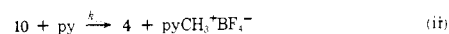
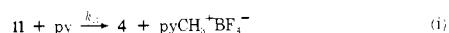


- stracts, V Symposium on Organic Sulphur Chemistry, Lund, Sweden, June 1972, No. 1B.1.
- (5) D. J. Cram, J. Day, D. R. Rayner, D. M. von Schriltz, D. J. Duchamp, and D. C. Garwood, *J. Amer. Chem. Soc.*, **92**, 7369 (1970); and A. Nudelman, *Int. J. Sulfur Chem., Part B*, **6**, 1 (1971), and references cited therein. See F. Wudl and T. B. K. Lee, *J. Amer. Chem. Soc.*, **95**, 6349 (1973), and F. G. Yamagishi, D. R. Rayner, E. T. Zwicker, and D. J. Cram, *ibid.*, **95**, 1916 (1973), and references cited therein for examples of retention.
- (6) The absolute configuration of a sulfonium salt has to the best of our knowledge never been established, unambiguously. See B. M. Trost and R. F. Hammen, *J. Amer. Chem. Soc.*, **95**, 962 (1973).
- (7) T. A. Whitney and D. J. Cram, *J. Org. Chem.*, **35**, 3964 (1970).
- (8) H. Kwart and E. R. Evans, *J. Org. Chem.*, **31**, 413 (1966).
- (9) J. J. Rigau, C. C. Bacon, and C. R. Johnson, *J. Org. Chem.*, **35**, 3655 (1970).
- (10) See, for example, R. M. Wing, J. J. Uebel, and K. K. Andersen, *J. Amer. Chem. Soc.*, **95**, 6046 (1973); R. R. Fraser, T. Durst, M. R. McClory, R. Viau, and Y. Y. Wigfield, *Int. J. Sulfur Chem., Part A*, **1**, 133 (1971); I. Karup-Nielsen and A. Kjaer, *Acta Chem. Scand.*, **26**, 852 (1972), and references cited therein.
- (11) The angular dependence of the induced pseudocontact shifts is in most cases only a minor contributor to the total observed shifts. Our results show that in this qualitative application it can be neglected.
- (12) P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert *J. Amer. Chem. Soc.*, **92**, 5734 (1970).
- (13) Our assignment is in agreement with that of W. H. Pirkle and T. A. Whitney, *Tetrahedron Lett.*, 2299 (1974).
- (14) A. Garbesi, N. Corsi, and A. Fava, *Helv. Chim. Acta*, **53**, 1499 (1970).
- (15) R. Annunziata, M. Cinquini, and S. Colonna, *J. Chem. Soc., Perkin Trans. 1*, 1231 (1973).
- (16) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N.Y., 1972, p 24.
- (17) C. R. Johnson and D. M. McCants, Jr., *J. Amer. Chem. Soc.*, **87**, 5404 (1965).
- (18) C. R. Johnson and W. G. Phillips, *J. Org. Chem.*, **32**, 1926 (1967).
- (19) K. K. Andersen, M. Cinquini, and N. E. Papanikolaou, *J. Org. Chem.*, **35**, 706 (1970).
- (20) We initially attempted to isolate **10** and **11** as the sulfonium bromides. The instability of these salts was shown to be due to nucleophilic attack of the bromide anion on **10** and **11** to give **4**.
- (21) Pure 1-thiachroman (**5**) was obtained by low-temperature ( $-78^\circ$ ) recrystallizations (heptane) of fractions enriched in **5** by careful fractional distillation: bp  $82-87^\circ$  (1 mm) [lit.<sup>8</sup> bp  $85-89^\circ$  (0.2 mm)]; nmr (CDCl<sub>3</sub>)  $\delta$  1.92 (m, 2, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.65 (t,  $J = 6.5$  Hz, 2, ArCH<sub>2</sub>), 2.85 (m, 2, SO<sub>2</sub>CH<sub>2</sub>), 7.0 (m, 4, ArH); ir (neat)  $\nu_{\max}$  3055 (m), 3000 (m), 2930 (s), 2845 (m), 1580 (m), 1560 (m), 1465 (s), 1425 (s), 1280 (m), 1265 (m), 1120 (m), 1070 (m), 1045 (m), 930 (m), 775 (m), 740 (s) cm<sup>-1</sup>.
- (22) Based on the two first-order reactions (eq i and ii), the following linear



eq iii was used.

