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1,2-DIPHENYLCYCLOPROPENE

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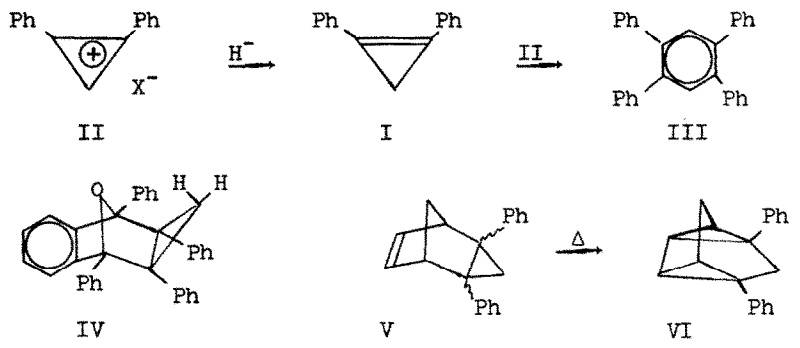
It is curious that among the diverse alkyl- and aryl-substituted cyclopropene hydrocarbons, 1,2-diarylcyclopropenes are completely unknown (1). Attempts to prepare the simplest cyclopropene of this type, 1,2-diphenylcyclopropene (I), have been singularly unsuccessful (2); moreover, an incidental reaction which likely generates I has not led to isolation of the compound (3). Hydride reduction of diphenylcyclopropenyl cation (II), an obvious route to I, affords only 1,2,4,5-tetraphenylbenzene (III) when the reduction is carried out in the usual manner (2a). We have offered evidence (2a) which indicates that in such reductions, III arises from the reaction of I, as generated, with cation II (4). With the knowledge of this mode of reaction for I we have examined the reduction of II by an inverse addition procedure and find that it results in the isolation of I in high yields. The availability of I now permits a direct test of several rearrangement processes in which its intermediacy has been implicated and has provided, in one of its adducts, an unexpected valence isomerization of the $(2\pi + 2\sigma)$ type.

A solution of 1.8 mmoles of 1,2-diphenylcyclopropenyl fluoroborate (II, $X = BF_4^-$) in acetonitrile was added over 2 hr to a solution of 2.4 mmoles sodium borohydride in the same solvent. After an additional two hr, the solvent was removed and the ether soluble portion of the residue subjected to preparative TLC (silica gel, cyclohexane). This afforded I (79% yield) as a waxy white solid (5) which softens with melting at 42-47°; nmr ($CDCl_3$) τ 8.48 (1, sharp s) and 2.1-3.0 (5, m); mass spectrum, m/e 192 (M^+, 100%) and 191 (95%); ir (KBr), 1820 cm^{-1}; uv (EtOH) λ_{max} (log ε). 228 (4.01), 236 (3.94),



309 (4.16), 318 (4.23), and 335 nm (4.09). Diimide reduction of I gives cis-1,2-diphenylcyclopropane, identical in all respects to authentic material (6).

The reaction of 1,2-diphenylcyclopropene with an equimolar amount of diphenylcyclopropenyl cation (II, X = BF_4^-) in acetonitrile affords 1,2,4,5-tetraphenylbenzene (III) in 85% yield, confirming our hypothesis (2a) concerning the formation of III in hydride reductions of II (4). Dehydrochlorination of 1,2-diphenyl-1-chlorocyclopropane using potassium amide in dimethoxyethane affords III rather than I (2d). Compound I is presumed (2d) to be an intermediate in this conversion. We find that I, when subjected to the described (2d) dehydrochlorination conditions, gives a complex mixture of products but III is not among them (7).

Reaction of I with 1,3-diphenylisobenzofuran gives the adduct IV (5), mp 235-236°. In addition to aromatic multiplets, the nmr spectrum exhibits coupled doublets (1 each, J = 4.7 Hz) at τ 7.06 and 8.20. The low field position of one of the doublets, presumably the methylene proton syn to oxygen (8), allows us to tentatively assign the exo stereochemistry to the adduct (9). More interesting is the adduct (V) (5), of unknown stereochemistry, from the reaction of I with cyclopentadiene. On warming to about 60°, in the solid state or in solution, V is quantitatively converted to a saturated isomer, apparently VI (5). Photochemical isomerizations of other tricyclo[3.2.1.$0^{2,4}$]-oct-6-enes to the tetracyclic system are well known (10). The first thermal example of this arrangement was described recently (11); it involves the iso-

merization (at 190°) of the adduct, argued to possess the endo configuration (12), of 1,2,3-triphenylcyclopropene and cyclopentadiene.

We are examining the stereochemistry of V and the detailed nature of the thermal isomerization. These studies and other aspects of the chemistry of I will be described in future publications.

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(5) Satisfactory elemental analyses and mass spectra were obtained for all new compounds. The assigned structures are consistent with nmr, ir and uv data.

(6) We are indebted to Dr. P. Sigal and Dr. E. W. Valyocsik for providing spectra of this compound.

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