

3,2-HYDRIDE SHIFTS IN THE NORBORNYL SYSTEM
UNDER ACETOLYSIS CONDITIONS*

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N.m.r. studies have shown that the 3,2-hydride shift in the norbornyl cation, generated in highly acidic media at low temperatures, is extremely slow in comparison with Wagner-Meerwein and 6,2-hydride shifts (1-3). Under solvolytic conditions, however, different behaviours could be obtained. Thus a significant extent of 3,2-hydride shift has been observed in the formolysis of 2-t-2-exo-norbornyl brosylate (exo-I-OBs-2-t)(4). In our earlier work on the acetolysis of exo- and endo-I-OBs-2-t (5), small amounts (about 1%) of the t-label was found at the C-3 position of the resulting product, exo-I-OAc-t, and it was concluded that most, if not all, of this overall 3,2-hydride shift could have resulted from subsequent ionization of the exo-I-OAc-t in the reaction mixture (5). We now wish to report further data, given in Tables I and II, in support of this conclusion.

Table I. Tritium Distributions in the exo-I-OAc-t Obtained from Duplicate Runs of Various Experiments.^a

Expt.	Reaction	Tritium Content, %			
		C-2	C-3	C-1,4,7	C-5,6
1	<u>exo</u> -I-OAc-2- <u>t</u> in HOAc-NaOAc 25°, 24 hr. ^b	96.0; 96.5	1.0; 1.1	2.2; 1.7	0.8; 0.7
2	<u>exo</u> -I-OAc-2- <u>t</u> in HOAc-NaOAc reflux, 20 hr.	90.7; 90.5	4.8; 4.1	3.2; 3.9	1.3; 1.4
3	<u>endo</u> -I-OBs-2- <u>t</u> in HOAc-NaOAc 30°, 64 days	41.4; 42.5	6.3; 4.7	32.8; 32.8	19.5; 20.0
4	<u>endo</u> -I-OBs-2- <u>t</u> in HOAc-NaOAc 30°, 2 days	54.0; 54.0	1.0; 0.2	25.0; 26.0	20.0; 19.8
5	Norbornene in TOAc-NaOAc reflux, 20 hr.	5.6; 2.2	51.8; 56.3	27.8; 23.8	14.8; 17.7

^aMethod of degradation given in Ref. 5.^bData from Ref. 5

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When exo-I-OAc-2-t** and 1.1 molar equivalents of NaOAc were stirred in HOAc under the conditions given for Expt. 1 and 2 in Table I, the results show that a higher temperature causes more extensive rearrangements. Of interest also is the relatively large proportion of activity found at C-3 in Expt. 2. The acetolysis of endo-I-OBS-2-t at reflux temperature has been reported in the previous study (5). When this acetolysis reaction was carried out at 30° for 64 days (approximately one half-life) (Expt. 3), the product showed extensive isotopic scrambling, with 4.7 and 6.3% of the activity found at C-3 in the duplicate runs. However, if the reaction time was reduced from 64 to 2 days (Expt. 4), the amount of net rearrangement from C-2 to C-3 was drastically decreased. These results, therefore, suggest that the exo-I-OAc-t, formed in the acetolysis, could undergo reactions in the acetolysis medium to give further isotopic scrambling, the extent of which being dependent on temperature and contact time, with the resulting material showing a relatively large proportion of the t-activity at C-3.

A possible route for locating the t-label at C-3 of the exo-I-OAc product is the addition of HOAc to norbornene formed during the acetolysis of 2-labeled brosylates. This possibility was investigated by a study on the addition of tritiated acetic acid (from $\text{Ac}_2\text{O} + \text{H}_2\text{O-t}$) to norbornene in the presence of NaOAc. Using the tritiated acid as solvent and NaOAc from 10% to 400% in excess of the norbornene, the yields of exo-I-OAc-t, obtained after refluxing the mixture for 20 hr., were found by isotope dilution calculations to be only 1-3%. The t-label in the resulting exo-acetate, however, was also extensively scrambled; a set of data is included in Table I (Expt. 5). Since only a small amount of norbornene is formed during acetolysis (6) and since only 1-3% of this small amount of norbornene could be converted to exo-I-OAc, addition of HOAc to norbornene likely is not the major pathway leading to the rearrangement of the t-label from C-2 to C-3.

