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A DEMONSTRATION OF CONSECUTIVE HYDRIDE SHIFTS DURING NORBORNYL REARRANGEMENTS*

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6,2-Migrations of hydrogen have been unequivocally demonstrated by Roberts (1) and co-workers, and by Doering and Wolf (2,3) during carbonium ion rearrangements of exo-2-norbornyl tosylate and of O-deuterated fenchol, respectively. In neither of these cases, however, is it possible to say if the hydrogen actually moves from the 6 to the 2 position, or whether a 6,1- and, subsequently, a 1,2-shift occurs. Berson and Grubb (4) recently showed that a 5-endo deuterium undergoes a transannular, intramolecular migration in the 2-carboxy-3-methyl-5-norbornyl cation (corresponding to a 6,2-shift in the norbornyl case).

We discussed previously (5) the stereospecific elimination of deuterium, and the stereospecific 5,4-migration of deuterium (corresponding to 6,1-migration in unsubstituted norbornyl) during hydrolysis of the dideutero-2-endo-phenyl-2-hydroxy-3-norbornyl tosylate 1, and mentioned that there were traces of another, then unidentified diol in the product. We

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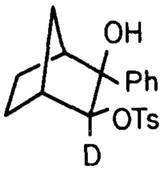
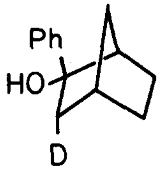
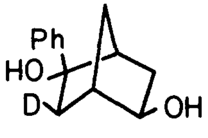
have already discussed the products arising from the presumed bridged ion intermediates A and B [Chart I] and the intermediate between them. The discovery of an additional diol* in very small yield after hydrolysis of 1a led to the intriguing possibility that this diol might be either 2a or 3a which conceivably *could be formed by consecutive shift of deuterium [A→B] and hydrogen [B→C].* The isotope position isomers 2b and 3b are also possible through a direct 5,3-migration of the *endo*-5 hydrogen [A→D]. In fact, the diol turned out to be 2ab which formed from *both* ions C and D, in the approximate proportions 9:1. This conclusion was confirmed by repeating the experiment with tosylate 1c, and isolating the mixture 2cd



1c



2c



2d

in about the same proportion.

The structure of 2 was confirmed by independent synthesis (4→5→2) and by analysis of its n.m.r. spectra recorded at 60 mc./sec. and at 100 mc./sec. Assignments of the signals and coupling constants were made with the aid of spin decoupling in the frequency sweep mode. The signals at 1.94 p.p.m. and

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*M.p. 163. *Anal.* calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.55; H, 7.97. Yield determinations by isotopic dilution methods will be reported later.

