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VALENCE ISOMERIZATION OF CIS-1,2-DIVINYLCYCLOPROPANES: A SIMPLE SYNTHESIS OF BICYCLO[3.2.1]OCTADIENE

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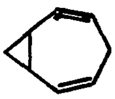
A reaction characteristic of hexa-1,5-dienes is their isomerization on heating (the Cope rearrangement) (2,3). The most facile of such thermal reorganization processes are undergone by cis-1,2-divinylcyclopropane and its derivatives (2-6). Isolation of cis-1,2-divinylcyclopropane itself has not been achieved, even from a reaction carried out at -45°; rearrangement to the observed product, cyclohepta-1,4-diene, presumably occurred even at that low temperature (5). Relief of strain in the three-membered ring and favorable π-orbital overlap between the double bonds in the quasi-boat transition state are factors responsible for the extreme ease of this transformation (3). Trans-1,2-divinylcyclopropane also rearranges to cyclohepta-1,4-diene, but temperatures of 190° are required (2,4). Besides various norcaradiene derivatives and analogs (7), few divinylcyclopropane derivatives have been reported (2,3), with the exception of the spectacularly degenerate examples, bicyclo[5.1.0]octa-2,5-diene (I)(5) and bullvalene (II).(6)

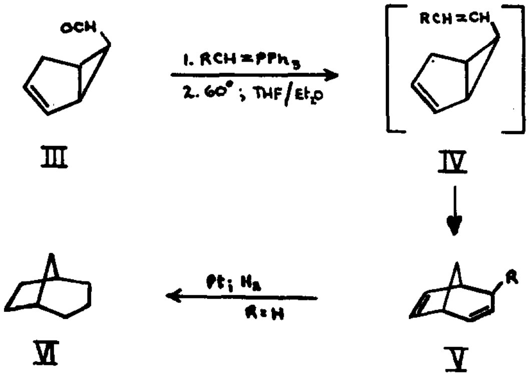


I

II

We wished to study this rearrangement and to explore its synthetic utility in non-degenerate systems. We report here observations which emphasize further the facility with which cis-1,2-divinylcyclopropanes isomerize.

The ready availability of bicyclo[3.1.0]hex-2-ene-6-carboxaldehyde (III) by peracid oxidation of norbornadiene (8) suggested a convenient route to 6-endo-alkenylbicyclo[3.1.0]hex-2-enes (IV) via a Wittig reaction (9) using alkylidenetriphenylphosphoranes [$RCH=P(C_6H_5)_3$]. Dienes of type IV should rearrange readily, possibly under the conditions of the Wittig reaction, to bicyclo[3.2.1]octa-2,6-dienes (V). We have realized this process with the parent hydrocarbons IV (R=H) and V (R=H), thereby achieving a more attractive synthetic route to bicyclo[3.2.1]octa-2,6-diene (V; R=H) than formerly available (10).



The aldehyde III was prepared as reported previously (8) and was purified through its bisulfite adduct. Treatment of this adduct under nitrogen with saturated aqueous sodium bicarbonate solution regenerated III in a satisfactory state of purity, as judged by gas chromatography. Addition of an ether solution of aldehyde III (0.04 mole) to methylenetriphenylphosphorane, which had been prepared in ether under a nitrogen atmosphere from methyltriphenylphosphonium bromide (0.20 mole) and phenyllithium (0.10 mole), caused immediate precipitation of the Wittig intermediate adduct (9). Decomposition of this adduct at 60° in refluxing tetrahydrofuran-ether and work-up in the usual fashion (9) gave crude hydrocarbon product in 70 per cent yield. Capillary gas chromatography of this crude material showed it to consist of 95 per cent of a single compound, which distilled unchanged at 121° (760 mm.). The remaining 5 per cent consisted of reaction solvents. Final purification by preparative gas chromatography yielded bicyclo[3.2.1]octa-2,6-diene (V, R=H), identified by comparison with an authentic sample (10, 11). The proton magnetic resonance spectra [1.5-2.7 δ(6H) complex; 5.03 δ(1H) broad doublet; 5.53 δ(1H) sharp quartet; 5.86 δ(1H) broad doublet; 6.07 δ(1H) sharp quartet] and infrared spectra (3040, 3025, 1629, 1590, 726 and 674 cm.$^{-1}$) of our synthetic V (R=H) and of the comparison specimen (11) were superposable and were identical with data reported for this compound (10). Reduction of diene V (R=H) over platinum catalyst at one atmosphere hydrogen pressure resulted in uptake of two molar equivalents of hydrogen to give bicyclo[3.2.1]octane (VI), m.p. 133-134° (lit. m.p. 133.5-135°(10), 133°(12) and 139.5-141°(13).

No evidence for the presence of 6-<u>endo</u>-vinylbicyclo[3.1.0]hex-2-ene

(IV, R=H), the presumed intermediate, was found under these reaction conditions. The apparently spontaneous rearrangement of IV (R=H) to V (R=H) at 60° suggests a simple route to 5-substituted bicyclo[3.2.1]octa-2,6-dienes (V) from the reaction of aldehyde III with other alkylidenetriphenylphosphoranes. Further research towards this end is now in progress.

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11. We wish to thank Professor N. LeBel, Wayne State University, for supplying us with an authentic sample of bicyclo[3.2.1]octa-2,6-diene (V, R=H).
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