *cis*-cyclopentane-1,3-dicarboxylic acid (III), mp 119–120° (lit.[2] 120–121°). *Anal.* Calcd for $C_7H_{10}O_4$: C, 53.10; H, 6.37. Found: C, 52.95; H, 6.30. III was converted to *cis*-cyclopentane-1,3-diamine which, in turn, was oxidized to succinic acid (IV), mp 185° (lit.[16b] mp 185°). *Anal.* Calcd for $C_4H_6O_4$: C, 40.67; H, 5.08. Found: C, 40.63; H, 5.01.

Samples of *exo*-I-OH-*t*, the semicarbazone of II, and acids III and IV were repeatedly recrystallized until their specific activities were constant. All calculations of isotopic rearrangements were based on the activities of these purified samples.

Rearrangement Studies with Carbon-14. XXVII. The Acetolysis and Formolysis of 2-(Δ^3-Cyclopentenyl)-2-^{14}C-ethyl *p*-Nitrobenzenesulfonate[1a]

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Abstract: The acetolysis and formolysis of 2-(Δ^3-cyclopentenyl)-2-^{14}C-ethyl *p*-nitrobenzenesulfonate were studied to provide data on isotope position rearrangements in the norbornyl cation generated by the π route. A comparison with earlier results on such rearrangements in the norbornyl cation generated by the σ route showed that differences do exist. A novel process which leads to a nonequivalent distribution of the tracer at C-3 and C-7 of the norbornyl product is noted for the π route. This process may be depicted as a concerted rearrangement involving hydride shift and reaction with solvent, and it occurs to a greater extent in acetolysis than in formolysis. An alternative explanation invoking product formation from edge-protonated nortricyclene is also discussed, but it appears to be the less preferable of the two possibilities.

In conjunction with the studies on the acetolysis of *exo*- and *endo*-2-*t*-2-norbornyl brosylates (*exo*- and *endo*-I-OBs-2-*t*),[2] an investigation was undertaken on the acetolysis and formolysis of 2-(Δ^3-cyclopentenyl)-2-^{14}C-ethyl *p*-nitrobenzenesulfonate (II-2-^{14}C) which gave norbornyl products by the π route.[3] It is expected that this work will provide data for a comparison between the processes that give rise to isotope position rearrangements in the norbornyl cation generated by the σ and π routes.

Results and Discussion

II-2-^{14}C was prepared from 4-bromocyclopentene[4] and diethyl 2-^{14}C-malonate[5] by procedures previously described.[6] Solvolyses of II-2-^{14}C were carried out at 60° for 30 hr in reagent grade glacial acetic acid or 98–100% formic acid. The product, *exo*-I-OAc-^{14}C or *exo*-I-OCHO-^{14}C, was treated with $LiAlH_4$ to give *exo*-I-OH-^{14}C which was degraded[7] by conversions to *cis*-cyclopentane-1,3-dicarboxylic acid (III) to *cis*-cyclopentane-1,3-diamine (IV) to succinic acid (V) to ethylenediamine (VI). Measurement of the ^{14}C activities of III, IV, V, and VI, with the diamines IV and VI assayed as their respective dibenzamides, gave the necessary data from which the ^{14}C-contents at C-2,3, C-1,4, C-7, and C-5,6 can be evaluated.[7] The results are summarized in Table I.

Table I. ^{14}C Distributions in *exo*-Norbornyl Products from Solvolyses of II-2-^{14}C

	^{14}C distribution, %[a]							
	C-2,3		C-1,4		C-7		C-5,6	
Reaction	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
Acetolysis	38.5	37.1	0.4	1.4	23.8	25.9	37.3	35.6
Formolysis	31.5	31.4	2.8	4.0	26.0	26.9	39.7	37.7

[a] Assayed by a liquid scintillation counter. For the various runs, 100% corresponded to specific activities ranging from about 33,300 to 61,400 counts/min/mmole.

If solvolyses of II-2-^{14}C were to give rise to the norbornonium ion VIIa (or its equivalent of a pair of rapidly equilibrating classical ions) without further rearrangements, the ^{14}C label would be located only at the C-5 position of the product. In view of the propensity for 6,2 (and the analogous 6,1) hydride shift, as well as the possibility of some 3,2 hydride shift, observed in the norbornyl cation generated by the σ route from solvolyses of *exo*-I-OBs-2-*t*[2] and *exo*-I-OBs-2,3-$^{14}C_2$,[7] it is not surprising to note the extensive isotopic rearrangements as recorded in Table I. Indeed, the solvolysis of II-1,1-d_2 in 80% aqueous acetic acid has been reported to give about 15% rearrangement of the deuterium label to C-1 and C-2 of the norbornyl product,[8] indicating the occurrence of some 6,2 hydride

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[1] (a) Supported by a grant from the National Research Council of Canada; (b) holder of a Canadian Industries Limited Fellowship, 1964–1966.

[2] C. C. Lee and L. K. M. Lam, *J. Am. Chem. Soc.*, 2831 (1966).

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[8] K. Humski, S. Borčić, and D. E. Sunko, *Croat. Chem. Acta*, **37**, 3 (1965).