$$\ln(C_{-11} - C_{11}) = k_{11}/k_{10} \ln(C_{-10} - C_{10}) + \text{constant} \quad (\text{iii})$$

## Isotopic Scrambling Processes in the Acetolysis of Labeled *exo*-Dehydro-2-norbornyl Brosylate

Choi Chuck Lee\* and Eric C. F. Ko

Contribution from the Department of Chemistry and Chemical Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada S7N 0W0. Received January 19, 1974

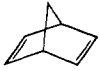
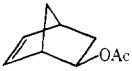
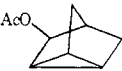
**Abstract:** Acetolysis of *exo*-dehydro-2-norbornyl-3-*exo-t* brosylate (**1-3-*exo-t*-OBs**) at 24, 45, or 65° gave in each case about 50% rearrangement of the label from C-2,3 to C-1,4,5,6,7 in the product, **1-*x-t*-OAc**, in agreement with the results from **1-3-*exo-d*-OBs** obtained by Cristol and coworkers. Degradation of the **1-*x-t*-OAc**, however, showed that the distribution of the T label was approximately 12, 38, 38, and 12%, respectively, at C-2, C-3, C-1,4,7, and C-5,6, not a 50:50 split over C-3 and C-7 as was previously assumed. It is suggested that the overall T distribution is the net result of a number of contributing processes, including (1) formation of product from an equilibrating mixture of the Wagner–Meerwein related homoallylic dehydronorbornyl cations **2a** and **2b**, (2) elimination to norbornadiene followed by addition of HOAc to give scrambled **1-*x-t*-OAc**, and (3) the occurrence of 3,2 hydrogen shift before product formation. A possible rationalization of the discrepancies reported by previous workers is discussed.

Discrepancies in the extents of isotopic scrambling observed in the *exo*-dehydro-2-norbornyl acetate obtained from acetolysis of <sup>14</sup>C- or D-labeled *exo*-dehydro-2-norbornyl brosylate have been reported by two groups of workers.<sup>1,2</sup> In 1955, Roberts, *et al.*,<sup>1</sup> found that in the acetolysis of *exo*-dehydro-2-norbornyl-2,3-<sup>14</sup>C<sub>2</sub> brosylate (**1-2,3-<sup>14</sup>C-OBs**) at 45° in the presence of KOAc, 38% of the <sup>14</sup>C label was rearranged from the C-2,3 positions to the rest of the carbon skeleton in the resulting *exo*-dehydro-2-norbornyl-*x*-<sup>14</sup>C acetate (**1-*x*-<sup>14</sup>C-OAc**). On the other hand, Cristol and coworkers<sup>2</sup> reported in 1966 that the acetolysis of *exo*-dehydro-2-norbornyl-3-*exo-d* brosylate (**1-3-*exo-d*-OBs**) at 24° in the presence of NaOAc gave a **1-*x-d*-OAc** product, the mass spectral analysis<sup>3</sup> of which showed an essentially 50% rearrangement of the D label from C-2,3 to C-1,4,5,6,7. These differences prompted Lee and Hahn<sup>4</sup> to study the reaction once more, using **1-2-*endo-d*-OBs** as the labeled reactant. It was found that both the results of Roberts<sup>1</sup> and of Cristol<sup>2</sup> were essentially correct, and it was thought that differences in reaction temperature might have played a role in giving rise to the different extents of rearrangement. Recently, however, Cristol and Beimborn<sup>5</sup> rein-

