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ACETOLYSIS OF 1:2,5:6-DIBENZOCYCLOHEPTA-1,3,5-TRIENYL-7-ETHYL TOSYLATE

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In our previous papers (1,2) it has been reported that the solvolysis of the 1:2,5:6-dibenzocyclohepta-1,3,5-trienyl-7-methyl tosylate (I-OTs) takes place to a small extent (nearly 10%) with participation of the double bond of the middle ring, giving rise to bridged products. A larger participation seemed more probable in the case of the higher homolog, II-OTs.

In order to check this hypothesis the acetolysis of 1:2,5:6-dibenzocyclohepta-1,3,5-trienyl-7-ethyl tosylate (II-OTs) was performed. This reaction proceeds 15 times faster than that of the saturated analog (3) giving rise mainly (about 85%) to bridged products (4). In the presence of sodium acetate the acetolysis led to the epimeric two-membered bridge alcohols 2:3,6:7-dibenzobicyclo[3.2.2]nona-2,6-dien-exo-4-ol (exo-III-OH), m. p. 120° and endo-III-OH, m. p. 134° [x]. These two compounds were found to equilibrate under the reaction conditions (the ratio endo/exo being about 2:1).

In the absence of sodium acetate, two hydrocarbons and a three-membered bridge alcohol made up the bulk of the reaction products, namely the 6:7,8:9-dibenzobicyclo[3.2.2]nona-2,6,8-triene (V), m. p. 165°, 2:3,7:8-dibenzotricyclo[$3.3.1.0^{4,6}$]nona-2,7-diene (VI), m. p. 97°, and 6:7,8:9-dibenzobicyclo[3.2.2]nona-6,8-dien-2-ol (IV-OH), m. p. 150-152°.

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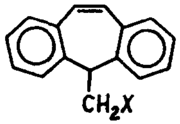
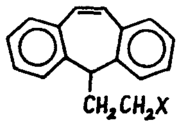
[x] All new compounds gave satisfactory elemental analysis.



I



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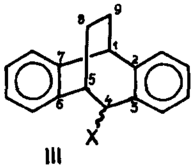

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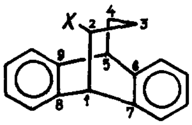

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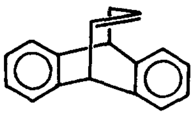

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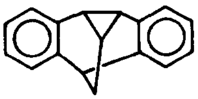


VI

The solvolysis mixture was analyzed by v.p.c. (see Table I) after conversion of the acetates to the corresponding alcohols (by treatment with $LiAlH_4$). The products were separated on aluminum oxide column. Some polymer (4-6%) was always formed during the unbuffered acetolysis.

Table I. Acetolysis products of II-OTs and IV-OTs at 117° (after reduction with $LiAlH_4$)

Tosylate (0.10 M)	NaOAc M	Time hr	% Products					
			V	VI	III-OH endo	III-OH exo	IV-OH	II-OH
II-OTs	-	5	6.	13	-	-	72	9
II-OTs	-	8	7.5	21	1	1	56	13.5
II-OTs	-	16	9.5	24	2	3	39.5	22
II-OTs	0.15	8	3.5	1	58	23.5	3.5	10.5
IV-OTs	-	8	3	5.5	1	6	75.5	9
IV-OTs	0.20	8	-	-	56.5	27.5	16	-

Both endo- and exo-alcohols yielded on oxidation with chromic anhydride in pyridine the same ketone which was transformed into the hydrocarbon III-H, m. p. 79°, by the method of Brown and White (5). Reduction of the ketone with $NaBH_4$ or $LiAlH_4$ led back to a mixture of the two alcohols III-OH. The IR, NMR and mass spectroscopy data are in agreement with the assigned endo and exo configuration.

Starting from the alcohol IV-OH and using the same procedure as before (oxidation followed by Kishner-Wolff reduction), the hydrocarbon IV-H was obtained, m. p. 100°, identical with that formed by hydrogenation of the olefin V. The NMR spectra confirm the structure ascribed.

The NMR spectrum of the hydrocarbon VI, containing a tricyclic median ring, shows : τ 2.98 (8 aromatic protons), 8.30 (triplet, 2 bridged protons), 7.30-8.10 (multiplet, 3 cyclopropanic protons) and 6.23 (sextet, one bridgehead proton). This structure was confirmed when the hydrocarbon VI was obtained from 2:3,7:8-dibenzotricyclo$[3.3.1.0^{4,6}]$nona-2,7-dien-9-one (6) by Kishner-Wolff reduction.

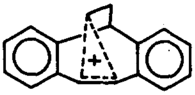
The distribution of the products obtained from II-OTs suggests thermodynamic control for the unbuffered acetolysis and kinetic control for the sodium acetate buffered one. In order to check this hypothesis the acetolysis of IV-OTs was performed, under the same conditions (Table I). The product distribution is similar enough to that obtained in the previous experiments to justify the view that the system IV is the thermodynamically more stable one. The system IV rearranges only in the presence of sodium acetate, giving rise to the kinetically controlled products endo-III-OH and exo-III-OH.

On the other hand, endo-III-OH or exo-III-OH, when refluxed for 8 hr in a solution of TsOH (0.05 M) in acetic acid gave products with the skeleton IV, together with the hydrocarbon VI. From endo-III-OH : 70.5% IV-OH, 8% V, 18% VI and 3.5% II-OH ; from exo-III-OH : 72% IV-OH, 8% V, 19% VI and 1% II-OH were obtained.

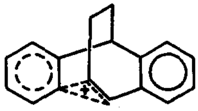
Starting from the alcohol IV-OH, under the same conditions, the following products were obtained : 4.5% V, 13% VI and 8.5% II-OH, together with the initial alcohol IV-OH. However, at a longer reaction time (24 hr) this distribution was found to alter to : 8% V, 17.5% VI, 21% II-OH, the rest being IV-OH. The increase of the proportion of hydrocarbon VI suggests that this product is formed by an irreversible side reaction. It should be pointed out that by replacing in the II-OTs solvolysis the acetic acid by propionic acid the yield in hydrocarbon VI reached 40%.

The presence of the alcohol II-OH among the reaction products of the acid-catalyzed acetolysis of the alcohols III-OH and IV-OH indicates retro-π-route.

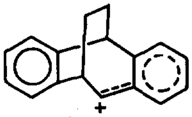
As regards the structure of the intermediates involved in the solvolysis reactions and the rearrangements described above, the kinetically observed anchimeric assistance by the double bond and the formation of the hydrocarbon VI and of the other bridged compounds, suggest the intervention of the bridged ion VII in the π- and retro-π-route conditions.



VII



VIII



IX

The ion VII could give rise to the more stable ion IX and to the nonclassical ion VIII. The ion VII is likely to possess a higher energy content, while IX should be the more stable one. The hydrocarbon VI could arise from the ion VII by elimination of one proton, in the same way as nortricyclene, the formation of which, in the solvolysis of *exo*-norbornyl brosylate, can better be explained by admitting a nonclassical cation (7). The formation of IV-OH and V involves the participation of the nonclassical cation VIII. The alcohols III-OH may result from the ion IX. The epimerization of *exo*-III-OH and *endo*-III-OH which takes place quite readily, is consistent with the intervention of the cation IX.

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