Some observations on isotopic scramblings accompanying acetolysis in the 2-norbornyl system

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Evidence is presented to show that in the acetolysis of isotopically labeled *exo*- or *endo*-2-norbornyl brosylate (*exo*- or *endo*-**1**-OBs) in NaOAc buffered HOAc, the initially formed product, *exo*-**1**-OAc, could undergo further isotopic scrambling during its subsequent contact with the reaction medium. These scramblings in the acetate apparently involved relatively large amounts of rearrangement of the label from C-2 to -3. After partial acetolysis of *exo*- or *endo*-**1**-OBs-2-*d*, n.m.r. analysis showed that the recovered *endo*-brosylate was unchanged, while the D-label in the recovered *exo*-brosylate has definitely rearranged from C-2 to -1 and probably also to C-6. Thus, in the acetolysis of labeled *exo*-**1**-OBs as commonly carried out in HOAc–NaOAc, isotopic scramblings could occur not only in the solvolysis reaction itself, but also prior to the reaction due to internal return giving rise to scrambled brosylate and subsequent to the reaction due to further scrambling in the initial product. Other mechanistic implications of the results are also discussed.

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In the original work on the acetolysis of *exo*-2-norbornyl-2,3-$^{14}C_2$brosylate (*exo*-**1**-OBs-2,3-^{14}C) (1, 2), because the label was present at both C-2 and -3, it was not possible to observe directly any 3,2-hydride shifts. In our earlier work on the acetolysis of *exo*- and *endo*-**1**-OBs-2-*t* (3), small amounts (about 1–2%) of the *t*-label were found at the C-3 position of the resulting product, *exo*-**1**-OAc-*x*-*t*. Since treatment of *exo*-**1**-OAc-2-*t* in HOAc–NaOAc at 25° also gave rise to some isotopic scrambling with about 1% of the label rearranged to C-3 (3), it was concluded that most, if not all, of the overall 3,2-hydride shifts observed in the acetolysis of the brosylate could have resulted from the subsequent ionization, in the reaction mixture, of the initially formed acetolysis product. The present paper deals with further studies confirming this conclusion, some of the data from these studies having been reported previously in preliminary form (4). It is well known that the acetolysis of *exo*-**1**-OBs is accompanied by internal returns (5, 6). The present paper also describes our attempts in evaluating the nature and extents of the isotopic scrambling arising from internal returns in the recovered brosylate after partial acetolysis.

Results and Discussion

Given in Table 1 are the *t*-distributions in the 2-norbornyl skeleton of the *exo*-**1**-OAc-*x*-*t* samples obtained from the various experiments using *t*-labeled materials. The methods of degradation from which these distributions were obtained have already been described (3). For comparison, some of the results (experiments I, II, and III) reported by Lee and Lam (3) are also included in Table 1. The data in Table 1 indicate that there was extensive isotopic scrambling not only in the acetolysis of *exo*- or *endo*-**1**-OBs-2-*t*, but also when the acetolysis product was allowed to be in contact with the reaction mixture. This was demonstrated by experiments III and IV when *exo*-**1**-OAc-2-*t* was stirred at 25° or heated under reflux in NaOAc buffered HOAc. More rearrangement was observed at the higher temperature; but interestingly, the relative increase in rearrangement is much greater to C-3 than to the other positions. In experiment V, the acetolysis of *endo*-**1**-OBs-2-*t* at 30° for 64 days was found to give 6.3 and 4.7% overall rearrangement of the *t*-label to C-3 in duplicate runs. The precision of these values was not as good as those obtained in experiments I–IV, possibly because of lesser reproducible control of the experimental conditions during the prolonged reaction time. However, the extent of rearrangement to C-3 in experiment V was greater than those observed in experiments I–III. When the reaction time in the acetolysis of *endo*-**1**-OBs-2-*t* was reduced from 64 to 2 days (experiment VI), the amount of net rearrangement to C-3 was greatly decreased, again suggesting that the acetolysis product, *exo*-**1**-OAc-*x*-*t*, could undergo subsequent ioniza-

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TABLE 1

Tritium distributions in the *exo*-2-norbornyl-*x*-*t* acetate (*exo*-1-OAc-*x*-*t*) from various experiments

