THE EFFECT OF 1,5-BRIDGING ON THE SOLVOLYTIC BEHAVIOR

OF THE BICYCLO[3.1.0]HEX-2-YL CATION[1]

Paul G. Gassman, Richard N. Steppel, and Eugene A. Armour

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

The generation of the bicyclo[3.1.0]hex-2-yl cation has been the subject of much recent

discussion.[2] In particular, considerable attention has been given to the question of whether

different cations result from the ionization of a suitable leaving group from the exo and endo

sides of the 2-position of the bicyclo[3.1.0]hexane nucleus.[2f] As part of our general interest

in the chemistry of strained ring systems, we have studied the solvolysis of certain bridged

bicyclo[n.1.0]alkane derivatives. In view of the extent of interest in the bicyclo[3.1.0]-

hex-2-yl cation, we now wish to report our results on the solvolysis of bicyclo[3.1.0]hex-2-ol

p-nitrobenzoates, which are bridged across the 1,5-positions.

Table 1 lists the rates of solvolysis of the p-nitrobenzoates 1-6 in 70:30 ^{v}/v acetone:

water. As can be seen from this data, bridging of the 1,5-positions of 5 and 6 provides for
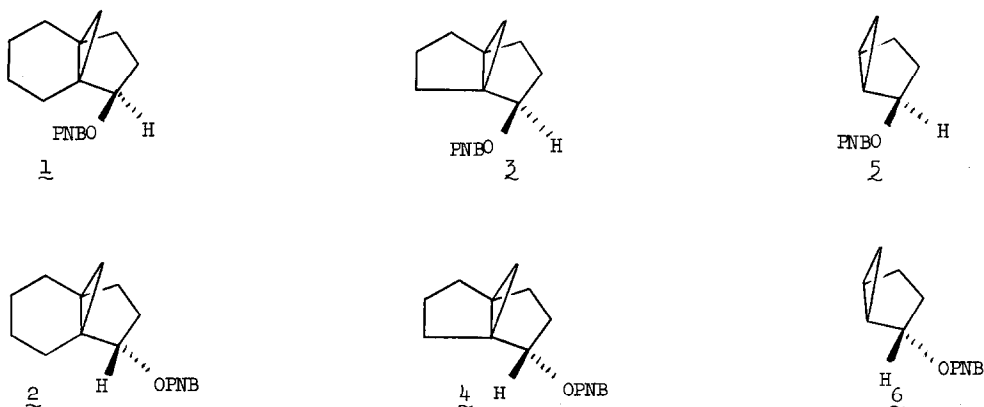
a considerable increase in the solvolysis rates. In the case of 2 and of 4, this acceleration

might conceivably be associated with the change in steric environment of the leaving group.

However, an analogous argument cannot be made for the similarly accelerated rates observed for

the solvolysis of 1 and 3 relative to 5. Examination of the rate ratios of the epimeric pairs

5 and 6, 3 and 4, and 1 and 2, shows that these ratios (3.8, 3.4, and 1.9, respectively) vary

Table 1. Rates of Solvolysis of Derivatives of Bicyclo[3.1.0]hexane in 70:30 $^V/v$ Acetone:Water

Compound	Temp (±0.02 °C)	Rate (sec^{-1})	k_{rel} @25°	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)
1	115.00	$(2.22 \pm 0.07) \times 10^{-3}$			
	100.00	$(6.82 \pm 0.09) \times 10^{-4}$		23.9	-9.5
	85.00	$(1.53 \pm 0.03) \times 10^{-4}$			
	25.0[a]	1.54×10^{-7}	1230		
2	115.00	$(1.12 \pm 0.02) \times 10^{-3}$			
	100.00	$(3.29 \pm 0.01) \times 10^{-4}$		23.7	-11.5
	85.00	$(7.89 \pm 0.01) \times 10^{-5}$			
	25.0[a]	8.26×10^{-8}	661		
3	130.00	$(2.75 \pm 0.02) \times 10^{-3}$			
	115.00	$(9.63 \pm 0.12) \times 10^{-4}$		22.9	-14.1
	100.00	$(2.56 \pm 0.07) \times 10^{-4}$			
	25.0[a]	9.02×10^{-8}	722		
4	130.00	$(1.66 \pm 0.01) \times 10^{-3}$			
	115.00	$(5.76 \pm 0.09) \times 10^{-4}$		24.6	-10.7
	100.00	$(1.31 \pm 0.01) \times 10^{-4}$			
	25.0[a]	2.62×10^{-8}	210		
5	160.00	$(8.91 \pm 0.04) \times 10^{-4}$			
	145.00	$(2.90 \pm 0.04) \times 10^{-4}$		26.7	-11.4
	130.00	$(8.21 \pm 0.16) \times 10^{-5}$			
	25.0[a]	4.78×10^{-10}	3.8		
6	160.00	$(8.30 \pm 0.13) \times 10^{-4}$			
	145.00	$(2.40 \pm 0.05) \times 10^{-4}$		29.2	-6.0
	130.00	$(6.20 \pm 0.03) \times 10^{-5}$			
	25.0[a]	1.25×10^{-10}	1.0		

a) Extrapolated from higher temperatures.

very little. This indicates that the effect of the trimethylene bridge in the tricyclo-[3.3.1.0^{1,5}]nonane derivatives and of the tetramethylene bridge in the tricyclo[4.3.1.0^{1,6}]-decane derivatives was probably the same for both the exo and endo p-nitrobenzoates.

