# Transannular Hydride Shifts in the Bicyclo[3,3,1]nonane System

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FROM *X*-ray and spectroscopic evidence,[1] the preferred ground-state conformation of bicyclo-[3,3,1]nonane appears to be a twin-chair form in which the severe transannular C(3)–C(7) non-bonded interaction is accommodated by an easing apart of these two centres. Transannular, C(3)–C(7) hydride shifts have been reported for this ring system[2] but, to date, all the examples were characterised by strongly acidic reaction conditions and a powerful thermodynamic driving force for the observed migration. It was therefore of interest to determine the extent of C(7)–C(3) hydride shift (if any) associated with the solvolysis of *exo*-3-bicyclo[3,3,1]nonane toluene-*p*-sulphonate (I; R = OTs).

Solvolysis of (I; R = OTs) and the corresponding *endo*-epimer (II; R = OTs)† was carried out in aqueous acetone–Li$_2$CO$_3$ and acetic acid–sodium acetate and the product distribution results and relevant kinetic data are summarised in Tables 1 and 2.

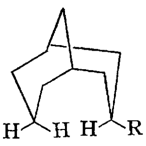
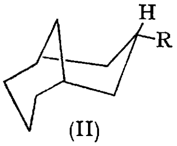
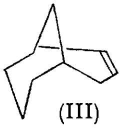
To detect the occurrence of hydride shifts a $^{14}$C-label was specifically inserted at C(3) in (I; R=OTs) and a satisfactory degradation of the major solvolysis product *viz.* bicyclo[3,3,1]nonene, was then devised (see the Scheme).

The relative molar activity of [(I; R = OH or OTs), (III), (IV; R = OH or OAc), and (V)] could not be determined accurately due to their extreme volatility, but the 2,4-dinitrophenylhydrazone of (V) and cyclohexane-1,3-dicarboxylic acid (VI) proved ideal for radioactive assay and the results are shown in Table 3.

The percentage of $^{14}$C-isotope present in the final degradation product (VI) represents the *total* extent of rearrangement occurring in each solvolytic medium, *e.g.* it is possible to devise pathways involving a combination of hydride shifts and Wagner–Meerwein rearrangement, which would convert (I; R = OTs) into (III) labelled at positions additional to C(3) and C(7). These

TABLE 1

*Solvolysis products* [a] (%)

| Compound | <br>(I) | <br>(II) | <br>(III) |
|---|---|---|---|
| (I) R=OTs[b] | 3·6 (R=OH) | 5·4 (R=OH) | 91 |
| (II) R=OTs[b] | 20·5 (R=OH) | 8·5 (R=OH) | 71 |
| (I) R=OTs[c] | 3 (R=OAc) | 2 (R=OAc) | 95 |
| (II) R=OTs[c] | 6·6 (R=OAc) | 2·8 (R=OAc) | 90·6 |

[a] These products were stable to the reaction conditions; [b] Aqueous acetone–Li$_2$CO$_3$; [c] Acetic acid–sodium acetate.

TABLE 2

*Acetolysis rate data* [a]

| Compound | *k*(sec.$^{-1}$)/25° | Relative rate |
|---|---|---|
| (I) R=OTs | 5·78 × 10$^{-5}$ | 1200 |
| (II) R=OTs | 7·4 × 10$^{-5}$ | 1500 |
| Cyclohexyl-OTs | 4·88 × 10$^{-8}$ | 1 |
| Cyclo-octyl-OTs | 2·82 × 10$^{-5}$ | 580 |

[a] Determined by modification of spectrometric method described by C. G. Swain and C. R. Morgan (*J. Org. Chem.*, 1964, **29**, 2097).

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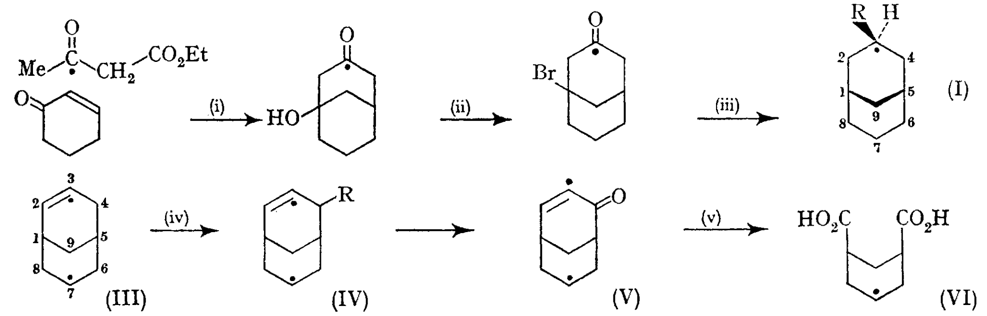
† The mode of synthesis and spectroscopic evidence fully substantiate the stereostructures indicated.