Experiment	Reaction	Specific activity of *exo*-1-OH-*x*-*t* (c.p.m./mmole)*		Tritium content (%)							
				C-2		C-3		C-1,4,7		C-5,6	
		Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
I†	*exo*-1-OBs-2-*t* in HOAc–NaOAc, 25°, 24 h	339 300	300 100	34.3	35.6	1.8	2.1	37.3	35.7	26.6	26.6
II†	*exo*-1-OBs-2-*t* in HOAc–NaOAc, 45°, 24 h	121 300	117 600	38.3	38.0	1.3	1.3	40.1	40.0	20.2	20.7
III†	*exo*-1-OAc-2-*t* in HOAc–NaOAc, 25°, 24 h	157 600	150 400	96.0	96.5	1.0	1.1	2.2	1.7	0.8	0.7
IV	*exo*-1-OAc-2-*t* in HOAc–NaOAc, reflux, 20 h	116 600	109 100	90.7	90.5	4.8	4.1	3.2	3.9	1.3	1.4
V	*endo*-1-OBs-2-*t* in HOAc–NaOAc, 30°, 64 days	141 300	135 800	41.4	42.5	6.3	4.7	32.8	32.8	19.5	20.0
VI	*endo*-1-OBs-2-*t* in HOAc–NaOAc 30°, 2 days	214 100	198 500	54.0	54.0	1.0	0.2	25.0	26.0	20.0	19.8
VII	Norbornene in HOAc-*O*-*t* – NaOAc reflux, 20 h	7 710	7 740	5.6	2.2	51.8	56.3	27.8	23.8	14.8	17.7

*The *exo*-1-OH-*x*-*t* was derived from the corresponding *exo*-1-OAc-*x*-*t* and was assayed as the α-naphthylurethan; it contained 100% of the *t*-activity.
†Data from ref. 3.

TABLE 2

Data from the treatment of norbornene with excess HOAc-*O-t* in the presence of NaOAc

Reactants used				*exo*-2-Norbornyl acetate					
HOAc-*O-t*				Carrier added (mmole)		Specific activity (c.p.m./mmole)		Yield (%)†	
Volume (ml)*	Specific activity (c.p.m./mmole)	Norbornene (mmole)	NaOAc (mmole)	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
25	525 300	20	22	19.5	22.0	9 120	13 600	1.7	2.9
30	923 400	20	100	17.5	19.5	23 300‡	33 100‡	2.3	3.6
50	774 400	7.5	270	18.9	24.3	4 070	2 130	1.3	0.9
100	774 400	7.5	1125	18.4	20.0	3 570	3 100	1.1	1.1

*Larger volumes were necessary to bring all reactants into solution in the experiments involving large amounts of NaOAc.
†Calculated from isotopic dilution, an illustration is given in the Experimental.
‡These samples were further diluted and degraded to give the isotopic distributions listed under experiment VII, Table 1.

tion in the reaction mixture to give isotopic scramblings which led to relatively larger amounts of overall rearrangement to C-3.

A possible route for locating the *t*-label at C-3 of the *exo*-**1**-OAc-*x-t* product would be via an elimination–addition process involving the addition of HOAc to the norbornene formed during the acetolysis of the 2-labeled brosylates. This possibility was investigated by a study on the addition of *O*-tritiated HOAc (HOAc-*O-t* from $Ac_2O + H_2O$-*t*) to norbornene in the presence of NaOAc. The results are given in Table 2. It can be seen that using NaOAc:norbornene molar ratios ranging from 1.1 to 150, refluxing in excess HOAc-*O-t* for 20 h resulted in the formation of only about 1–4% *exo*-**1**-OAc-*x-t* based on the norbornene. Since the acetolysis of *exo*-**1**-OBs gave rise to only 4% elimination products consisting of 98% nortricyclene and 2% norbornene (7), and since only 1–4% of the norbornene could be converted to *exo*-**1**-OAc under the acetolysis conditions, addition of HOAc to norbornene likely is not a major pathway responsible for the rearrangement of the label from C-2 to -3 in the acetolysis of *exo*- or *endo*-**1**-OBs-2-*t*.

If no rearrangement occurs in the addition of HOAc-*O-t* to norbornene, the resulting tritiated *exo*-**1**-OAc should have all the *t*-label located at the C-3 position. The two samples of *exo*-**1**-OAc-*x-t* obtained from the treatment of norbornene with the HOAc-*O-t* of highest specific activity (Table 2) were degraded and the isotopic distributions are given in Table 1 as experiment VII. The extensive isotopic scramblings observed in these samples further indicate the great propensity of the 2-norbornyl system to undergo cationic rearrangements, even when the cationoid species were generated from the reaction of norbornene with NaOAc buffered HOAc.

