

Concerted and Non-concerted Transformations of Cyclopropyl to Allyl; the Solvolysis of *endo*- and *exo*-7-chloro-7-*p*-substituted-phenylbicyclo[4,1,0]heptanes

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Summary. Activation parameters have been obtained for the acetolysis of epimeric 7-chloro-7-*p*-substituted-phenylbicyclo[4,1,0]heptanes; the evidence suggests concerted dis(2) and non-concerted dis(0) modes of ring opening for the *endo*- and *exo*-chloro-epimers, respectively.

In a recent communication the silver ion-assisted methanolysis of a mixture of *exo*- and *endo*-7-phenyl-7-chlorobicyclo[4,1,0]heptanes has been described.¹ On the basis of the products isolated (*exo*- and *endo*-7-phenyl-7-methoxybicyclo[4,1,0]heptanes and 2-phenyl-3-methoxycycloheptene), it was suggested that the *exo*-chloro-epimer, in which a straightforward dis(2) ring opening is sterically unfavourable, proceeds *via* a non-concerted process.

We report that, on the evidence of product distribution

alone from a *mixture* of epimeric starting materials, the assignment of a non-concerted reaction pathway for the *exo*-chloro-isomer is not unambiguous and we present some preliminary results of our more detailed investigations of a related system. We have prepared and separated the epimers of 7-*p*-substituted-phenyl-7-chlorobicyclo[4,1,0]heptanes, Scheme, X = H, Cl, Me, F, and for both epimers have determined the activation parameters for acetolysis in acetic acid-sodium acetate at 100 and 125°.

The epimers were separated with great difficulty by dry-column chromatography on alumina.² The configurations of starting materials and products were assigned on the basis of 220 and 100 MHz. ¹H n.m.r. spectra with the aid of decoupling experiments, and by g.l.c. For comparison the parent *exo*- and *endo*-7-chlorobicyclo[4,1,0]heptanes have

TABLE I

<i>endo</i> -7-Chloro- bicyclo[4,1,0]heptane	k_{rel} (125°)	${}^a\Delta H^\ddagger$ kcal./mole	${}^a\Delta S^\ddagger$ e. u.
(I) R=H, X=H	1	34.43 ± 0.08	-7.00 ± 0.19
R=H, X=F	35.5	29.75 ± 0.09	-11.60 ± 0.23
R=H, X=Me	33.1	30.04 ± 0.11	-10.89 ± 0.29
R=Ph, X=H	114.2	29.79 ± 0.25	-9.09 ± 0.65
R=Ph, X=H	472.0	28.12 ± 0.09	-10.18 ± 0.23

^a From measurements at 100 and 125° for the phenyl-substituted epimers and 125 and 150° for the *endo*-chlorobicyclo[4,1,0]heptane.

also been studied. The results are collected in Tables 1 and 2.

Considering first the *endo*-chloro-series (Table 1), the parent compound, 7-chlorobicyclo[4,1,0]heptane, has previously been studied³ and a concerted dis(2)† mode of ring opening postulated. For the *p*-substituted-phenyl derivatives the product consists of ring-opened diene, and the small substituent effect and rate enhancement with respect to the parent compound are entirely consistent with a concerted ring opening by the favoured dis(2) mode. The rate differences result from a subtle interplay of both enthalpy and entropy effects. In the transition state for the dis(2) ring opening the positive charge is extensively delocalized^{4,5} and this is confirmed by the relatively small rate-enhancing effect of a bridgehead phenyl substituent, Scheme, (I), R = Ph.

of a partially opened cation is quite small, and hence it is not unreasonable that a mixture of the two ethers be formed with the *exo*-isomer predominating. This is a plausible alternative to the explanation suggested by Ledlie and Nelson,¹ and hence their evidence cannot be taken as unambiguous for a non-concerted ring opening.