SCHEME

(i) *cf.* P. Rabe, *Ber.*, 1904, **37**, 1671; P. Rabe, R. Ehrenstein, and M. Jahr, *Annalen*, 1908, **360**, 265; P. Rabe and K. Appuhn, *Ber.*, 1943, **76**, 979; (ii) $PBr_3$; (iii) Li–$NH_3$; (iv) $SeO_2$; (v) $H^+$–$KMnO_4$.

possibilities, however, seem remote since they require the intermediacy of isomeric carbonium ions and the g.l.c. analysis employed would have detected the products known to be found from such species. Hence it seems reasonable to correlate the percentage $^{14}$C-retention in (VI) with a specific transannular C(7)–C(3) hydride shift although the final di-acid has not been degraded further to locate the precise position(s) of the isotopic label. The low percentage hydride shift (0·64 in aqueous acetone and 3·56% in NaAc–HOAc) detected in the olefin (III) produced from solvolysis of (I; R = OTs) is far beyond experimental error but shows that transannular C(7)–C(3) hydride shift cannot be considered as a major reaction pathway in the solvolysis of *exo*-3-bicyclo[3,3,1]nonyl derivatives under kinetically controlled conditions, at least as far as the major product (III) is concerned.

TABLE 3

*Relative molar activity* (cpm./mM)

| Compound | Observed | Calc. |
|---|---|---|
| (I) R=OTs | $3{\cdot}75 \times 10^{4\,a}$; $7{\cdot}0 \times 10^{4\,b}$ | $4{\cdot}5 \times 10^{4\,a}$ |
| (V) [c] | $4{\cdot}31 \times 10^{4\,c}$; $9{\cdot}96 \times 10^{4\,b}$ | $4{\cdot}5 \times 10^{4\,a}$ |
| (VI) | $2{\cdot}74 \times 10^{2\,a}$; $3{\cdot}55 \times 10^{3\,b}$ | |

% $^{14}$C-retention of (VI) relative to (V) = 0·64 [a] – 3·56 [b].

[a] Aqueous acetone–$Li_2CO_3$; [b] Acetic acid–sodium acetate; [c] Assayed as the corresponding 2,4-dinitrophenylhydrazone.

The buffered acetolysis of [1,2,2,8,8-$^2H_5$]cyclo-octyl bromobenzene sulphonate has been shown[3] to produce cyclo-octyl acetate (53%) and *cis*-cyclo-octene (47%) in both of which a specific 1 : 5-transannular hydride shift had occurred to the extent of ~50%. This is a striking result when compared with the extent of C(7)–C(3) shift detected in the corresponding solvolysis of the 1,5-methanocyclo-octyl-3-derivative, *viz.* (I; R = OTs). One explanation for this difference is based on the reasonable assumption that transannular hydride shifts occur when the termini of migration are within a critical distance and an examination of models suggests that in the cyclo-octyl cation the required C(5) to C(1) approach need not entail a large amount of additional angle and non-bonded strain, whereas the bridging C(9) methylene group in the bicyclo[3,3,1]nonyl-3-cation restricts the corresponding C(7) to C(3) movement by imposing severe angle strain.

Acetolysis of the *exo*-isomer (I; R = OTs) has a rate constant 1200 times that of cyclohexyl toluene-*p*-sulphonate and this marked reactivity[4] can be ascribed purely to steric acceleration due to the relief of strain associated with the charge at C(3) from $sp^3$ to $sp^2$ hybridisation during ionisation. A certain fraction of this rate enhancement might be due to participation by the *endo*-C(7)–H but the above hydride shift results suggest that this effect, if operative, must be small. The *endo*-isomer (II; R = OTs) is even more reactive and here again this is due to strain relief during ionisation, probably from a boat–chair conformation.[5] Labelling experiments have not yet been performed on (II; R = OTs) but from the above result and the small amount of hydride shift (~10%) found[6] in the solvolysis of *trans*-5-methyl-cyclo-octyl toluene-*p*-sulphonate as compared with the *cis*-isomer (90%), it seems improbable that a C(7)–C(3) shift would occur to any significant extent during the solvolysis of (II; R = OTs).

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