In a study on the π-route to the norbornyl cation from the solvolysis in HOAc–urea of 2-(Δ^3-cyclopentenyl)-2-^{14}C-ethyl *p*-nitrobenzenesulfonate (**2**-ONs-2-^{14}C), the resulting *exo*-**1**-OAc-*x*-^{14}C product was found to have the ^{14}C-label located essentially only at the C-3, -5, and -7 positions (*exo*-**1**-OAc-3,5,7-^{14}C) (8). This observation indicated that in this reaction, the amount of 3,2-hydride shift that took place in the resulting 2-norbornyl cation was negligible (the maximum extent of such 3,2-shifts could be no more than about 0.5%). If the *exo*-**1**-OAc-3,5,7-^{14}C obtained from such a reaction were treated with HOAc–NaOAc and the isotopic distribution in the recovered *exo*-**1**-OAc-*x*-^{14}C was ascertained, the data could provide an unequivocal demonstration that 3,2-shifts have occurred in the recovered acetate. The results from such an experiment, together with the earlier data of Lee and Hahn (8), are given in Table 3. These results clearly confirmed the conclusion that further isotopic scramblings in the initially formed acetolysis product could take place during its subsequent contact with the reaction medium. They also indicated that these further scramblings definitely gave rise to some overall 3,2-shifts, resulting, in the case with *exo*-**1**-OAc-3,5,7-^{14}C, in the rearrangement of some ^{14}C-label from C-3 to -2.

In the studies on internal returns, initially, it was intended to subject *exo*- and *endo*-**1**-OBs-2-*t* to partial acetolysis and then degrade the recovered brosylate to ascertain the nature and extent of the isotopic scrambling that might have resulted from the return processes. This was

TABLE 3

^{14}C-Distributions in the *exo*-2-norbornyl-*x*-^{14}C acetate (*exo*-**1**-OAc-*x*-^{14}C) from various experiments

Experiment	Reaction	Specific activity for 100% ^{14}C (c.p.m./mmole)*		^{14}C-Content (%)									
				C-2		C-3		C-1,4		C-7		C-5,6	
		Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
VIII†	**2**-ONs-2-^{14}C in HOAc–urea 60°, 30 h	87 800	98 400	0.0	0.0	27.8	27.9	0.0	0.0	24.1	22.8	48.1	49.3
IX‡	As in VIII	92 800		0.0		27.3		0.0		23.7		49.0	
X	*exo*-**1**-OAc-3,5,7-^{14}C from IX in HOAc–NaOAc 25°, 24 h	153 400	153 800	2.8	1.7	21.5	21.7	1.4	0.9	27.4	28.2	46.9	47.5

*Corresponding to the specific activity of the *cis*-cyclopentane-1,3-dicarboxylic acid derived from the degradation of the *exo*-**1**-OAc-*x*-^{14}C.
†Data from ref. 8.
‡Part of the *exo*-**1**-OAc-3,5,7-^{14}C product was diluted with inactive carrier and then degraded; the remainder was utilized for the two runs in experiment X.

accomplished with the *endo*-epimer. After acetolysis at 75° for approximately one half-life, the recovered *endo*-brosylate was treated with anhydrous tetramethylammonium acetate in dry acetone to give *exo*-**1**-OAc-2-*t* (3) which on subsequent conversion to norcamphor (3) results in the loss of more than 99% of the *t*-activity. This finding indicated that the recovered brosylate was essentially unrearranged *endo*-**1**-OBs-2-*t*, confirming the conclusion of no rearrangement or racemization due to return to *endo*-brosylate, which was arrived at from the equality of the titrimetric and polarimetric rates for the acetolysis of *endo*-**1**-OBs (9).

Incidentally, in the direct displacement reaction of *endo*-**1**-OBs-2-*t* with $(CH_3)_4NOAc$ in acetone, under strictly anhydrous conditions, it was possible to obtain *exo*-**1**-OAc-2-*t* with about 99.5% of the *t*-label accounted for at C-2 (3). Such samples of *exo*-**1**-OAc-2-*t* were used in experiments III and IV (Table 1), and it could also be converted to *exo*-**1**-OBs-2-*t* and utilized in experiments I and II (Table 1) (3). However, this reaction of *endo*-**1**-OBs-2-*t* with $(CH_3)_4NOAc$ could give rise to samples of *exo*-**1**-OAc-*x*-*t* with varying amounts up to about 10% of the *t*-label rearranged from C-2 to the rest of the norbornyl skeleton. Possibly, failure of maintaining absolutely anhydrous conditions during the reaction could have contributed to the formation of cationic pathways which led to isotopic scrambling (the $(CH_3)_4NOAc$ is extremely hygroscopic and its exposure to the atmosphere such as in weighing may require further drying for several days under vacuum over P_2O_5 before its use). B. L. Murr (private communications) has also noted such scramblings in the reaction between *endo*-**1**-OBs-2-*d* and $(CH_3)_4NOAc$, and he has found that the use of tetrabutylammonium acetate in benzene, instead of $(CH_3)_4NOAc$ in acetone, would eliminate this difficulty.