vestigated the acetolysis of **1-3-*exo-d*-OBs** under various experimental conditions including the different temperatures used by Lee and Hahn. Again about 50% rearrangement was observed in all cases. Professor Cristol also indicated that he has examined the data from the thesis of Hahn, found no errors in the calculations, and was unable to rationalize the difference between their results and those of Lee and Hahn.<sup>4</sup> Since the mass spectral analysis of the **1-*x-d*-OAc** from either **1-3-*exo-d*-OBs** or **1-2-*endo-d*-OBs** gave only the overall rearrangement of the D label from C-2,3 to C-1,4,5,6,7 based on fragmentation by the retrograde Diels–Alder reaction,<sup>3</sup> we have decided to repeat the investigation using **1-3-*exo-t*-OBs** and degrade the **1-*x-t*-OAc** product in order to obtain more detailed information which may help to explain the apparent discrepancies in the published results.

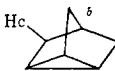

In the acetolysis of **1-2,3-<sup>14</sup>C-OBs**,<sup>1</sup> reaction *via* a rapidly equilibrating pair of enantiomeric homoallylic ions **2a** and **2b**, or the intervention of a symmetrical ion such as **3**, would give rise to 50% rearrangement of the label from C-2,3 to C-1,7 in the resulting **1-*x*-<sup>14</sup>C-OAc**. Since less than 50% rearrangement was observed,<sup>1</sup> a relatively slow equi-

**Table I.** Yields of Products Calculated from Isotopic Dilution for Duplicate Runs in the Acetolysis of 1-3-*exo-t*-OBs

Reaction temp, °C	% yield		
			
24 <sup>a</sup>	0.75; 0.45	5.4; 6.1	57.2; 69.7
45 <sup>b</sup>	0.60; 0.47	6.6; 8.6	75.3; 83.6
65 <sup>a</sup>	0.32; 0.56	6.8; 7.8	88.6; 87.3

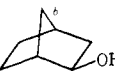
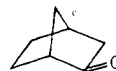
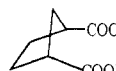
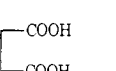
<sup>a</sup> Data on yields obtained from experiments different from those whose products were degraded to give the data in Tables II and III. <sup>b</sup> Data on yields and on isotopic scrambling (Tables II and III) were derived from the same experiments.

**Table II.** Specific Activities of Degradation Products of 3-Nortricyclenyl-*x-t* Acetate (4-*x-t*-OAc) from Duplicate Acetolyses of 1-3-*exo-t*-OBs

Reaction temp, °C	Specific activity, <sup>a</sup> dpm/mmol × 10 <sup>-6</sup>	
		
24	14.1; 17.2	14.0; 17.0
45	25.9; 36.8	26.0; 37.0
65	23.1; 22.7	23.1; 22.8

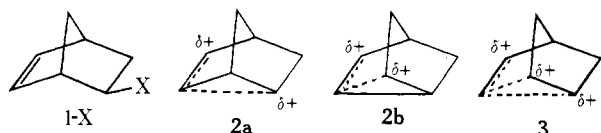
<sup>a</sup> Measured by a liquid scintillation counter. <sup>b</sup> Assayed as the  $\alpha$ -naphthylurethane. <sup>c</sup> Assayed as the semicarbazone.

