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DEHYDRATION REACTION OF 1,2-BIS(DIPHENYLHYDROXYMETHYL)SPIRO-[2,6]NONA-4,6,8-TRIENE : THE INTRAMOLECULAR RING-CYCLIZATION OF A 10π ELECTRONS SYSTEM[1]

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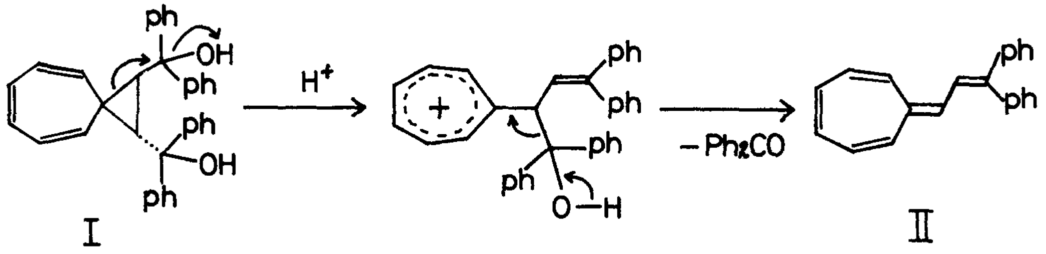
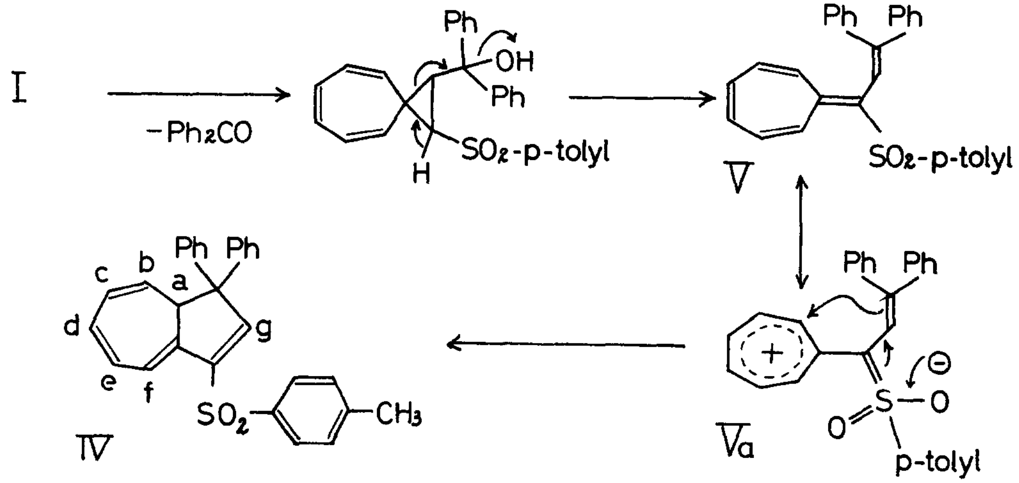
Previously it has been reported that in general spiro[2,6]nona-4,6,8-trienes derivatives, on treating with dilute acids, transformed into heptafulvene derivatives (2,3). In addition, we found that 1,2-bis(diphenylhydroxymethyl)spiro[2,6]nona-4,6,8-triene (I) behaved as a precursor of vinylheptafulvenes when it was treated with acids or even with silica gel. Thus 8-(2,2-diphenylvinyl)heptafulvene (II) obtained from I was unstable, whereas a derivative possessing a sulfonyl group underwent the 10π electrons cyclization and led to a dihydroazulene derivative (IV)(4,5,6). We wish to report an outline of our results concerning this intramolecular cyclic reaction.

The reaction of dimethyl spiro[2,6]nona-4,6,8-triene-1,2-dicarboxylate (2,3) with phenyl lithium (8 equivalent) afforded a diol (I)(7), mp 225°, in 85% yield, although the reaction using phenyl magnesium bromide gave a complex mixture of tarry products. The diol (I) was stable to alkalis, but so labile towards acids that treatment of a benzene solution of I with 0.1 N mineral acids or even with silica gel, under separation of 1 equivalent of benzophenone, afforded 8-(2,2-diphenylvinyl)heptafulvene (II) as a very unstable oil. Although II turned to a polymer on standing in air for less than one hour, a fresh material of II shows uv spectrum similar to that of heptafulvene derivatives (8,9) ; uv (MeOH), 225 (sh), 255 and 385 nm. In addition, the exhaustive catalytic hydrogenation of II (fresh one) afforded 1,1-diphenyl-3-cycloheptylpropane (III) as an oil, which structural identity was based on the following spectral data : mass, m/e, 292 ($M=C_{22}H_{28}$, 9%) and 167 (Ph_2CH, 100%); nmr (60 MHz, CCl_4), 1.8-2.3 ppm (multiplet, 17 H), 3.8 (triplet, 1 H) and 7.2 (singlet, 10 H). The reaction pathway for the formation of II from I could be explained as follows :



