Acetolysis of Phenyl-substitute *endo*- and *exo*-Bicyclo[*n*,1,0]alkyl Chlorides; Evidence for Concerted dis(2), Nonconcerted dis(0) and Partially Ring-opened Carbonium-ion Mechanisms

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Summary A study of the effect of phenyl-substitution on the rate of reaction and products produced in the acetolysis of bicyclo[*n*,1,0]alkyl chlorides provides evidence for three different modes of ring-opening in the transformation of the cyclopropyl to allyl system.

THE acetolysis of the *exo*-bicyclo[*n*,1,0]alkyl toluene *p*-sulphonates ($n = 4, 5, 6$), for which the favoured dis(2)† concerted mode of ring-opening is sterically unfavourable, have been postulated to occur through the intermediacy of a partially ring-opened cyclopropyl cation.[1] However, even this pathway is energetically expensive for the bicyclo[3,1,0] isomer which solvolyses at least 100 times slower than cyclopropyl toluene *p*-sulphonate itself (at 100°).[1]

Both nonempirical all-electron[2] and semiempirical all-valence-electron SCF-MO calculations[3] agree that the other possible concerted disrotatory mode, dis(1), which on steric grounds should be the more favourable, is energetically as bad as a conrotatory ring opening con(1), and the

† Nomenclature of ref. 2 and 3.

solvolytic inertness[1] of the *exo*-bicyclo[3,1,0]hexyl toluene *p*-sulphonate provides striking confirmation for this.

by dry-column chromatography[5] on alumina. In the case of the 6-chloro-6-phenylbicyclo[3,1,0]hexane only the

TABLE 1

n	R	k_{rel} 125°	k^1_{rel} 100° (toluene-*p*-sulphonates)	$\Delta H^{\ddagger}$ kcal./mole	$\Delta S^{\ddagger}$ e.u.	Products
3	H	$2{\cdot}594 \times 10^4$	$4{\cdot}03 \times 10^2$	$25{\cdot}86 \pm 0{\cdot}07$	$-2{\cdot}76 \pm 0{\cdot}3$	*cis*-Cyclohex-2-enyl acetate[a]
4	H	1	1	$34{\cdot}43 \pm 0{\cdot}08$	$-1{\cdot}89 \pm 0{\cdot}19$	*cis*-Cyclohept-2-enyl acetate[b]
5	H	$3{\cdot}826 \times 10^{-2}$	$5{\cdot}0 \times 10^{-2}$	$35{\cdot}39 \pm 0{\cdot}10$	$-6{\cdot}04 \pm 0{\cdot}23$	*cis*-Cyclo-oct-2-enyl acetate[c]
		k_{rel} 125° (R=Ph/R=H)$_n$				
3	Ph	—		—	—	—
4	Ph	$0{\cdot}355 \times 10^2$		$29{\cdot}75 \pm 0{\cdot}09$	$-6{\cdot}52 \pm 0{\cdot}30$	2-Phenylcyclohepta-1,3-diene[d]
5	Ph	$1{\cdot}043 \times 10^2$		$31{\cdot}33 \pm 0{\cdot}08$	$-6{\cdot}93 \pm 0{\cdot}20$	2-Phenylcyclo-octa-1,3-diene[e]

[a] At 75°, activation parameters from measurements at 50° and 75°. [b] At 125°, activation parameters from measurements at 125° and 150°. [c] At 150° as well as small amounts of the 1,3-diene, activation parameters from measurements at 150° and 175°. [d] At 125° activation parameters from measurements at 100° and 125°. [e] At 125°, activation parameters from measurements at 125° and 150°.

TABLE 2

n	R	k_{rel} 125°	k^1_{rel} 100° (toluene *p*-sulphonates)	$\Delta H^{\ddagger}$ kcal./mole	$\Delta S^{\ddagger}$ e.u.	Products
3	H	$<10^{-2}$[a]	$<10^{-2}$	—	—	—
4	H	1[b]	1	—	—	—
5	H	$5{\cdot}26 \times 10^4$	$1{\cdot}47 \times 10^3$	$28{\cdot}37 \pm 0{\cdot}12$	$-14{\cdot}23 \pm 0{\cdot}30$	*cis*-Cyclo-oct-2-enyl acetate,[c] *cis*-Cyclo-octyl 1,3-diacetate.
		k_{rel} 125° (R=Ph/R=H)$_n$				
3	Ph	$<1{\cdot}5 \times 10^8$		$29{\cdot}59 \pm 0{\cdot}03$	$-4{\cdot}31 \pm 0{\cdot}10$	2-Phenylcyclohexa-1,3-diene,[d] *exo*- and *endo*-6-Acetyl-6-phenylbicyclo-[3,1,0]hexanes.
4	Ph	$1{\cdot}5 \times 10^6$		$30{\cdot}98 \pm 0{\cdot}10$	$-0{\cdot}84 \pm 0{\cdot}26$	2-Phenylcyclohepta-1,3-diene,[e] *exo*- and *endo*-7-Acetyl-7-phenylbicyclo-[4,1,0]heptanes.
5	Ph	$1{\cdot}43 \times 10^2$		$22{\cdot}42 \pm 0{\cdot}50$	$-19{\cdot}00 \pm 1{\cdot}22$	2-phenylcyclo-octa-1,3-diene,[f] *cis*-2-phenylcyclo-octyl 1,3-diacetate.