**Table III.** Tritium Distributions in the 1-*x-t*-OAc Product from Duplicate Acetolyses of 1-3-*exo-t*-OBs

Reaction temp, °C	Specific activity, <sup>a</sup> (dpm/mmol) × 10 <sup>-3</sup>				Tritium content, %					
					C-2 <sup>d</sup>	C-3 <sup>e</sup>	C-1,4,7 <sup>f</sup>	C-5,6 <sup>g</sup>	C-2,3	C-1,4,5,6,7
24	1375 (100)	1205 (87.6)	709 (51.6)	158 (11.5)	12.4	36.0	40.1	11.5	48.4	51.6
	1230 (100)	1080 (87.8)	626 (50.9)	156 (12.7)	12.2	36.9	38.2	12.7	49.1	50.9
45	2400 (100)	2120 (88.3)	1243 (51.8)	313 (13.0)	11.7	36.5	38.8	13.0	48.2	51.8
	2950 (100)	2650 (89.8)	1485 (50.3)	399 (11.5)	10.2	39.5	38.8	11.5	49.7	50.3
65	1050 (100)	912 (86.9)	507 (48.3)	153 (14.6)	13.1	38.6	33.7	14.6	51.7	48.3
	818 (100)	723 (88.4)	410 (50.1)	122 (14.9)	11.6	38.3	35.2	14.9	49.9	50.1

<sup>a</sup> Measured by a liquid scintillation counter; numbers in parentheses are the activities expressed as a percentage of the total activity in the 2-norbornanol. <sup>b</sup> Assayed as the  $\alpha$ -naphthylurethane. <sup>c</sup> Assayed as the semicarbazone. <sup>d</sup> % activity in 2-norbornanol - % activity in 2-norbornanone. <sup>e</sup> % activity in 2-norbornanone - % activity in *cis*-cyclopentane-1,3-dicarboxylic acid. <sup>f</sup> % activity in *cis*-cyclopentane-1,3-dicarboxylic acid - % activity in succinic acid. <sup>g</sup> Equal to the % activity in the succinic acid.

bration was postulated so that the initially formed homoallylic ion **2a** would be partly trapped by solvent before its isomerization to **2b** or to **3**. On the other hand, the 50%



rearrangement observed by Cristol, *et al.*,<sup>2,5</sup> in the acetolysis of 1-3-*exo-d*-OBs, was interpreted as in support of **3** or rapidly equilibrating **2a** and **2b**, and it was assumed by these workers that the 1-*x-d*-OAc product would have a 50:50 distribution of the D label over C-3 and C-7. However, the present work with 1-3-*exo-t*-OBs (*vide infra*) shows that the scrambling of the T label in the 1-*x-t*-OAc product is much more complex than an equal distribution over C-3 and C-7, the T activity being present at C-2, C-3, C-1,4,7, and C-5,6. These results thus indicate the occurrence of scrambling processes other than, or in addition to, the previously assumed reaction *via* **3** or equilibrating **2a** and **2b**.

1-3-*exo-t*-OBs was prepared from the corresponding alcohol obtained from hydroboration of norbornadiene as de-

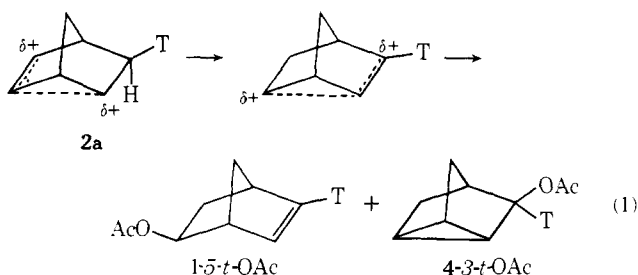
scribed by Cristol and coworkers<sup>2,6</sup> except that the source of label was NaBH<sub>4</sub>-*t* instead of LiAlD<sub>4</sub>. Acetolysis was carried out with about 0.5 M 1-3-*exo-t*-OBs in the presence of a 10% excess of KOAc at 24, 45, and 65°, respectively, for 11, 1, and 1 hr.<sup>4</sup> The yields of products, as estimated by isotopic dilution, are given in Table I. It is of interest to note that besides the previously reported products, *exo*-dehydro-2-norbornyl acetate (1-*x-t*-OAc) and 3-nortricyclenyl acetate (4-*x-t*-OAc), small amounts of the elimination product, norbornadiene (5-*x-t*), were also detected. Since isotopic dilution gave the actual yields of the tritium containing products, it may be pointed out that the relative yields of 1-*x-t*-OAc to 4-*x-t*-OAc for the reaction at 24°, for example, would be 5.4:57.2 and 6.1:69.7 or 8.6:91.4 and 8.0:92.0, for the duplicate runs, and this is in complete agreement with a product ratio of 8:92 reported by Cristol, *et al.*,<sup>2</sup> for a typical solvolysis at 24°.