Recently, the solvolyses of 7 and 8 were found to be 22 and 18 times faster than those of the corresponding non-methylated cases.[2f] Although this was interpreted in terms of a highly delocalized structure such as 9, the authors indicated that the effect of methyl substitution was primarily an entropy effect. Our data indicate that the trimethylene bridge in the case of 3 and 4, and the tetramethylene bridge in the case of 1 and 2 do not have much of an effect on the entropy of the reaction, even though rate accelerations of greater then 10^2 result from

this bridging.
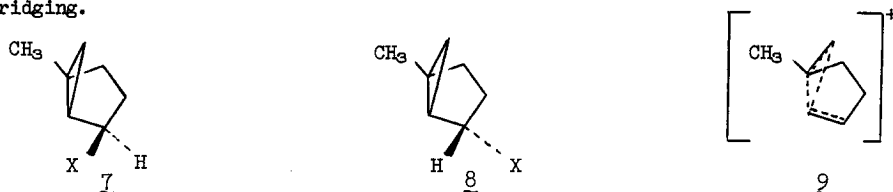
Product studies on 3 and 4 at 100° indicated that both 3 and 4 gave a 1:2 mixture of 10

and 11 on solvolysis in aqueous acetone. Solvolysis at higher temperatures, or the heating of

10 and 11 in the presence of acid, resulted in the formation of small amounts of additional

products, which were not identified. These studies indicated that 3 and 4 probably solvolyzed

to give the same ion.

Product studies on 1 and 2 were somewhat more complicated because the ratio of products

changed during the course of the reaction due to the instability of some of the products under

the reaction conditions. Thus, after ten half-lives at 85°, 1 gave 12 (59%), 13 (5%), 14 (7%),

and 15 (20%). In contrast, after 10% reaction the ratio of 12:13:14:15 was 70:25:4:1. This
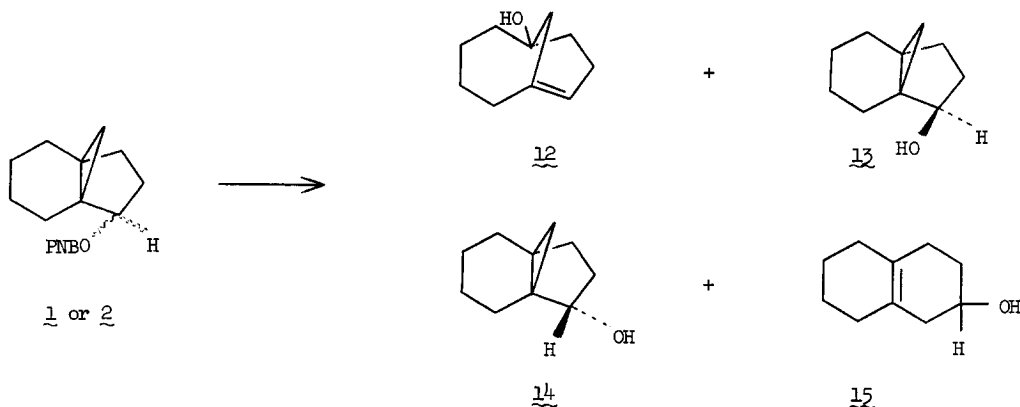
indicated to us that 12 and 13 were the primary products of the solvolysis and that they were

converted into 14 and 15 under the reaction conditions. After ten half-lives at 85°, 2 also

gave 12 (63%), 13 (8%), 14 (6%), and 15 (14%). At 10% reaction the ratio of 12:13:14:15

from 2 was 68:30:1:trace, which shows that the product ratios from the solvolysis of 1 and 2

are essentially within experimental error of each other. This indicates that the primary

products from both 1 and 2 are the same, and suggests that 1 and 2 probably ionize to give the same cationic intermediate.

The structures of 13 and 14 were established by comparison with the authentic samples[3] used in the preparation of 1 and 2. Comparison of 15 with an authentic sample prepared according to the literature procedure[4] established the structure as bicyclo[4.4.0]dec-1(6)-en-3-ol. A combination of spectral and chemical evidence was used to elucidate the structure of 12. Nmr and ir spectral data established the presence of a tertiary alcohol and of a trisubstituted double bond [one proton triplet at τ 4.46 (J = 5.5 Hz)]. In addition, the nmr spectrum showed six allylic type protons at τ 7.66–8.15. Hydrogenation of 12 gave a saturated tertiary alcohol, whose ir spectrum compared well with that reported for bicyclo[4.3.1]decan-1-ol.[5]

The similar product ratios obtained from 1 and 2, and from 3 and 4, indicate to us that the epimeric pairs of compounds are solvolyzing to the same intermediates. The significant difference in the primary products obtained from the two tricyclic ring systems is of interest. The formation of 12 as the major product from 1 and 2 and the absence of analogous products from 3 and 4 can be rationalized in terms of the nine-membered ring of 12 being able to sustain a trans double bond. If a similar product were to be formed from 3 and 4, a *trans*-cyclooctene would be incorporated into the bicyclic skeleton.[6] The added strain energy, which would result from such a trans double bond is probably sufficient to inhibit formation of products containing this moiety.

<div align="center">REFERENCES</div>

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