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SOLVOLYTIC π-ROUTE TO DIBENZOBICYCLO[2.2.2]OCTADIENE AND DIBENZOBICYCLO[3.2.1]OCTADIENE DERIVATIVES

E. Ciorănescu, A. Bucur, F. Badea, M. Rentzea and
C. D. Nenitzescu

Institute of Organic Chemistry of the Romanian Socialist Republic Academy, Bucharest, Romania

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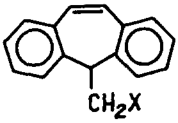
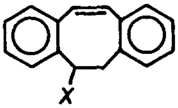
Some years ago (1,2) we have reported that the acetolysis of 1:2,5:6-dibenzocyclohepta-1,3,5-trienyl-7-methyl tosylate (I-OTs), carried out in the presence of sodium acetate, led to dibenzocyclooctatrien-7-ol acetate (II-OAc). The unbuffered acetolysis of I-OTs, as well as the reaction of II-OH with p-toluenesulfonic acid or other strong acid in acetic acid led to I-OAc together with a small amount of dibenzocyclooctatetraene (III).



I



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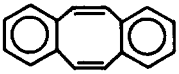
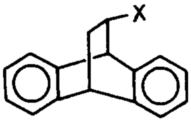
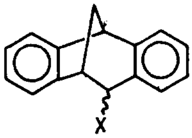


III

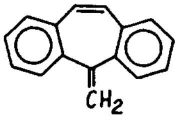
We now wish to report about some reactions giving rise, through π-route, to bridged products, accompanying those mentioned above. The products were detected by v.p.c., performed after alkaline hydrolysis, authentic samples being used as internal references (3,4). The reaction mixture of the unbuffered acetolysis of I-OTs was found to contain, in addition to the compounds mentioned above, dibenzobicyclo[2.2.2]octa-2,5-dien-7-ol (IV-OH), whereas in the case of the buffered acetolysis, the pair of epimeric alcohols exo- and endo-dibenzobicyclo[3.2.1]octa-2,6-dien-4-ol (V-OH) was found. In both reactions the hydrocarbons III and VI were also formed. The product distribution is shown in Table I (entries 2 and 7).



IV



V



VI

When the acetic acid solvent was replaced by higher homologs, the distribution of the products obtained from I-OTs changed. The yields of the bridged alcohol and of the two hydrocarbons increased from acetic acid to pivalic acid (Table I ; entries 2 to 5). These differences cannot be explained only by the raise of temperature, because in acetic acid, at 140° (entry 6) the product distribution differs from that obtained in propionic acid, at the same temperature. In formic acid (strongly ionizing but poorly nucleophilic medium), the bridged alcohols practically were not found (entry 1). Under these conditions double bond does not assist the ionization.

<u>Table I</u>. Solvolysis products of I-OTs [a)] in different acids as solvents (after alkaline hydrolysis)

	Acid (reaction temp.)	III	VI	IV-OH	V-OH exo+endo	II-OH	I-OH
1	Formic (100°)	-	-	1	-	-	99
2	Acetic (117°)	7	3	8.5	-	-	81.5
3	Propionic (141°)	10.5	1.5	16	-	-	72
4	Isobutiric (154°)	14	4	17	-	-	65
5	Pivalic (163°)	18	11	19	-	-	52
6	Acetic (140°)	1	1	6	-	-	92
7	Acetic (117°) [b)]	3	1	-	2+4.5	85.5	4

a) 0.13 M I-OTs ; 24 hr b) 0.4 M NaOAc added.

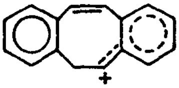
It could be assumed that the acetic, propionic, isobutyric and pivalic acids have about the same carbonium ion-solvating power. However, the steric requirements of the solvent molecules increase considerably along this series ; the life of the carbonium ion should likewise increase. This would explain the raise of the yield of bridged alcohol IV-OH. At the same time the yield of hydrocarbons increases also, suggesting that the elimination occurs within the cation of a solvated ion pair.

The failure to prepare II-OTs, in order to make a comparison with I-OTs, led to the investigation of the already known (5) corresponding bromide (II-Br). In aqueous acetone II-Br was found to hydrolyze faster than the corresponding saturated bromide by a factor of 9 x 10^4 suggesting anchimeric assistance by the double bond. The attempts to acetolyze II-Br (1 hr at reflux) led by internal return to the very unreactive bromide I-Br, formed in practically quantitative yield.

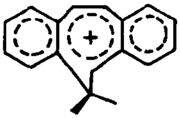
It seems that in order to account for the various bridged and unbridged products formed in the reactions described so far, several intermediates must be taken into consideration.

In the reactions of interconversion of the systems I $\rightleftarrows$ II, by ring expansion or contraction, the intervention of the phenonium ion VII seems plausible. The cation VII should undergo rapid rearrangement to the much more stable benzylic ion VIII.

VII



VIII



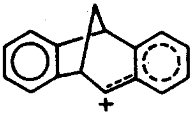
IX

The difference in solvolysis rate between II-Br and the saturated analog is so great (s. above) that another explanation may be possible. Instead of a benzylic ion, it seems more probable that the eight-membered intermediate is the dibenzohomotropylium cation IX. This hypothesis is supported by the generation of IX from II-OH, I-Br and I-Cl in very strongly acidic media (FSO_3H – SbF_5 in sulfur dioxide) and its detection by means of n.m.r. spectroscopy (6). The cation IX is an isomer of the dibenzohomotropylium cation obtained by Childs and Winstein (7).

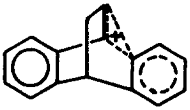
When bridged products are formed from I-OTs, the intervention of a bridged nonclassical ion X, arising by double bond participation, is plausible. This ion should rearrange to the more stable benzylic ion XI which can give rise to the bridged phenonium ion XII.

The rearrangement of VII to X should be energetically unfavourable ; therefore we may assume that these ions do not equilibrate. It is more likely that they arise directly from I-OTs, by two independent ionization routes : a phenonium route leading to unbridged ions (VII-IX), and a π-route leading to bridged ions (X-XII).

X



XI



XII

In these two series of carbonium ions, under kinetic control conditions the more favoured homotropylium ion IX and benzylic ion XI are probably attacked. Accordingly, the products are derivatives of systems II and V. Under thermodynamic control conditions, owing to repeated reionisation, the more stable systems I and IV accumulate in the long run.

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