The acetate products, separated by preparative vpc, were degraded. Conversion of the 4-*x-t*-OAc to the alcohol followed by its oxidation to 3-nortricyclenone<sup>7</sup> showed no significant loss in T activity (Table II), indicating no detectable amount of T label at the C-3 position of the 4-*x-t*-OAc product. The 1-*x-t*-OAc was hydrogenated to give *exo*-2-norbornyl-*x-t* acetate which was converted to the alcohol and degraded the usual way<sup>1,8</sup> through oxidation to 2-norbornanone and to *cis*-cyclopentane-1,3-dicarboxylic acid which in turn was converted to succinic acid to give the data

summarized in Table III.

While the data in Tables I and III do show some variations between different experiments in both per cent yields of the three products and T contents in the various positions of the 1-*x-t*-OAc product, in all cases the overall rearrangement of the T label from C-2,3 to C-1,4,5,6,7 did turn out to be about 50%. These experiments in effect have reproduced the results of Cristol and Beimborn,<sup>5</sup> but the T distribution in the 1-*x-t*-OAc is certainly much more complex than the assumption of a 50:50 split over C-3 and C-7. All previous interpretations<sup>1,2,4,5</sup> of the isotopic scrambling data are, therefore, inadequate since the possibility of extensive scramblings as found in the present work has never been considered.

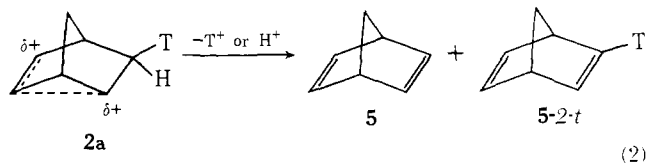
Examination of the data in Table III suggests that the only discernible trend may be that the rearrangements of the label to C-1,4,7 and to C-5,6, respectively, are somewhat lower and somewhat higher at the higher temperature of 65°. If this trend is real, it could suggest a somewhat higher activation energy for the scrambling to C-5,6 than to C-1,4,7. A possible route for the scrambling of the label to C-5,6 may be a 6,2 (or 5,3) type of hydrogen shift, for example, involving ion **2a** (eq 1). Such a process would predict that the resulting 3-nortricyclenyl acetate should contain



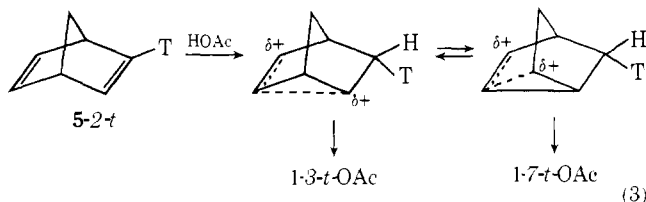
some T label at C-3. The data given in Table II indicate that this is not the case, thus effectively eliminating 6,2 type of shifts as a factor in accounting for the T activity at C-5,6.

Since norbornadiene (**5**-*x-t*) is found as a minor product in the reaction (Table I), a plausible pathway for locating the T label at C-5,6 is a process of elimination-addition. Cristol and coworkers<sup>6,9</sup> have shown that HOAc could add to **5**, with or without catalysis by mineral acid, to give **1-OAc** and **4-OAc** and some scrambling of the D label from C-2,3 to C-1,4,5,6,7 was also observed in the **1-OAc**-*x-d* when the reaction was carried out with HOAc-*O-d*. In the present work, it was found that when ordinary, unlabeled **1-OBs** was solvolyzed in HOAc-*O-t*, tritium activity was taken up in both acetate products, **1-OAc** and **4-OAc**, as given in Table IV. These findings thus lend further support to the occurrence of the elimination-addition process during the acetolysis of **1-OBs**.