When *exo*-**1**-OBs-2-*t* was treated with anhydrous $(CH_3)_4NOAc$ in dry acetone, instead of obtaining only the product of direct displacement, *endo*-**1**-OAc-2-*t*, both *exo*- and *endo*-**1**-OAc were produced (about 70% *exo*- and 30% *endo*-), and the *t*-label in this mixed product was found to be extensively scrambled upon degradation. These behaviors are analogous to the observations of Schaefer and Weinberg (10, 11), who noted that the reaction of optically active *endo*-**1**-OH with triphenylphosphine and bromine gave optically active *exo*-**1**-Br via a bimolecular displacement, while the same reaction utilizing optically active *exo*-**1**-OH resulted in the formation of only some optically active *endo*-**1**-Br, the major product being racemic *exo*-**1**-Br (some nortricyclene was also formed). Obviously, any degradation of *exo*-**1**-OBs-*x*-*t* involving treatment with $(CH_3)_4NOAc$ could not give meaningful results.

Closson and coworkers (12) have reported that *exo*-**1**-OTs may be cleaved without rearrangement to give *exo*-**1**-OH by treatment with sodium naphthalene anion radical in tetrahydrofuran solution. When *exo*-**1**-OBs-2-*t* was treated by this method, the resulting *exo*-**1**-OH-*x*-*t* was also found to show extensive isotopic scrambling. Presumably, H–T exchange under these highly basic conditions could have contributed to the apparent lability of the *t*-label. The use of *exo*-**1**-OBs-2-*t* as a substrate thus is unlikely to lead to a successful study on the problem of internal returns. An alternative is to employ ^{14}C-labeled *exo*-**1**-OBs and cleave the recovered brosylate after partial acetolysis by sodium naphthalene. H. L. Goering (private communication) has indicated to us that he is planning to study internal returns in the 2-norbornyl system utilizing ^{14}C as label.

In order to avoid the necessity of degrading the recovered brosylate in the internal return studies, D-labeling and n.m.r. analysis could be employed, although such a method would be of less accuracy than analogous studies utilizing radioactive tracers. Experiments were carried out using *endo*- or *exo*-**1**-OBs-2-*d*, prepared as previously reported (13). After the substrate was acetolyzed in the presence of NaOAc for approximately one half-life, the recovered brosylate was examined by n.m.r. The spectra obtained are shown in Fig. 1. With *endo*-**1**-OBs-2-*d*, the spectra before and after partial acetolysis were essentially identical (Fig. 1*A*). There was no detectable H-absorption for the C-2 proton (4.7 p.p.m. region), indicating no rearrangement due to returns to *endo*-brosylate, in complete accord with the results obtained from studies with *endo*-**1**-OBs-2-*t*.

The *exo*-**1**-OBs-2-*d* employed in the partial acetolysis (Fig. 1*B*) appeared to contain traces of H-absorption at C-2 (4.4 p.p.m. region). After acetolysis at 25° for 100 min, the recovered *exo*-**1**-OBs-*x*-*d* (Fig. 1*C*) definitely showed a

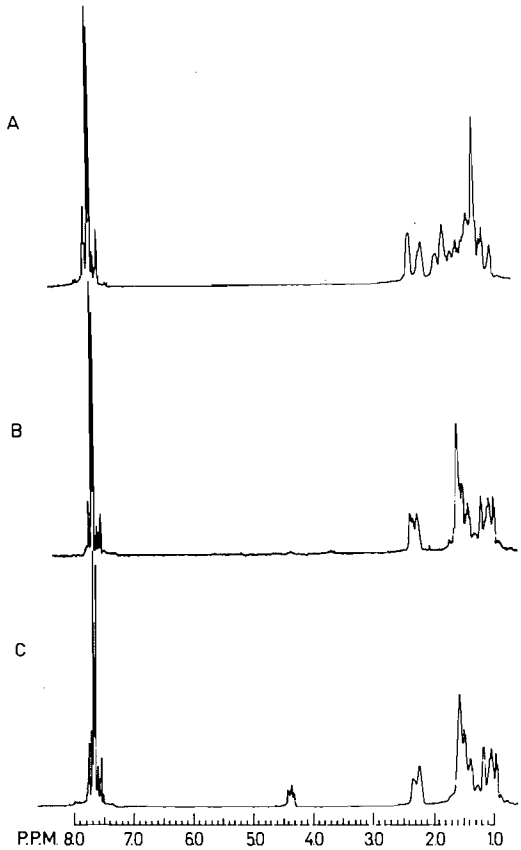
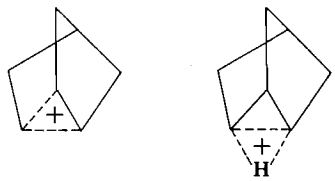


FIG. 1. The n.m.r. spectra. *A*, *endo*-2-Norbornyl-2-*d* brosylate (*endo*-**1**-OBs-2-*d*) before acetolysis and the same compound recovered after partial acetolysis; *B*, *exo*-**1**-OBs-2-*d* before acetolysis; *C*, *exo*-**1**-OBs-*x*-*d* recovered after partial acetolysis of *exo*-**1**-OBs-2-*d*.

