

THE REACTION OF TRANS-1,2-BIS(DIPHENYLHYDROXYMETHYL)-
SPIRO[2,6]NONA-4,6,8-TRIENE WITH SODIUM HYDRIDE

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It has been known that spiro[2,6]nona-4,6,8-triene derivatives rearrange to indane derivatives upon thermolysis (1,2). In addition, they are very unstable toward acids and rearrange to heptafulvene derivatives even with the treatment by very weak acids such as silica gel (1,3). Although they are fairly stable toward bases (4), we found the formation of five-membered ether ring compounds from trans-1,2-bis(diphenylhydroxymethyl)spiro[2,6]nona-4,6,8-triene (I)(3) by the reaction with sodium hydride. We wish to report the structural determination of the products and the reaction mechanism for the formation of the products.

Treatment of I with sodium hydroxide or pyridine resulted in the quantitative recovery of the starting substance. On the other hand, when I was treated with sodium hydride in absolute dioxane for 300 hr at room temperature, an ether compound (II), mp 115°, was obtained in 63% yield, accompanied by 12% yield of I. Two other ether compounds III, mp 164°, and IV, mp 180°, were obtained in 44 and 17% yields respectively, in addition to 4% yield of II, when the same reaction mixture was refluxed for 6.5 hr. Prolonged heating (20 hr) gave IV in 43% yield, and neither II nor III were isolated.

All the products II, III and IV possess the same molecular formula, $C_{35}H_{30}O_2$, and the same molecular ion at m/e 482 in their mass spectra. Thus, they are isomers of the starting substance and isomeric each other. Treatment of II, III and IV with dilute acids afforded 8-(2,2-diphenylvinyl)heptafulvene (V), which

was also obtained by the acidic treatment of I (3). The chemical shift of protons at C₁ and C₂ of the products II, III and IV is similar to that of the cyclopropane protons of I. These nmr spectral data indicate that the C₁ and C₂-protons are located at cyclopropane ring and coupling constants suggest that they are in trans configurations (5). The chemical evidence and the nmr spectral data of II, III and IV suggest that they possess the spiro[2,6]nonadiene skeleton.

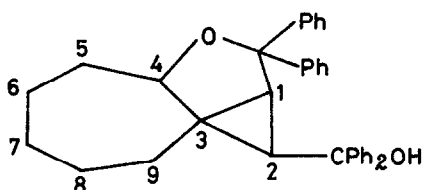
NMR spectral data of II, III and IV. (in C₆D₆, 100 MHz, δ ppm)*

	C ₁	C ₂	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	OH	ph
II	1.84	2.78	4.55	5.92	5.46	5.21	5.21	2.52, 2.96	1.65	6.8~7.5
III	1.67	2.99	4.22	2.60, 2.85	5.5	5.5	5.5	5.92	1.93	6.8~7.5
IV	2.02	2.80		5.87	5.63	5.41	1.9(2H)	2.0(2H)	1.62	6.8~7.5

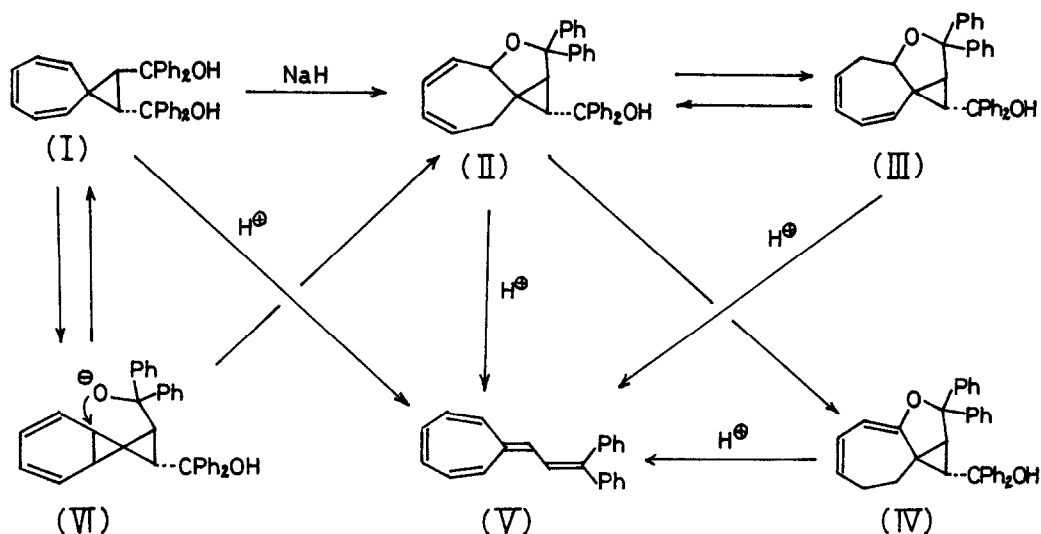
Coupling constants of II, III and IV in Hz.*

	J ₁₂	J ₄₅	J ₅₆	J ₆₇	J ₇₈	J ₈₉	
II	4.0	2.0	11	4	ca. 9	4 and 1	J _{99(gem)} =20, J ₄₆ =2
III	4.5	4.5 and 8	3	11	ca. 3	11	J _{55(gem)} =18, J ₇₉ =3
IV	4.5		7	12	4 and 6		

* Numbering in the structure of the products is represented as shown below.



The interconversion between II and III, and the formation of IV from II was observed when II, III and IV were heated with sodium hydride in absolute dioxane. These transformations can be explained by the thermal 1,5-hydrogen shifts, and IV which possesses a vinyl ether linkage is the thermally most stable isomer. The evidence mentioned above support the structures assigned which are shown in the following Scheme.



The formation of II from I can be explained by the alkoxide oxygen attack on the double bond of the cycloheptatriene. However, the nucleophilic attack on the carbon-carbon double bond by an alcohol oxygen is only observed upon irradiation or under acidic conditions (6-8), and the reported examples of such nucleophilic addition reactions are very few. For instance, the addition of alkyl lithium to 1,1-diphenylethylene (9,10), and of ethylamine to diphenylene-ethylene (11) are known. Therefore, the addition of the alkoxide oxygen to the cycloheptatriene would be irrational. To explain our finding, we propose an idea that the alkoxide anion attacks the cyclopropane ring of the norcaradiene (VI), instead of the cycloheptatriene (I). It is well known that the cycloheptatrienes exist in equilibrium with the norcaradienes (12-16). Thus, the nucleophilic attack of alkoxide anion occurs on the unstable cyclopropane ring of norcaradiene form (VI) and the driving force for the formation of II is ascribed to the strain relief of the [2,2] spiro system (VI). Dreiding model indicates that, the distance between the alkoxide anion and C_4 of VI is less than 2.3 Å and therefore the reaction seems favorable from the view point of the geometry factor. The resulted diene-ether systems seem strainless compared with I and VI.

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