By contrast, our results presented in Table 2 are open to a reasonable interpretation only in terms of a non-concerted dis(0) ring opening in which a free cyclopropyl carbonium ion is formed prior to rearrangement. This is based on three lines of argument: firstly, the large rate enhancement in going from the parent to phenyl-substituted bicyclo[4,1,0]heptanes, secondly, the large effect of *p*-substituents, and thirdly, the formation of returned acetates, Scheme, (II). The entropy changes involved in the case of the *exo*-epimers are significantly lower than those for the

TABLE 2

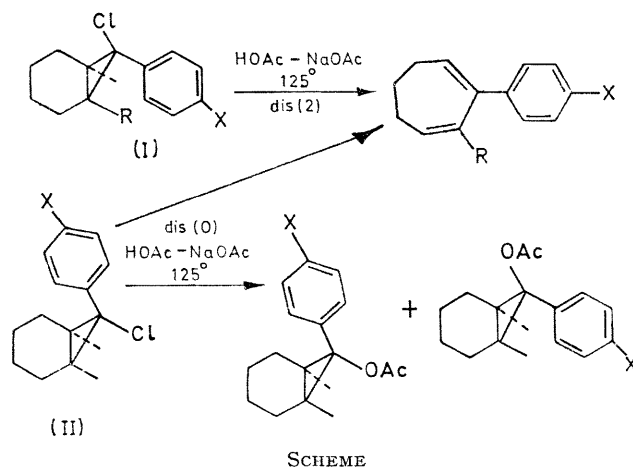
<i>exo</i> -7-Chloro- bicyclo[4,1,0]heptane	k_{rel} (125°)	${}^a\Delta H^\ddagger$ kcal./mole	${}^a\Delta S^\ddagger$ e. u.
(II) X=H	1 ^a	—	—
X=F	1.50 × 10 ⁶	30.98 ± 0.10	-6.18 ± 0.26
X=Cl	1.92 × 10 ⁶	29.78 ± 0.28	-8.32 ± 0.73
X=Me	0.67 × 10 ⁶	30.52 ± 0.09	-8.79 ± 0.23
X=Me	26.71 × 10 ⁶	28.00 ± 1.5	-7.0 ^b ± 3.9

^a This is an estimated upper limit, based on no solvolysis at 175°, with a detectable lower limit of chloride (estimation *ca.* 0.5%).

^b 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.

For the *exo*-chloro series (Table 2), the acetolysis of the parent 7-chlorobicyclo[4,1,0]heptane is immeasurably slow even at 175°; however in the case of the corresponding tosylate,⁶ reaction does proceed to produce returned acetate, and ring opened *trans*-cyclohept-2-enyl acetate, which adds acetic acid to produce the cycloheptane-1,3-diyl diacetate. The postulated pathway^{6,7} for this involves an initial dis(2) ring opening to produce a partially ring opened carbonium ion in a potential minimum,^{4,5,8} which then adds acetate to produce returned or ring opened acetate. (Non-empirical calculations⁵ indicate that the dis(1) and con(1) modes have almost identical activation barriers). In the absence of any other evidence, a similar route could be postulated for the methanolysis of the *exo*-7-chloro-7-phenylbicyclo[4,1,0]heptane. The partially ring-opened carbonium ion can add methanol to produce returned ether and the initially formed *trans*-2-phenyl-3-methoxycycloheptene, isomerized to the thermodynamically more stable *cis*-isomer.

The first *ab initio* calculation on an organic reaction co-ordinate has recently been completed,⁵ on the cyclopropyl to allyl cation rearrangement, and this indicates quite clearly that the energetic preference for *exo*-addition



corresponding *endo*-isomers. In the case of the *exo*-7-chloro-7-phenylbicyclo[4,1,0]heptane the returned acetate amounts to *ca.* 60% of the total product and consists of an

† Nomenclature of ref. 4.

approximately 1:1 mixture of the *exo*- and *endo*-acetates. Models of the carbonium ion indicate that approach from both sides is hindered and that an equal mixture of the two epimeric acetates is not unreasonable. This is supported by the results for the corresponding bicyclo[3,1,0] and [5,1,0] compounds.⁹

Large effects of *p*-substituents have also been noted by Depuy¹⁰ in the solvolysis of 1-phenylcyclopropyl tosylate and suggests strongly that this is also a non-concerted dis(0) ring opening, since a large rate enhancement relative to cyclopropyl tosylate was also observed. The non-concerted reaction was rejected on the grounds that no phenylcyclopropyl acetate was isolated. This emphasizes the fact that the formation of returned material depends on

many factors, the most important of which are the nucleophilicity of the leaving group, and potential entering group, solvating power of the medium and activation barrier for the rearrangement of the carbonium ion. It is significant that a large amount of rearranged tosylate is produced in the acetolysis of 1-phenylcyclopropyl tosylate which subsequently undergoes acetolysis in a second step.

Satisfactory analyses were obtained on all new compounds.

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