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STEREOSELECTIVE THERMAL REARRANGEMENTS OF 2-PHENYL-ALKENYLIDENECYCLOPROPANES

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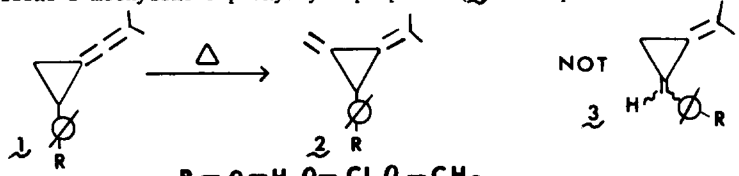
Alkenylidenecyclopropanes have been pyrolyzed to yield dimethylenecyclopropanes.[2,3] A similar but stereoselective thermal rearrangement of 1-(2-methylprop-1-enylidene)-2-phenylcyclopropanes (**1**)[4] to 1-isopropylidene-2-methylene-3-phenylcyclopropanes (**2**) is reported here.

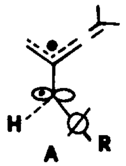


R = p-H, p-Cl, p-CH_3

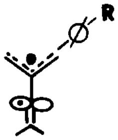
Rearrangement of **1** to **2** occurs nearly quantitatively on vpc at 170° or by heating **1** in mesitylene solution at 130°.

Identification of **2** was accomplished by spectral methods. The PMR ($CDCl_3$, 60 MHz) spectrum of **2**(R=H) displayed peaks at τ 2.84 (5H, phenyl), 4.80 and 4.60 (1H each, vinyl), 7.00 (1H, benzylic), and 7.97, 8.12 (3H each, methyl). The IR spectrum of **2**(R=H) showed characteristic dimethylenecyclopropane absorptions at 5.57 and 5.83 μ.[5] Spectral data for **2**(R=Cl, CH_3) were also consistent with the proposed structure. All new compounds gave satisfactory elemental analysis.

Several mechanisms can account for the conversion of **1** to **2**[2,3,6,7]. Using the elegant Doering-Roth mechanism[7] to account for the stereoselectivity, one can predict that non-planar diradical structures A-C would be expected to be in the path leading to products from the thermolysis of **1**. Since **2** is the only detected product, it must arise from the ring closure of a benzylic-vinyl-allylic diradical (Structure A) or from a vinylic-benzylallylic diradical (Structure B). Other diradical ring closures possible in A-C are not operative probably because they represent higher energy diradical ring closures, thus explaining the absence of **3**.[8]



A



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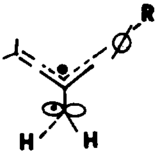
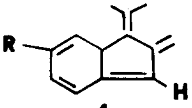


C

The fact that **1** and **2**, 2-phenylisopropylidenecyclopropane[9] and 2-phenylmethylenecyclopropane[10] do not rearrange to indene derivatives supports the suggestion that two phenyl groups are necessary for the thermal rearrangements of 2,2-diphenylmethylenecyclopropanes to indenes.[10] Also the lack of rearrangement of **1** or **2** to an indene may be due to strain in **4**, a possible intermediate needed to form an indene derivative.[11]



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1. We thank the Research and Projects division of S.I.U.-Edwardsville for financial support of this work.
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8. The absence of **3** is concluded on the basis that only one compound (**2**) was detected by vpc on several colums. In each vpc run, **2** was identified by its nmr spectrum. Heating **1** in mesitylene solution at 100° for 10 minutes led to a mixture containing mesitylene, **1** and **2**.
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11. Heating pure degassed samples of **1** or **2** in sealed, steam cleaned tubes at 320-370° for up to 12 hours resulted in recovery of pure **2**.