In the preceding communication (7), it was reported that the acetolysis of 2-(Δ^3 -cyclopentenyl)-2- ^{14}C -ethyl *p*-nitrobenzenesulfonate (II-2- ^{14}C) in the presence of 2.0 molar equivalents of urea gave exo-I-OAc- ^{14}C with scrambling of the ^{14}C -label only among the C-3, C-7 and C-5 positions, indicating no 3,2-hydride shift. when the

** The exo-I-OAc-2-t used in the present work was prepared from reaction between endo-I-OBS-2-t and $(\text{CH}_3)_4\text{NOAc}$ in dry acetone; about 99.5% of its t-label was found to be located at C-2 (5). In some instances, however, such a preparation gave exo-I-OAc-t with varying amounts of rearrangement of the label, possibly because the acetone was not absolutely dry. In a private communication, Professor Brown L. Murr informed us that such isotopic scramblings can be eliminated if the preparation were effected between labeled endo-I-OBS and Bu_4NOAc in benzene. When exo-I-OBS-2-t was treated with $(\text{CH}_3)_4\text{NOAc}$ in dry acetone, both endo- and exo-I-OAc-t, with extensive isotopic scrambling, were obtained.

exo-I-OAc-¹⁴C obtained from such an acetolysis (Expt. 6) was treated with HOAc-NaOAc (Expt. 7), the isotopic distributions in the recovered exo-I-OAc-¹⁴C, given in Table II, unequivocally show the occurrence of some 3,2-hydride shifts.

Table II. ¹⁴C-Distributions in the exo-I-OAc-¹⁴C Obtained from Various Experiments.^a

Expt.	Reaction	¹⁴ C-Content, %				
		C-2	C-3	C-1,4	C-7	C-5,6
6	II-2- ¹⁴ C in HOAc-Urea 60°, 30 hr. ^b	0.0	27.3	0.0	23.7	49.0
7	<u>exo</u> -I-OAc-C ¹⁴ from Expt. 6 in HOAc-NaOAc 25°, 24 hr.	2.8; 1.7	21.5; 21.7	1.4; 0.9	27.4; 28.2	46.9; 47.5

^aMethod of degradation given in Ref. 7.

^bThe results from this experiment are in good agreement with the data reported in Ref. 7.

The above results clearly indicate that further isotopic scrambling in the labeled exo-I-OAc product can take place in the acetolysis reaction medium, and that the processes involved are capable of giving rise to significant amounts of 3,2-hydride shifts. Possibly, in the ionization of exo-I-OAc in HOAc-NaOAc, there is little or no anchimeric assistance and the driving force required, such as assistance by solvation, could produce an ion-pair with an essentially classical norbornyl cation in which 3,2- and 6,2-hydride shifts as well as Wagner-Meerwein rearrangements can occur.

It may also be worthwhile pointing out that in contrast to the isotopic distribution of more ¹⁴C-label at C-3 than C-7 in the acetate from Expt. 6, the exo-I-OAc-¹⁴C from Expt. 7 has more ¹⁴C-label located at C-7 than C-3 (Table II). These results suggest the probable occurrence of 6,2-hydride shifts followed by Wagner-Meerwein rearrangement, thus converting the C-5 position of the initial acetate from Expt. 6 into the C-7 position of the acetate from Expt. 7. It is of interest to note that from studies of the n.m.r. spectra of exo-I-OH in F₃CCOOH-H₂SO₄ under various conditions, Fraenkel and coworkers (8) have concluded that, in contrast to the behaviour of the norbornyl cation generated in highly acidic media (1-3), under their conditions, 3,2- and 6,2-hydride shifts take place faster than Wagner-Meerwein rearrangements. Apparently, there may be some similarities in the behaviours of the cation or ion-pair generated from exo-I-OAc in the present work and from exo-I-OH by Fraenkel and coworkers (8).

References

1. 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).
2. M. Saunders, P. von R. Schleyer, and G. A. Olah, J. Am. Chem. Soc., 86, 5680 (1964).
3. F. R. Jensen and B. H. Beck, Tetrahedron Letters, 4287, (1966).
4. C. C. Lee and L. K. M. Lam, J. Am. Chem. Soc., 88, 5355 (1966).
5. C. C. Lee and L. K. M. Lam, J. Am. Chem. Soc., 88, 2831 (1966).
6. S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, J. Am. Chem. Soc., 87, 376 (1965).
7. C. C. Lee and B.-S. Hahn, The preceding communication in this journal.
8. G. Fraenkel, P. D. Ralph, and J. P. Kim, Can. J. Chem., 43, 674 (1965).