An attempted tosylation of I by refluxing with tosyl chloride in pyridine resulted in the another type of the dehydration, i.e., in the formation of pale yellow crystals (IV) with formula $C_{29}H_{24}O_2S$, mp 192°, (40% yield) accompanied by the formation of 1 equivalent of benzophenone. The assignment of the structure of 1,1-diphenyl-3-(p-tosyl)-1,9-dihydroazulene for IV is based on the following spectral data and chemical evidence : Mass spectrum, m/e, 436 (M, 16%), 281 ($M-C_7H_7SO_2$, 100%) and 203 ($281-C_6H_6$, 46%) ; uv (MeOH), 235 nm (log ε, 3.01) and 325 (2.90) ; ir (KBr), no carbonyl group, 1330 and 1140 (sulfonyl)(10), 1090 and 750 cm^{-1}. The nmr spectra (100 MHz, C_6D_6) and decoupling experiment permitted the following assignment for the signals of IV (chemical shift in δ) and provided the following coupling constants (in Hz) ; 1.86 (singlet, CH_3), 3.61 (broad doublet, Ha), 4.48 (quartet, Hb), 5.60 (multiplet, Hc), 6.15 (quartet, Hd), 6.39 (quartet, He), 6.71 (doublet, 2 H of p-tolyl), 6.86 (doublet, Hf), 6.8-7.2 (multiplet, 10 H of phenyl), 7.50 (singlet, Hg) and 7.75 (doublet, 2 H of p-tolyl) ; $J_{a,b}=4.5$, $J_{a,c}=2.0$, $J_{a,f}=0.5$, $J_{b,c}=10.0$, $J_{b,d}=0.5$, $J_{c,d}=5.5$, $J_{c,e}=0.5$, $J_{d,e}=11.0$, $J_{d,f}=0.5$, $J_{e,f}=6.0$ and J (protons in p-tolyl)=8.5. Especially the signals due to the cycloheptatriene moiety of IV was very similar to those of the addition product of tropone and diphenylketene (11). Furthermore, the stability of IV toward hydrolysis with alkali may support the existence of the sulfone function instead of the sulfenyl ester group. These facts including above spectral data account for the correctness of the assigned structure for IV (12).

For the formation of IV from I by tosylation, the reaction pathway depicted below would be proposed. An intermediate V, which formation has still some ambiguity, would undergo the thermally allowed intramolecular cyclization in which process 10 π electrons participate (5) and thus dihydroazulene IV be formed. However, it should be noted that there is a difference in the cyclization behavior between II and V, depending on the electron attractive group existed. For the cyclization process, contribution of the polar resonance structure like Va, which is attributed to the electron attracting group such as p-tosyl group, seems fairly important. A reported example in which although at high temperature 8-(2,2-dicyanovinyl)heptafulvene underwent the same type of cyclization would also be the case (6). Nevertheless, whether the cyclization takes place in concerted or ionic stepwise mechanism is still in important doubt.



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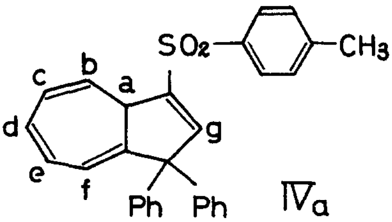
12. Another possible structure IVa which was also suggested from the observed evidence would be ruled out on basis of the following nmr spectral data as well as of the course of the cyclization of V. That is, singlet due to Hg shows big shift (0.98 ppm) in C_6D_6 compared with that in $CDCl_3$, whereas signals ascribed to Ha did not show such big shift (0.06 ppm) in the same solvent. This indicates that Hg is located more near by the sulfonyl group than Ha.



IVa