significant increase in H-absorption at C-2. This was accompanied by a decrease in absorption for one of the bridge-head protons, the peak at 2.35 p.p.m. has decreased while the one at 2.25 p.p.m. remained essentially unchanged. These findings definitely indicated the scrambling of the D-label from C-2 to -1 in the recovered brosylate. Integration of Fig. 1*C*, using the absorption of the aromatic protons as an internal standard of 4.0 H, gave an estimated D-distribution of 0.4 ± 0.1 D at C-2, 0.4 ± 0.1 D at C-1,4 and 0.3 ± 0.1 D for the rest of the norbornyl skeleton (the integrated H-absorptions in the 0.8–1.8 p.p.m. region having changed from about 8.0 H in Fig. 1*B* to about 7.7 H in Fig. 1*C*). Although the small changes in integrated areas in the 0.8–1.8 p.p.m. region of Fig. 1*B* and *C* do not constitute a conclusive proof of 6,2-shifts, the probable presence of some D-label at C-3,5–7 does tend to suggest that scrambling of the D-label from C-2 to -6, as well as to C-1, has occurred as a result of internal returns during the acetolysis of *exo*-**1**-OBs-2-*d*.

From the above results, it is apparent that in the acetolysis of *exo*-**1**-OBs as commonly carried out in HOAc–NaOAc, isotopic scramblings could occur not only in the solvolysis reaction itself, but also prior to the reaction due to internal returns that gave rise to scrambled *exo*-**1**-OBs, and subsequent to the reaction due to ionization in the reaction medium of the initially formed product. Detailed quantitative analysis of the overall isotopic distributions obtained from labeled substrates would thus be fairly complicated. In interpreting such results, Roberts and coworkers (1, 2), and Lee and Lam (3) have used a qualitative approach. In treating the results such as those from experiments I and II (Table 1), Lee and Lam (3) have partitioned the overall *t*-distribution into contributions from processes in which C-1 and -2 are equivalent (Wagner–Meerwein shift), C-1, -2, and -6 are equivalent (Wagner–Meerwein and 6,2-shifts), and all carbon positions are equivalent (Wagner–Meerwein, 6,2- and 3,2-shifts). From more quantitative analyses of the data, such as by the elegant method of Collins and Lietzke (14), rate ratios for cation–anion collapse to 6,2- or 3,2-shifts (k_s/k_6 or k_s/k_3) could be evaluated. In this treatment, however, no provision was made for the possibility of further scrambling of the initial product in the solvolysis medium. When the reaction conditions are more likely to lead to kinetic control, such as in the π-route formation of the norbornyl cation from solvolysis of **2**-ONs-2-^{14}C in HOAc–urea or H_2O–acetone–$NaHCO_3$ (8), essentially no 3,2-shift was detected, and treatment of the scrambling data using the method of Collins and Lietzke (14) has led to the conclusion that both the norbornonium ion (corner-protonated nortricyclene) (**3**) and edge-protonated nortricyclene (**4**) are involved in product formation, and that ion **3** is the more stable of the two species.

Goering and Schewene (15) have studied the energy difference between the classical and non-classical norbornyl cations by investigating the $HClO_4$-catalyzed ionization of *exo*-**1**-OAc in HOAc. In the present work, isotopic scramblings have been found in the labeled *exo*-**1**-OAc even in NaOAc buffered HOAc (experiments III and



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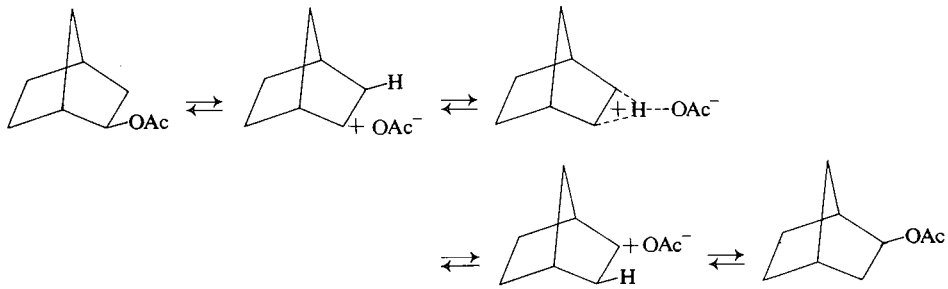
IV, Table 1). Data from such studies indicated that proportionally an extraordinarily large amount of net rearrangement from C-2 to -3 has occurred. In interpreting these results, even a qualitative partitioning into different contributing processes is not possible because all the apparent 3,2-shifts did not lead to all carbon positions becoming equivalent. In these cases, it appears that the process responsible for the rearrangement of the label from C-2 to -3 may be faster than other scrambling processes such as Wagner–Meerwein and 6,2-shifts. On the other hand, the formolysis of *exo*-**1**-OBs-2-*t* at 25° has been found to give a net rearrangement of about 6% of the label from C-2 to -3 (16). The overall *t*-distribution in the product from this formolysis reaction, however, could be rationalized qualitatively by the different contributing processes, with the assumption that 3,2-shifts together with Wagner–Meerwein and 6,2-shifts would result in the complete equivalence of all carbon positions. This apparent difference in the interpretation of the effects of 3,2-shifts in the formolysis of *exo*-**1**-OBs-2-*t* and in the reaction of *exo*-**1**-OAc-2-*t* in HOAc–NaOAc would appear to require some explanation. In this regard, it is pertinent to consider some spectroscopic data from the literature.