The stereochemistry of the elimination-addition reaction under the conditions of the acetolysis is not known. If only cis elimination occurs with **1-3-exo-t-OBs**, only unlabeled norbornadiene (**5**) would be formed, and this seems unlikely since T containing **5** was found as a product (Table I). Purely trans elimination would give rise to **5-2-t**, while in an elimination proceeding *via* the initially formed ion **2a**, loss of T<sup>+</sup> or H<sup>+</sup> from C-3 could occur resulting in the formation of **5** and **5-2-t** (eq 2).



Addition of HOAc to **5-2-t** would give rise to a **1-x-t-OAc** product with the T label located at C-2,3 and C-5,6, and possibly also at C-1,7 if rearrangement occurs in the addition *via* equilibrating **2a** and **2b** (e.g., eq 3).



In selected experiments carried out for the comparison, the specific activity of the **1-x-t-OAc** product, undiluted by any inactive carrier, was found to be about 1.5% less than the corresponding starting material, **1-3-exo-t-OBs**, indicating the possibility of a slight loss of T activity, probably *via* elimination to unlabeled **5**. On the other hand, the specific activity of the major product, **4-x-t-OAc**, was nearly the same (more than 99.5%) as that of the reactant, **1-3-exo-t-OBs**, suggesting that elimination-addition may be relatively much less important in the formation of this major product. Since the product ratio of **1-x-t-OAc** to **4-**

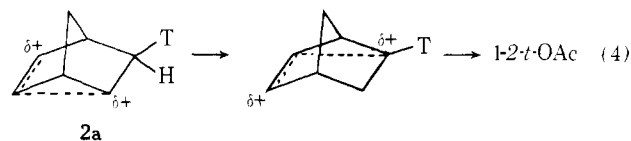
**Table IV.** Tritium Uptake in the Products, *exo*-Dehydro-2-norbornyl Acetate (**1-OAc**) and 3-Nortricyclenyl Acetate (**4-OAc**), from Acetolysis of **1-OBs** in HOAc-*O-t*

Reaction temp, °C	Specific activity, (dpm/mmol) × 10 <sup>-3</sup>				% exchange <sup>a</sup>			
	HOAc- <i>O-t</i>		<b>1-OAc</b>	<b>4-OAc</b>	<b>1-OAc</b>		<b>4-OAc</b>	
45	9870; 9870	420; 380	170; 228	4.3; 3.9	1.7; 2.3			
65	9870; 9870	413; 410	162; 216	4.2; 4.2	1.6; 2.2			

<sup>a</sup> Specific activity of **1-OAc** or **4-OAc** as a per cent of specific activity of the HOAc-*O-t*.

*x-t-OAc* is about 8:92, a minor process such as elimination-addition could materially affect the overall T distribution in the **1-x-t-OAc** while exerting relatively little influence on the overall T distribution in the **4-x-t-OAc**. In this connection, it may be pointed out that even if the addition of HOAc to **5-2-t** were to give rise to some **4-x-t-OAc** besides the **1-x-t-OAc**, since elimination-addition is a relatively minor process, and since only one-fourth of the T activity from this minor process could end up at C-3 of **4-x-t-OAc**, the net amount of T activity at the C-3 position of this major product, **4-x-t-OAc**, should be negligibly small, as was observed (Table II).

From Table III, it is seen that the averaged T distribution in the **1-x-t-OAc** product derived from the acetolysis of **1-3-exo-t-OBs** is approximately 12, 38, 38, and 12%, respectively, for C-2, C-3, C-1,4,7, and C-5,6. If it is assumed that the activity at C-5,6 is derived from elimination-addition, the process should give rise to a similar amount of activity at C-2,3. Since the activity at C-2 alone is about the same as the sum of the activities at C-5 and C-6, some additional process leading to more scrambling to C-2 is required. Such a process may be a 3,2 hydrogen shift, possibly involving ion **2a** as depicted by eq 4. It may be noted that eq



