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ION PAIRS AS INTERMEDIATES IN THE REARRANGEMENTS OF THE DIBENZOCYCLOHEPTATRIENYL-METHYL AND DIBENZOCYCLOOCTATRIENYL SYSTEMS

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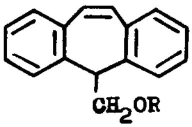
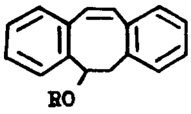
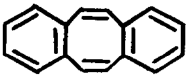
By acetolysis of the 1:2.5:6-dibenzocyclohepta-1.3.5-trienyl-7-methyl tosylate (Ib) in glacial acetic acid the unrearranged acetate Ic was obtained together with a small amount of dibenzocyclooctatetraene (III). On the other hand 1:2.5:6-dibenzocycloocta-1.3.5-triene-7-ol acetate (IIb) was the only product if solvolysis proceeds in the presence of sodium acetate (1). In both cases maximum yields are more than 90%. The proportions of the products corresponding to different concentrations of sodium acetate are given in table I.



Ia ($R=H$)
Ib ($R=Ts$)
Ic ($R=Ac$)



IIa ($R=H$)
IIb ($R=OCH_3$)



III

It is possible to return to derivatives of the initial sevenring system, from the eightring product thus obtained. By heating the alcohol IIa (whose tosylate could not be prepared)' in acetic acid solution in the presence of a strong acid (p-toluenesulfonic acid, sulfuric acid or boron fluoride) the acetate Ic was obtained again, in nearly quantitative yield.

Table I. Products of the acetolysis of tosylate Ib +)

Mole %	AcONa :	0	0.5	0.75	0.90	1.0	1.2	3.0
Mole %	Ia :	92.5	88	87	50	13.5	5	0
Mole %	IIa :	0	0	0	45	86.5	95	100
Mole %	III :	7.5	12	13	5	0	0	0

+) The raw reaction products were submitted to alkaline hydrolysis and composition was determined through their IR spectra.

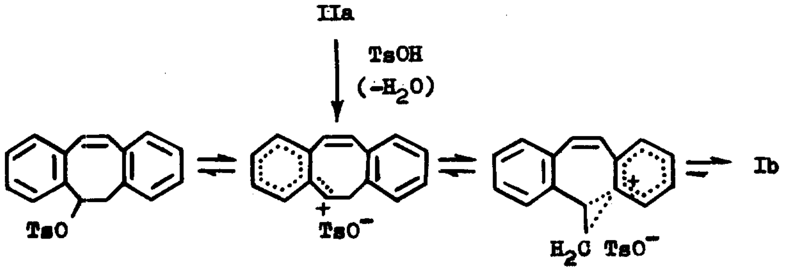
To realize the rearrangement at will in one sense or the other is only possible if acetic acid is used as solvent. In formic acid, with or without sodium formate, only Ia is obtained (after alkalic hydrolysis). On the contrary the alcohol IIa gives by refluxing with 10 wt % methanolic sulfuric acid the unrearranged methyl ether. Under the same conditions the tosylate Ib remains unchanged. Obviously it is not the acidity of the solution that determines the occurence of the rearrangement.

The first order rate constant of the acetolysis of Ib in the presence of sodium acetate has aproximately twice the value compared to that determined in its absence. An increase of the same magnitude of the rate constant has been noticed when lithium perchlorate is added. But in that case the reaction product is the unrearranged acetate Ic.

A supposed effect of the neighbouring group of the sevenring double bond in Ib was eliminated by preparing the saturated analog of Ia. His tosylate undergoes acetolysis about twice as fast as Ib. Therefore the sevenring double bond rather slows down the reaction, due to some conjugation effect with one of the benzene rings. The possibility of a tropylium ion intermediate was also excluded by determination of the UV spectra of the alcohols Ia and IIa in anhydrous sulfuric acid. By comparing these spectra with those of authentic dibenzotropylium compounds, marked differences were observed.

The collected data seem to require two cationic intermediates, existing in solution as intimate ion pairs with the tosylate anions (2) and equilibrating rapidly. Both ion pairs are supposed to be able to undergo internal return, but only one of the so formed covalent tosylates is practically stable (non-ionisable) under the conditions used.

From the alcohol IIa the ion pair V is formed, perhaps through an intermediate oxonium salt. The cation of V is a highly stabilised secondary benzylium ion. Through ionization, Ib should give a primary carbonium ion, which is very likely to stabilize to the phenonium ion VI (a similar effect has been convincebly demonstrated in the case of benzocyclooctene-3-ol) (3). At the equilibrium V $\rightleftharpoons$ VI, V evidently would predominate, but as IV ionises rapidly (in fact IV could not be isolated) the sole stable product of the covalent return would be Ib.



IV V VI

The actual occurence of this mechanism could be proved by isolating tosylate Ib in yields as high as 80%, from the reaction between alcohol IIa and p-toluenesulfonic acid in acetic acid, when heated at 116° for a short time (1 hour). On prolonged heating (24 hrs.) the reaction proceeds to give acetate Ic. This seems to be the first known case of the formation of a sulfonic ester in a direct reaction between a sulfonic acid and an alcohol. But of course this is not likely to be generalized.

The observed salt effects of sodium acetate and lithium perchlorate on the rate of the acetolysis of the tosylate Ib suggests a "specific electrophilic assistance to ionization" as Winstein put it recently in other cases (4). This salt ion pair-assisted ionization leads to ion quadruplets as :

$$\left[R^+TsO^-Na^+AcO^-\right] \quad \text{and} \quad \left[R^+TsO^-Li^+ClO_4^-\right]$$

The first of these ion quadruplets undergoes an irreversible internal covalent return by combination of the strong nucleophilic AcO^- ion with R^+ (this last ion in its more stable equilibrium form V). As the carbonium ion V can form no covalent bond with the perchlorate ion and only a weak one with the tosylate ion, the second ion quadruplet is likely to collapse in the same way as in the absence of any salt.

By using instead of acetic acid the highly ionizing, weak nucleophilic formic acid (5), Ia-formate was obtained as shown above. The formate ester of IIa ionizes probably in formic acid in the same manner as IV and therefore will disappear in favour of the formation of stable Ia-formate. On the contrary, the strong nucleophilic methanol is traping the stable ion V prior to its rearrangement to VI.

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