From the examination of the n.m.r. spectra of *exo*-**1**-OH in F_3CCOOH–H_2SO_4 under various conditions, with the amount of H_2SO_4 ranging from 5–60% and the temperature ranging from 0–40°, Fraenkel and coworkers (17) have concluded that under these conditions, 3,2- and 6,2-hydride shifts take place faster than Wagner–Meerwein rearrangements. Thus it appears that there could be some similarities in the processes of scrambling in the reaction of *exo*-**1**-OAc in HOAc–NaOAc and in the treatment of *exo*-**1**-OH in F_3CCOOH–H_2SO_4. In sharp contrast to the findings of Fraenkel and coworkers (17), the norbornyl cation generated in "super acid" by Schleyer and coworkers (18, 19) behaved quite differently. At temperatures between −5 and +37°, a one-peak n.m.r. spectrum was observed, indicating the equivalence of all protons on the n.m.r. time scale. When the temperature was lowered to −60°, the 3,2-hydride shift could be "frozen out", and it was estimated that at −120°, the 3,2-shift was slower than the 6,2-shift and the Wagner–Meerwein rearrangement by a minimum factor of $10^{8.8}$ (however, *cf.* ref. 20).

From considerations of data from Raman spectroscopy, ^{13}C n.m.r. and ^{1}H n.m.r. at very low temperatures down to −156°, Olah and coworkers (21–23) have recently concluded that the stable norbornyl cation is the nonclassical norbornonium ion or corner-protonated nortricyclene **3**, with its geometry corresponding to that of nortricyclene rather than that of norbornane. The 6,2,1-hydrogen migrations about the cyclopropane ring would, therefore, involve little if any change in the carbon skeleton of **3**. On the other hand, the 3,2-shift would require a lengthening of the 6,2 C—C bond distance in the transition state, resulting in a higher activation energy and a loss of σ-delocalization energy. It was further suggested that in the limiting case, when all the delocalization energy is lost prior to the transition state for the 3,2-shift, the classical ion could be considered an intermediate. In the formolysis of *exo*-**1**-OBs-2-*t* at 25° (16), subsequent ionization of the formate product probably contributed to some extent to the observed 6% overall 3,2-shifts. However, formolysis is likely to follow a **Lim** solvolysis mechanism (24, 25), involving relatively extensive dissociation and a long lifetime for the carbonium ion. Analogous to the behavior in super acid at room temperature, any 3,2-shift together with the 6,2,1-shifts would render all carbon positions equivalent. In the reaction of *exo*-**1**-OAc in HOAc–NaOAc, which involves a poor leaving group in a buffered medium, the degree of dissociation is likely not very extensive. Tight ion-pairs may be produced with the cationoid species retaining the norbornane geometry. 3,2-Shifts may occur at the ion-pair stage. Since *endo–endo* 3,2-hydride shifts are very unlikely (26–28), the process would involve *exo–exo* 3,2-shifts with the hydrogen migration occurring on the same side as the acetate group. Professor P. v. R. Schleyer has suggested to us that by hydrogen bonding-type of solvation, *exo–exo* 3,2-hydride shifts at the ion-pair stage may be facilitated. The mechanism of such a *cis*-shift would be analogous to that



SCHEME 1

proposed by Cram and Tadanier (29) in their interpretation of the stereochemistry of hydrogen participation in the solvolysis of the tosylates of the diastereomeric 3-cyclohexyl-2-butanols. The processes involved may be depicted by Scheme 1.

