

GAS CHROMATOGRAPHIC EVIDENCE FOR INTRAMOLECULAR

HYDROGEN BONDING WITH DOUBLE BONDS

C. H. DePuy and P. R. Story

Department of Chemistry, Iowa State College, Ames, Iowa

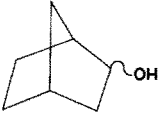
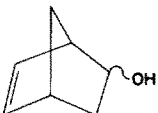
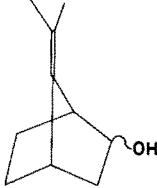
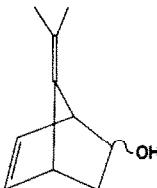
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IN recent publications it has been shown that intramolecular hydrogen bonds between hydroxyl groups and carbon-carbon double bonds may be detected by infrared spectra.¹ We wish to report data which show that unsaturated bicyclic alcohols which are capable of internal hydrogen bonding show strikingly shorter retention times than epimers or dihydro derivatives which cannot so interact.

Analysis of the data in Table 1 shows that exo and endo norborneol (I) have similar retention times. Introduction of a double bond into the exo isomer has practically no effect on the retention time. Introduction of a double bond into the endo isomer (to give endo-II, the only member of the series capable of intramolecular hydrogen bonding^{1c}) sharply decreases its retention time.

^{1a} D. S. Trifan, J. L. Weinmann and L. P. Kuhn, J. Amer. Chem. Soc. 79, 6555- (1957); ^b A. W. Baker and A. T. Shulgin, Ibid. 80, 5358 (1958); ^c P. von R. Schleyer, D. S. Trifan and R. Bacskai, Ibid. 80, 6691 (1958).

Table 1. GLPC Retention Times^(a)

			
I	II	III	IV
<u>endo</u> 104 ^(b)	79 ^(b)	38 ^(c)	30 ^(c)
<u>exo</u> 96	94	28	33

^(a) Retention times in minutes determined on a 12 ft x $\frac{1}{4}$ in. column packed with 23% by weight Ucon No. 50HB 2000, available from Union Carbide, on Celite.

^(b) At 160° and 30 mL/min of He.

^(c) At 210° and 41 mL/min of He.

Exo and endo-7-isopropylidene-dehydronorborneol (IV),² in both of which intramolecular hydrogen bonding may reasonably be assumed, have similar retention times. Reduction of the 5,6-double bond in the exo isomer results in a decrease in retention time. Removal of this same double bond in the endo isomer (to give endo-III, the only member of the series incapable of intramolecular hydrogen bonding) results in an increase in retention time. The net effect of intramolecular hydrogen bonding is to decrease the retention time by nearly $\frac{1}{3}$.

These observations constitute the first nonspectral evidence for such intramolecular hydrogen bonding and suggest that GLPC will be an important adjunct to I.R. in the determination of the configurations of unsaturated alcohols.

² C. H. DePuy and P. R. Story, submitted to J. Amer. Chem. Soc.