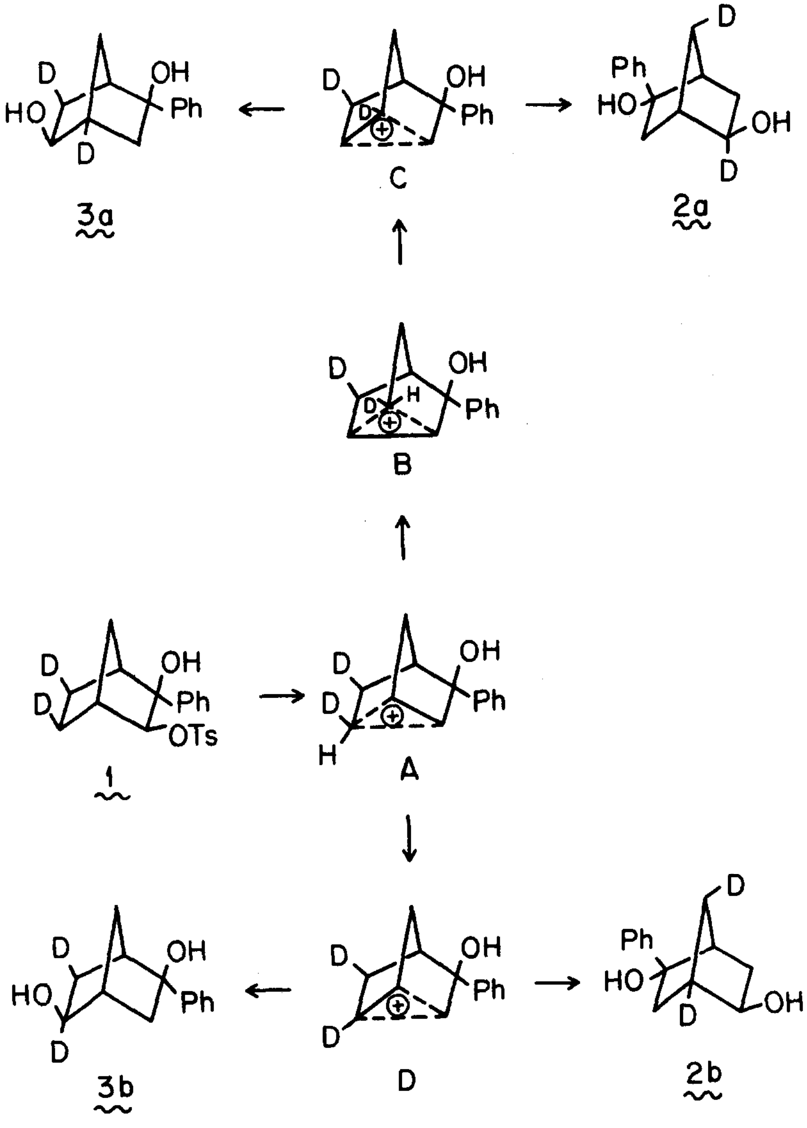
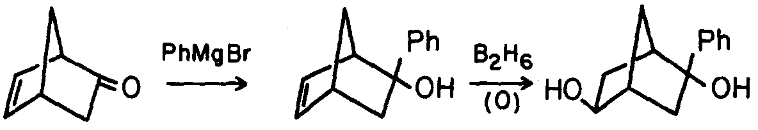


CHART I

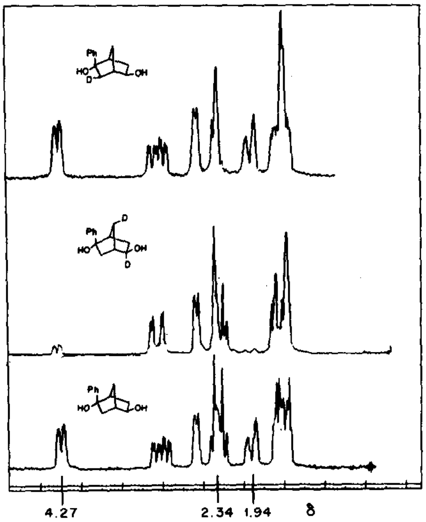


4 5 2

4.27 p.p.m. (Fig. 1) arise from the 7-*syn** and 5-*endo*

FIG. 1

The 100 mc./sec. spectra of 2, 2ab, and 2cd taken at 60°C in pyridine solution using TMS as standard at $\delta = 0$. The sample giving the spectrum in the center is composed of approximately 80% 2a, 10% 2b, and 10% 2. The sample giving the spectrum at the top is composed of about 80% 2d, 10% 2c, and 10% 2.



***Syn* to the 5-*exo* hydroxyl. We estimate our error in deuterium determinations to be not more than ± 3 percent.

hydrogens, respectively. In the spectrum of 2ab the signal for 7-syn-H is almost totally absent and the signal for 5-endo-H is only partly visible. From the integrated intensities of the signals and because the starting tosylate contained about ten percent protium in the 5-exo and 6-exo positions it is clear that approximately ninety percent of 2a is formed through A→B→C and ten percent of 2b is formed through A→D. In the spectrum of 2cd the quartet (at 2.34 p.p.m.) arising from 3-exo-H is considerably attenuated thus further confirming the course of reaction.

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References

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

2. W. von E. Doering and A. P. Wolf, Chem. Abstr. **46**, 7080 (1952).

3. J. A. Berson, Molecular Rearrangements, Chap. 3, p. 141, Interscience Publishers (New York) Ed. P. de Mayo (1963).

4. J. A. Berson and P. W. Grubb, J. Amer. Chem. Soc. **87**, 4016 (1965).

5. Ben M. Benjamin and C. J. Collins, J. Amer. Chem. Soc. **88**, 1556 (1966); B. M. Benjamin, B. W. Ponder and C. J. Collins, ibid. **88**, 1558 (1966).