4 involves an endo-endo 3,2 hydrogen shift, which has been regarded as an unfavorable process in the analogous *exo*-2-norbornyl system. However, endo-endo 3,2 hydrogen shifts have been reported by Wilder and coworkers<sup>10</sup> and more recently by Olah and Liang.<sup>11</sup>

While it is difficult to devise a detailed mechanism to account for all the results recorded in Tables I, II, and III, it is clear from the above discussion that, qualitatively, a number of scrambling processes may be considered as contributing to the overall T distribution in the acetolysis product, **1-x-t-OAc**. Following the suggestion of Story and Clark<sup>12</sup> that homoallylic ions should be formulated as simply as possible, the present results may be interpreted in terms of the Wagner-Meerwein related ions **2a** and **2b** without invoking ion **3**. The extensive isotopic scrambling in the **1-x-t-OAc** could arise from product formation after (1) equilibration of **2a** with **2b**, (2) **2a** undergoing elimination-addition, and (3) **2a** undergoing 3,2 hydrogen shift. The suggested occurrence of elimination-addition (process 2) and 3,2 shift (process 3) besides equilibration between **2a** and **2b** (process 1) could also provide a possible rationalization for the discrepancies reported by Roberts<sup>1</sup> and Cristol.<sup>2</sup> In the work of Cristol with **1-3-exo-d-OBs**,<sup>2</sup> as in the present work with **1-3-exo-t-OBs**, both elimination-addition (process 2) and 3,2 shift (process 3) could involve either H or the labeled atom at C-3. On the other hand, when the

label is  $^{14}\text{C}$  at the C-2,3 positions, neither of these two processes would directly involve the isotopic label. Therefore, the net rearrangement from C-2,3 to C-1,4,5,6,7 in the two reactions should be different since the relative contributions from processes 1, 2, and 3 to the overall label distribution would be different in the two cases. On the other hand, agreement was noted when the labeled reactant was 1-2-*endo-d*-OBs<sup>4</sup> and 1-2,3- $^{14}\text{C}$ -OBs<sup>1</sup> since processes 2 and 3 also would not affect the label in the reaction with 1-2-*endo-d*-OBs. Finally, it may be repeated that the present work with 1-3-*exo-t*-OBs and the work of Cristol, *et al.*,<sup>2,5</sup> with 1-3-*exo-d*-OBs are in agreement insofar as the 50:50 gross distribution between C-2,3 and C-1,4,5,6,7 is concerned, but the scrambling of the labeled atom is shown to be much more extensive than simply an equal distribution between C-3 and C-7.

### Experimental Section

**Solvolyses.** A solution of 4.0 to 8.0 g of 1-3-*exo-t*-OBs and 1.1 equiv of KOAc in 25-50 ml of HOAc was allowed to react at 65, 45, or 24° for 1, 1, or 11 hr, respectively. The resulting material was poured into cracked ice and then extracted with petroleum ether. The extract was washed with H<sub>2</sub>O, Na<sub>2</sub>CO<sub>3</sub> solution, and again with H<sub>2</sub>O and then dried over anhydrous MgSO<sub>4</sub>. After removal of the solvent, the main products, *exo*-dehydro-2-norbornyl-*x-t* acetate (1-*x-t*-OAc) and 3-nortricyclenyl-*x-t* acetate (4-*x-t*-OAc), were recovered by preparative vpc (25% Carbowax 20M on Chromosorb P at 150° or 20% Ucon polar 50-HB-2000 on Chromosorb P at 160°). When necessary, ordinary 1-OAc and 4-OAc were added as carriers to give sufficient amounts of these products for degradation.

As an illustration of the use of isotopic dilution in the estimated of yields, the following example gives the data from which one set of yields given in Table I was calculated.

After treatment of 214 mg of 1-3-*exo-t*-OBs, specific activity 187,000,000 dpm/mmol, at 24° for 11 hr, 1011 mg of norbornadiene (5), 125 mg of 1-OAc, and 860 mg of 4-OAc were added as carriers. Samples of these three diluted products were obtained by vpc, and their specific activities were found to be 83,000, 7,800,000, and 11,450,000 dpm/mmol, respectively, for the recovered 5, 1-OAc, and 4-OAc.