Finally, with regard to isotopic scramblings accompanying internal returns, the present studies indicated the probable rearrangement of the label from C-2 to both C-1 and -6. This finding could be explained by a mechanism involving 6,2,1-hydrogen shifts in the nonclassical ion **3** before return to covalent brosylate. An alternative or concurrent mechanism could involve returns to brosylate from both **3** and **4**, and such a mechanism would also suggest the competitive formation of **3** and **4** from *exo*-**1**-OBs. The possibility of competitive formations of two ions in the acetolysis of *exo*-**1**-OBs may be of some mechanistic significance. Recently, Lee and Hahn (30) have shown that in the acetolysis of 2-labeled *exo*-dehydro-2-norbornyl brosylate, the different results on the extent of isotopic scrambling previously reported by two groups of workers (31, 32) are both correct, the difference being attributable to a temperature effect due to the competitive formation of two intermediate ions. It is of interest to note that in experiments I and II (Table 1), significant differences in the *t*-distributions in the products were found for the acetolysis of *exo*-**1**-OBs-2-*t* carried out at 25 and 45°. Comparing the data from the two temperatures, it appears that the acetolysis at 25° resulted in more rearrangement of the label to C-5,6 and less to C-1,4,7, while at 45°, there was more rearrangement to C-1,4,7 and less to C-5,6. When these data were first reported (3), no explanation for these differences was offered. With the precedent established on the effects of temperature in the *exo*-dehydro-2-norbornyl system (30), and in view of the possibility of competitive formations of **3** and **4**, there is the possibility that in the acetolysis of *exo*-**1**-OBs, at lower temperatures, more product is formed from edge-protonated nortricyclene **4**, while at higher temperatures, more product is produced from the more stable ion **3**. Further studies to clarify or confirm these suggestions regarding competitive reactions and temperature effects in the 2-norbornyl system would appear to be worthwhile.

Experimental

*Acetolysis of endo-**1**-OBs-2-t and Treatment of Labeled exo-**1**-OAc in HOAc–NaOAc*

The methods for the preparation of *endo*-**1**-OBs-2-*t* and *exo*-**1**-OAc-2-*t* and for the degradation of the *exo*-**1**-OAc-*x*-*t* product from the various experiments are the same as those previously described by Lee and Lam (3). The treatment of *exo*-**1**-OAc-2-*t* in HOAc–NaOAc and the acetolysis of *endo*-**1**-OBs-2-*t* (experiments IV–VI, Table 1) also followed the procedures of Lee and Lam (3) except for the changes in reaction temperature and reaction time as given in Table 1.

The acetolysis of **2**-ONs-2-^{14}C in HOAc–urea (experiment IX, Table 3) and the degradation of the acetate product to establish the ^{14}C-distribution followed the same procedures described by Lee and Hahn (8). The treatment of *exo*-**1**-OAc-3,5,7-^{14}C in HOAc–NaOAc (experiment X, Table 3) was carried out under the same conditions used by Lee and Lam for experiment III (3).

Addition of HOAc-O-t to Norbornene

HOAc-*O*-*t* was prepared by the dropwise addition of a slight excess of Ac_2O to H_2O-*t* followed by refluxing the resulting material for 2 h. The HOAc-*O*-*t*, b.p. 118–119°, was recovered by fractional distillation in the presence of about 1% $KMnO_4$.

In a typical experiment, 1.88 g (20 mmole) of norbornene and 1.80 g (22 mmole) of NaOAc were dissolved in 25 ml of HOAc-*O*-*t* and the resulting material was refluxed for 20 h. Periodically during the refluxing, the small amount of norbornene that had collected on the condenser was rinsed down with some of the reaction mixture. At the end of the 20 h, cracked ice was introduced and a known weight of inactive *exo*-**1**-OAc was added as carrier. Most of the HOAc-*O*-*t* was then removed by fractionation and the residue was extracted several times

with 25-ml portions of petroleum ether. The combined extract was washed successively with water, 10% K_2CO_3 solution, and again water. After drying over $MgSO_4$, the solution was concentrated using a rotatory evaporator. From the residue, pure *exo*-**1**-OAc-*x*-*t* was recovered by preparative v.p.c. (3/8 in. copper column packed with 25% Carbowax 20M on Chromosorb P, operating at 150°).

As an illustration of the isotope dilution calculations, for the experiment described above, the specific activity of the HOAc-*O*-*t* was 525,300 c.p.m./mmole; the amount of *exo*-**1**-OAc carrier added was 19.5 mmole; and the specific activity of the recovered *exo*-**1**-OAc-*x*-*t* was 9120 c.p.m./mmole. If *x* mmole of active *exo*-**1**-OAc was formed before its dilution by the inactive carrier, then

$$525\,300\,x = (x + 19.5)9120$$

$$x = 0.34 \text{ mmole}$$

The yield was $(0.34/20) \times 100 = 1.7\%$.

Internal Return Studies

The *endo*- and *exo*-**1**-OBs-2-*d* were prepared as described by Lee and Wong (13).