[a] Based on footnote b and the results for the corresponding tosylates.[1] [b] This is an estimated upper limit $k = 1{\cdot}0 \times 10^{-10}$, based on the limit of detectable chloride ion, no solvolysis at 175°. [c] At 150°, activation parameters from measurements at 150° and 175°. [d] At 125°, activation parameters from measurements at 100° and 125°. [e] At 125°, activation parameters from measurements at 100° and 125°. [f] At 125°, activation parameters from measurements at 125° and 150°. It has so far proved impossible to obtain an absolutely pure sample of this isomer and these figures are based on a computer fit to the experimental data on samples containing a small amount of the *endo*-epimer. The errors are therefore somewhat larger.

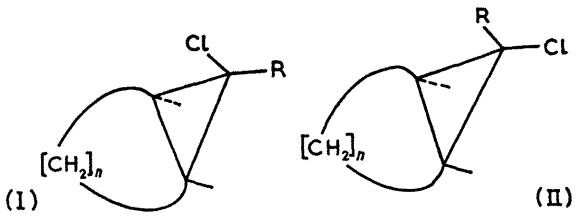
In a recent communication[4] we have presented evidence that 7-*exo*-chloro-7-*p*-substituted-phenylbicyclo[4,1,0]heptanes undergo a nonconcerted ring-opening by a dis(0) mode. Although the evidence for a dis(0) mode in this case is compelling it is important to rule out completely a mechanism involving an initial dis(2) ring-opening with formation of a partially-ring-opened carbonium ion. Since although the unsubstituted *exo*-bicyclo[4,1,0]alkyl chloride is solvolytically inert the corresponding toluene *p*-sulphonate has been shown, [1] as we have outlined above, to undergo ring-opening by this mechanism.

We have therefore prepared the corresponding bicyclo-[3,1,0] and [5,1,0] compounds and determined the activation parameters for acetolysis in acetic acid–sodium acetate. For comparison we have also investigated the *endo*-epimers together with the corresponding parent alkyl chlorides. The synthesis of these compounds proceeded along standard routes, the epimers of the parent alkyl chlorides being separated by g.l.c. and the phenyl-substituted compounds

exo-chloro-isomer was isolated. This is not too surprising since extrapolation of our results[4] for the corresponding [4,1,0]heptanes indicates that solvolysis of the *endo*-epimer would be extremely easy. The configurations of starting materials and products were assigned on the basis of 220 and 100 MHz. ^{1}H n.m.r. spectra with the aid of decoupling experiments, and by g.l.c. The results are collected in Tables 1 and 2. For the *endo*-series Figure, (I), Table 1, the relative rates for the parent bicyclo[*n*,1,0]alkyl chlorides are mirrored in the results for the toluene *p*-sulphonates as determined by Schollkopf and co-workers.[1] For the [4,1,0] and [5,1,0] compounds the relatively small rate-enhancement on replacing hydrogen by phenyl and the nature of the product are entirely consistent with a favoured dis(2) concerted ring-opening.

The results for the *exo*-series Figure, (II), Table 2 are striking. Both the [3,1,0] and [4,1,0] parent alkyl chlorides are solvolytically inert at 175° whilst the [5,1,0] compound rearranges rapidly even at 125°. The products.

ring-opened cyclo-octenyl acetate and *cis*-1,3-cyclo-octyl diacetate, are consistent with the data for the corresponding toluene *p*-sulphonate, for which a mechanism involving a partially-ring-opened cyclopropyl cation has been postulated.[1] The effect of replacing hydrogen by phenyl differs markedly both in terms of rate-enhancement and product distribution, for the [3,1,0] and [4,1,0] compounds on the



FIGURE

one hand and the [5,1,0] on the other. For the [3,1,0] isomers, for which an initial dis(2) opening to produce a partially-ring-opened cation is energetically most improbable, the large rate-enhancement on phenyl-substitution and formation of returned acetates is entirely consistent with a nonconcerted dis(0) mechanism. This behaviour is paralleled in the [4,1,0] case and lends considerable support to our assignment of a nonconcerted mechanism for the phenyl-substituted isomers previously discussed.[4]

By contrast the results for the [5,1,0] compounds clearly require a different interpretation. The products isolated and the similarity in rate enhancements on phenyl-substitution for both the *exo*- and *endo*-epimers, are consistent with an initial dis(2) ring-opening to produce a partially-ring-opened cation. This is supported by the large negative entropies of activation for both the parent and phenyl-substituted-bicyclo[5,1,0]octyl chlorides.

To summarize these results; for the *endo*-bicyclo[*n*,1,0]-alkyl chlorides solvolysis proceeds by a concerted dis(2) mechanism, and replacement of hydrogen by phenyl gives a relatively small rate-enhancement and does not change the mechanism. On the other hand for the *exo*-series when the favoured route involving a partially-ring-opened cyclopropyl carbonium ion is energetically very expensive ($n = 3, 4$), introduction of a phenyl-substituent alters the mechanism to a nonconcerted dis(0) process. However, for $n = 5$, where the parent *exo*-compound actually undergoes solvolysis by the partially-ring-opened carbonium ion mechanism faster than the *endo*-isomer by the concerted dis(2) mode, introduction of a phenyl-substituent again has a relatively small rate-enhancement and the mechanism does not change.

Satisfactory analyses were obtained on all new compounds.

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