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THE PHOTOCHEMISTRY OF 1,3-DIPHENYLPROPENE-2-d

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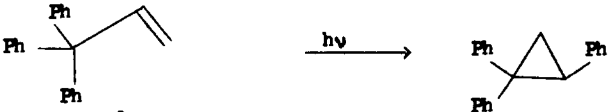
The photochemical rearrangement of arylpropenes to cyclopropanes was first reported by Griffin in 1965.[1a] This rearrangement appears to be quite general in that the migrating group may be aryl (1 → 2),[2] hydrogen (3 → 4),[2] or alkyl (5 → 6).[3] Although the reaction is formally the same in all three cases, it is very probable that the detailed mechanisms differ. Whereas the migration of alkyl and hydrogen can perhaps best be visualized as $\sigma^2s + \pi^2s$ cycloadditions, it seems quite likely that the aryl groups take advantage of



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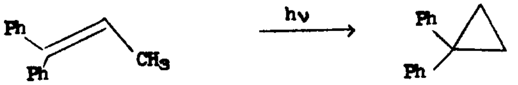

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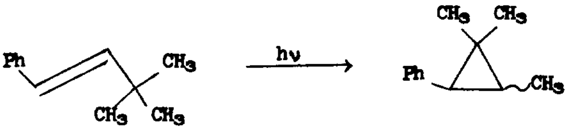

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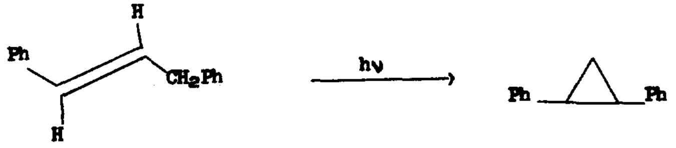
their π systems and rearrange in a different manner as discussed by Zimmerman.[4] A knowledge of the relative migratory aptitudes of the various groups would be very helpful in understanding the details of the rearrangement.

The rearrangement of 1,3-diphenylpropene (7) to 1,2-diphenylcyclopropane[1a,b] (6) is interesting in that product formation could conceivably occur by either hydrogen or phenyl migration. In the unlabeled olefin these pathways are indistinguishable. Since we are interested in studying migratory aptitudes in such acyclic systems which undergo photochemical 1,2-shifts, we have studied the photolysis of 1,3-diphenylpropene-2-d (7-d). Rearrangement of 7-d via a hydrogen shift (path a) would give diphenylcyclopropane with deuterium at the methylene position; a phenyl shift (path b) would give product with deuterium at a benzylic position.



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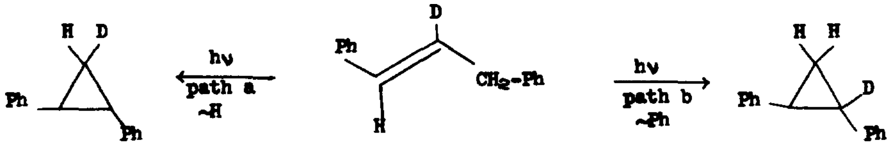
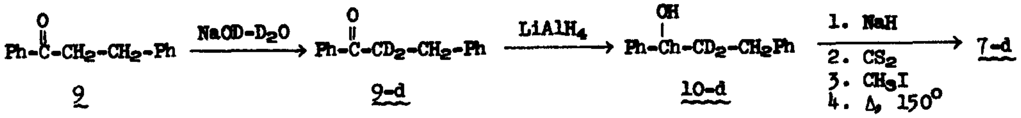


7-d

Two exchanges of β-phenylpropiophenone (9) with NaOD-D_2O in dioxane gave β-phenylpropiophenone-α, α-d_2 (9-d). Lithium aluminum hydride reduction of 9-d gave alcohol 10-d. Pyrolysis of the methyl xanthate of 10-d gave a crude product which, after distillation and four recrystallizations from methanol, afforded pure trans-7-d, containing 1.0 deuterium atom at C-2 (nmr).



$$\underset{\mathbf{2}}{Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}CH_2\text{-}Ph} \xrightarrow{NaOD\text{-}D_2O} \underset{\mathbf{9\text{-}d}}{Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}CD_2\text{-}CH_2\text{-}Ph} \xrightarrow{LiAlH_4} \underset{\mathbf{10\text{-}d}}{Ph\text{-}\overset{OH}{\overset{|}{Ch}}\text{-}CD_2\text{-}CH_2Ph} \xrightarrow[\substack{2.\ CS_2\\ 3.\ CH_3I\\ 4.\ \Delta,\ 150^{\circ}}]{1.\ NaH} \mathbf{7\text{-}d}$$

The irradiation of 7-d (1g) in cyclohexane (400 ml) was carried out under nitrogen using Corex-filtered light from a Hanovia 450 W medium pressure mercury arc. The conversion to cyclopropane was kept low (~13%) to avoid deuterium scrambling via the known sequence:[1a,b]

$$\text{Olefin } \mathbf{7} \xrightarrow{h\nu} \text{cyclopropane } \mathbf{8} \xrightarrow[\sim H]{h\nu} \text{olefin } \mathbf{7}$$

yet high enough to obtain enough product for nmr analysis.

After photolysis remaining olefin was removed via $KMnO_4$ oxidation and column chromatography, and the trans-1,2-diphenylcyclopropane product was isolated via preparative g.c. Examination of the nmr spectrum of the cyclopropane revealed a multiplet for the benzylic hydrogens integrating for 1.05 hydrogens; 1.95 hydrogens were present at the methylene position.

Thus the photochemical rearrangement of 7 to diphenylcyclopropane (8) proceeds almost entirely (95±5%) if not exclusively via phenyl migration (path b).[5,6] We conclude that the photolysis of 7 provides a further example of the now well established di-π methane rearrangement,[7] and that, as previously noted,[2,4] σ-π interaction is inefficient relative to π-π interaction in such systems.

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3. H. Kristinsson and G. W. Griffin, *J. Amer. Chem. Soc.*, **88**, 378 (1966).

4. H. E. Zimmerman, P. Hackett, D. F. Juers, J. M. McCall, and B. Schröder, *ibid.*, **93**, 3653 (1971); H. E. Zimmerman and G. E. Samuelson, *ibid.*, **91**, 5307 (1969).

5. The occurrence of a very small amount of hydrogen migration cannot be ruled out since our method of analysis is not sufficiently sensitive. Moreover, a small amount of the scrambling reaction cannot be differentiated from hydrogen migration.

6. Since submission of this manuscript for publication, Professor Gary Griffin has informed us that he has observed that photorearrangement of $PhCH = C^{14}HCH_2Ph$ to the cyclopropane **7** and subsequent oxidatitive degredation (CrO_3 + HOAc) gave C-14 labeled benzoic acid whose activity was consistent with exclusive phenyl migration: G. W. Griffin, R. C. Petterson, and P. Groves, unpublished results.

7. See Reference 3 and references cited therein.