The *endo*-**1**-OBs-2-*d* (3.0 g, 9 mmole), in 30 ml of HOAc containing NaOAc (0.82 g, 10 mmole), was heated at 75° for 60 min (approximately one half-life estimated from the rate of solvolysis (9) of *endo*-**1**-OBs in HOAc–KOAc). The resulting material was poured into ice–water and extracted with ether. The extract was washed with water and $NaHCO_3$ solution, dried over $MgSO_4$ and concentrated by the removal of practically all of the ether. From the residue, about 1.0 g of brosylate was recovered upon crystallization from ether – petroleum ether.

The *exo*-**1**-OBs-2-*d* (3.0 g) was also subjected to partial acetolysis and about 1.0 g of brosylate was recovered as described above for the *endo*-epimer except that the temperature used was 25° and the reaction time was 100 min (approximately one half-life estimated from the rate of solvolysis (5) of *exo*-**1**-OBs in HOAc–KOAc).

The n.m.r. spectra of the various samples of deuterated *endo*- and *exo*-**1**-OBs were determined in CCl_4 solution using an HA100 spectrometer.

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1. J. D. Roberts and C. C. Lee. J. Amer. Chem. Soc. **73**, 5009 (1951).
2. J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr. J. Amer. Chem. Soc. **76**, 4501 (1954).
3. C. C. Lee and L. K. M. Lam. J. Amer. Chem. Soc. **88**, 2831 (1966).
4. C. C. Lee, B.-S. Hahn, and L. K. M. Lam. Tetrahedron Lett. 3049 (1969).
5. S. Winstein and D. Trifan. J. Amer. Chem. Soc. **74**, 1154 (1952).
6. S. Winstein and K. C. Schreiber. J. Amer. Chem. Soc. **74**, 2165 (1952).
7. S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger. J. Amer. Chem. Soc. **87**, 376 (1965).
8. C. C. Lee and B.-S. Hahn. J. Amer. Chem. Soc. **91**, 6420 (1969).
9. S. Winstein and D. Trifan. J. Amer. Chem. Soc. **74**, 1147 (1952).
10. J. P. Schaefer and D. S. Weinberg. J. Org. Chem. **30**, 2635 (1965).
11. J. P. Schaefer and D. S. Weinberg. J. Org. Chem. **30**, 2639 (1965).
12. W. D. Closson, P. Wriede, and S. Bank. J. Amer. Chem. Soc. **88**, 1581 (1966).
13. C. C. Lee and E. W. C. Wong. J. Amer. Chem. Soc. **86**, 2752 (1964).
14. C. J. Collins and M. H. Lietzke. J. Amer. Chem. Soc. **89**, 6565 (1967).
15. H. L. Goering and C. B. Schewene. J. Amer. Chem. Soc. **87**, 3516 (1965).
16. C. C. Lee and L. K. M. Lam. J. Amer. Chem. Soc. **88**, 5355 (1966).
17. G. Fraenkel, P. D. Ralph, and J. P. Kim. Can. J. Chem. **43**, 674 (1965).
18. P. v. R. Schleyer, W. E. Watts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah. J. Amer. Chem. Soc. **86**, 5679 (1964).
19. M. Saunders, P. v. R. Schleyer, and G. A. Olah. J. Amer. Chem. Soc. **86**, 5680 (1964).
20. C. J. Collins and C. E. Harding. J. Amer. Chem. Soc. **91**, 7194 (1969).
21. G. A. Olah, A. Commeyras, and C. Y. Lui. J. Amer. Chem. Soc. **90**, 3882 (1968).
22. G. A. Olah and A. M. White. J. Amer. Chem. Soc. **91**, 3954 (1969).
23. G. A. Olah and A. M. White. J. Amer. Chem. Soc. **91**, 3956 (1969).
24. S. Winstein, E. Grunwald, and H. W. Jones. J. Amer. Chem. Soc. **73**, 2700 (1951).
25. S. Winstein and H. Marshall. J. Amer. Chem. Soc. **74**, 1120 (1952).
26. P. v. R. Schleyer. J. Amer. Chem. Soc. **89**, 699 (1967).
27. G. E. Gream. Rev. Pure Appl. Chem. **16**, 25 (1966).
28. J. L. Fry and G. J. Karabatsos. *In* Carbonium ions. Vol. II. G. A. Olah and P. v. R. Schleyer, *editors*. Interscience Publishers, New York, 1970. Pp. 521–571.
29. D. J. Cram and J. Tadanier. J. Amer. Chem. Soc. **81**, 2737 (1959).
30. C. C. Lee and B.-S. Hahn. J. Amer. Chem. Soc. **92**, 2583 (1970).
31. J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr. J. Amer. Chem. Soc. **77**, 3034 (1955).
32. S. J. Cristol, T. C. Morrill, and R. A. Sanchez. J. Amer. Chem. Soc. **88**, 3087 (1966).