If  $x = \text{mg of } 5 \text{ produced in the reaction, } 187,000,000(x/92.1) = 83,000[(x + 1011)/92.1]$ , and  $x = 0.45 \text{ mg}$ .

Since the theoretical yield of 5 from 214 mg of 1-OBs is 59.3 mg, the yield of 5 is  $(0.45/59.3) \times 100 = 0.75\%$ .

Similarly, the yields of 1-OAc and 4-OAc, respectively, were

calculated to be 5.4 and 57.2% for this experiment.

**Degradation.** Treatment of 4-*x-t*-OAc with LiAlH<sub>4</sub> gave 4-*x-t*-OH which was oxidized to the corresponding ketone with CrO<sub>3</sub> in HOAc as described by Schaeffer.<sup>7</sup> The samples of 1-*x-t*-OAc were hydrogenated to give *exo*-2-norbornyl acetate,<sup>1</sup> converted to *exo*-2-norbornanol by reaction with LiAlH<sub>4</sub>, and then degraded to give the T distribution as described previously.<sup>1,8</sup> The degradation involved the oxidation of part of the *exo*-2-norbornanol with CrO<sub>3</sub> in HOAc to 2-norbornanone and the oxidation of another portion of the *exo*-2-norbornanol with alkaline KMnO<sub>4</sub> to *cis*-cyclopentane-1,3-dicarboxylic acid which in turn was converted to *cis*-cyclopentane-1,3-diamine followed by oxidation to succinic acid. When the 1-3-*exo-t*-OH used to prepare the starting material, 1-3-*exo-t*-OBs, was hydrogenated to *exo*-2-norbornanol-3-*exo-t*, as expected its oxidation to 2-norbornanone showed essentially no loss of activity, while its conversion to *cis*-cyclopentane-1,3-dicarboxylic acid resulted in the complete loss of the T label. To ascertain that there was no complication arising from isotopic exchange during the degradation, it was found that oxidation of unlabeled *exo*-2-norbornanol with CrO<sub>3</sub> in HOAc-*O-t* resulted in an inactive 2-norbornanone and that conversion of unlabeled *cis*-cyclopentane-1,3-dicarboxylic acid to succinic acid in the presence of H<sub>2</sub>O-*t* showed that the succinic acid, recrystallized from H<sub>2</sub>O, was not radioactive.

**Acknowledgment.** The financial support given by the National Research Council of Canada is gratefully acknowledged.

### References and Notes

- (1) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **77**, 3034 (1955).
- (2) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Amer. Chem. Soc.*, **88**, 3087 (1966).
- (3) S. J. Cristol, R. A. Sanchez, and T. C. Morrill, *J. Org. Chem.*, **31**, 2738 (1966).
- (4) C. C. Lee and B.-S. Hahn, *J. Amer. Chem. Soc.*, **92**, 2583 (1970).
- (5) S. J. Cristol and D. A. Beilborn, *J. Amer. Chem. Soc.*, **95**, 3651 (1973).
- (6) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.*, **31**, 2726 (1966).
- (7) J. P. Schaeffer, *J. Amer. Chem. Soc.*, **82**, 4091 (1960).
- (8) C. C. Lee and L. K. M. Lam, *J. Amer. Chem. Soc.*, **88**, 2831 (1966).
- (9) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.*, **31**, 2719, 2733 (1966).
- (10) A. W. Bushell and P. Wilder, Jr., *J. Amer. Chem. Soc.*, **89**, 5721 (1967); P. Wilder and W.-C. Hsieh, *J. Org. Chem.*, **36**, 2552 (1971).
- (11) G. A. Olah and G. Liang, *J. Amer. Chem. Soc.*, **96**, 189 (1974).
- (12) P. R. Story and B. C. Clark, Jr., "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N.Y., 1972, pp 1007-1098.