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REARRANGEMENT OF PHENYLCYCLOPROPYL RADICALS

J. C. Chen*

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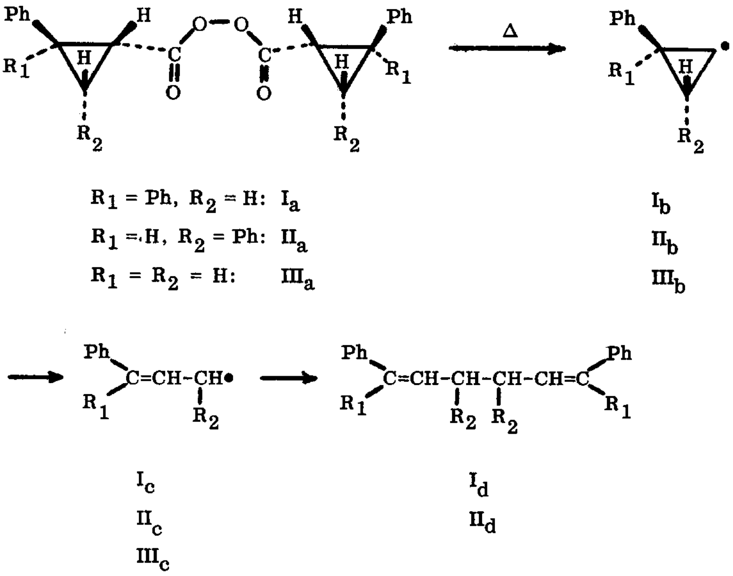
Cyclopropyl radicals have been generated from appropriate precursors in both the vapor and liquid phases. When cyclopropyl radicals were generated in the vapor phase, a mixture of unrearranged and rearranged products have resulted. But in liquid phase reactions only unrearranged products were observed except in the case[1] of 2,2-diphenylcyclopropyl radical (I_b).



$R_1 = Ph$, $R_2 = H$: I_a I_b I_c I_d

$R_1 = H$, $R_2 = Ph$: II_a II_b II_c II_d

$R_1 = R_2 = H$: III_a III_b III_c

In the isomerization of I_b to the allyl radical I_c, it has been suggested that the substitution of two phenyl rings in the 2-position markedly lowers the energy barrier to isomerization. However, the substitution may affect the isomerization of I_b by releasing steric interaction of the two phenyl rings[2] by leading to a highly resonance stabilized I_c, or a combination of both. In order to clarify these possibilities as well as search for an additional isomerization reaction of a cyclopropyl radical, the systems of <u>trans</u>-2,3-diphenylcyclopropyl radical

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*Current Address: Department of Chemistry, Boston University, Boston, Massachusetts 02215.

(II_b) and 2-phenylcyclopropyl radical (III_b) were investigated.

The precursors for the desired radicals, trans-2,3-diphenylcyclopropanecarbonyl peroxide (II_a) and trans-2-phenylcyclopropanecarbonyl peroxide (III_a) were synthesized by the method described by Greene and Kazen[3] from trans-2,3-diphenylcyclopropanecarboxylic acid[4] and trans-2-phenylcyclopropanecarboxylic acid (Aldrich). The thermal decomposition of II_a in benzene (0.02 M) at 80° for 24 hrs afforded ~30% yield of 1,3,4,6-tetraphenyl-1,5-hexadiene[5] (II_d). Under the same reaction conditions but in the presence of iodine II_a gave no II_d. This result is in accord with the thermal decomposition[1] of I_a. The formation of II_d obviously resulted from the isomerization of II_b to II_c followed by coupling of II_c. However, in the presence of a good radical trapping reagent such as iodine the isomerization of II_b to II_c was prevented. The thermal decomposition of III_a under the same reaction conditions as that of II_a (benzene, 0.02 M) gave only phenylcyclopropane. The analogous dimeric product resulting from the possible intermediate from III_c was not detected in the reaction mixture. Therefore the isomerization of III_b to III_c might not be a favorable pathway.

The present result leads one to conclude that the formation of highly resonance stabilized allylic radicals is the main factor in lowering the activation energy in the isomerization. Unlike the radical I_c, the radical II_c has little apparent steric interaction between the two phenyl rings[2] even though both have comparable resonance energies which are lower than that of III_c. The fact that the formation of a highly resonance stabilized radical lowers the activation energy has been seen in the other free radical reactions and has been well described by Huyser.[6]

Approximate calculations[7] of π-electron energy (E_π) show that III_c has an E_π of $9\alpha + 11.968\beta$. Therefore, in order to obtain an isomerization product in solution, a cyclopropyl radical must have substituents which would lead to an allylic radical possessing an E_π value larger than $9\alpha + 11.968\beta$.

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References

1. H.M. Walborsky and J.C. Chen, J. Am. Chem. Soc., 92, 7573 (1970)
2. The steric interaction of I_b can possibly be rationalized by the fact that phenyl nmr absorption of I_a showed a multiplet while I_d showed a singlet for the aromatic protons. The nmr spectrum of II_a showed a singlet in the phenyl region.

3. F.D. Greene and J. Kazan, J. Org. Chem., 28, 2163 (1963).

4. The acid was prepared by the reaction of trans-stilbene and ethyl diazoacetate in the presence of copper bronze followed by saponification.

5. The spectral data, molecular weight determination and element analysis were consistent with the proposed structure.

6. E.S. Huyser, Free Radical Chain Reaction, p. 75 and 93, Wily Interscience, New York, New York (1970).

7. M.J.S. Dewar, The Molecular Orbital Theory of Organic Chemistry, chapter 6 and references therein. McGraw-Hill, New York, N.Y. (1969).