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# THE PHOTOSENSITIZED DIMERIZATION OF 1,2,3-TRIPHENYLCYCLOPROPENE

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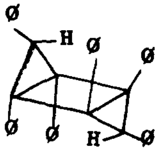
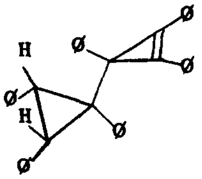
There have been two recent reports on the photodimerization of substituted cyclopropenes. H. H. Stechl has found[1] that 1,3,3-trimethylcyclopropene, on irradiation in the presence of benzophenone, produces two isomeric dimers, both tricyclo[3,1,0,0$^{2,4}$]-hexane derivatives. Obata and Moritani[2] report that 1,2-diphenylcyclopropenyl methyl ketone also dimerizes to a tricyclohexane on irradiation. We have been examining the photochemistry of some cyclopropenes, and wish to report on a subtle but interesting facet of the dimerization of 1,2,3-triphenylcyclopropene.

When a degassed 0.04 M solution of 1,2,3-triphenylcyclopropene (I) in benzene is irradiated with 3130 Å light there are no reactions of quantum yield greater than $10^{-2}$. If a sensitizer such as benzophenone is added to the solution and filtered light of 3660 Å used to insure that only the sensitizer is excited, a high quantum yield reaction occurs giving the two dimeric products shown below (II and III).



II 60%



III 40%

It is clear that the dimerization occurs *via* the triplet state of triphenylcyclopropene. We find there is no change in the ratio of the two products with sensitizers of different triplet energy and different

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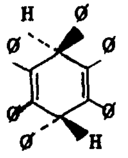
*NIH Postdoctoral Fellow, 1965-66. Present address: Research Laboratories, Eastman Kodak Company, Rochester, New York structure (vide infra), nor does the product ratio depend on the extent of conversion of the starting material. This implies a mechanism involving the triphenylcyclopropene triplet as a true intermediate, free and independent of the sensitizer molecule.

The tricyclohexane II is a white, crystalline, ether-insoluble substance melting between 330 to 350°, with a phase change occurring around 200°. The mass spectrum shows a parent peak at 536 mass units; the UV spectrum shows only end absorption beginning around 285 mmicrons. The NMR spectrum of II shows a singlet at 4.10$\delta$ and a multiplet near 7.2 $\delta$ in a ratio of 1:15. The extremely low field of the cyclopropane protons leads us to believe that II is the stereoisomer shown, with the cyclopropane protons deshielded by the phenyl rings opposite. This assignment is consistent with mechanistic considerations below.

When II is heated to the melting point and then cooled and the solid recrystallized from acetone-water, it affords IV, m. p. 340-355°. The NMR spectrum of IV shows a singlet at 5.00$\delta$ and a multiplet near 7.2 $\delta$ ; the UV spectrum shows absorption beginning at about 300 mmicrons and having shoulders at 273 ($8.6 \times 10^3$), 265 ($1.45 \times 10^4$), and 260 ($2.1 \times 10^4$).



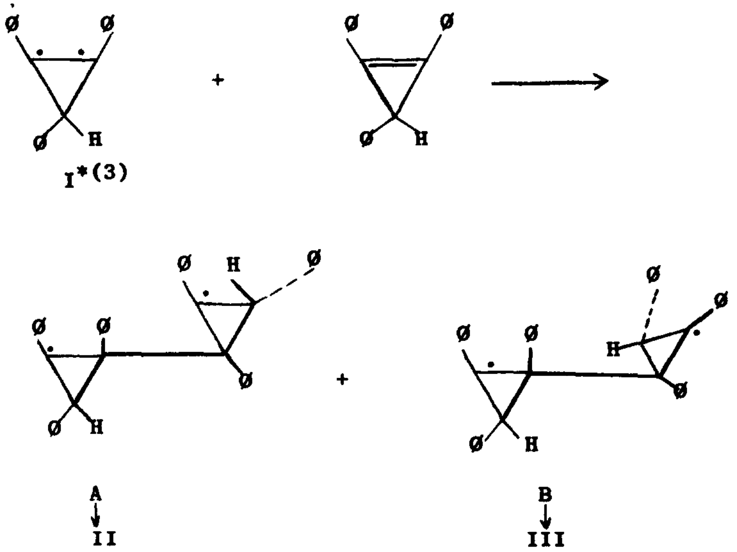
IV

When IV is treated with bromine, in refluxing chloroform, hexaphenylbenzene is formed in good yield.

Product III is an ether-soluble substance which was separated from undimerized starting material by chromatography on alumina. Its structure was established by comparison with an authentic sample.[3]

Since Dimer III is formed by hydrogen transfer, while II is not, we have determined the deuterium isotope effect to see whether the hydrogen transfer occurs during the product determining step. A mixture of

1,2,3-triphenylcyclopropene and 1,2,3-triphenylcyclopropene-3-d was dimerized and the isotopic composition of the starting material and of dimers II and III was determined by mass spectroscopy. No detectable isotope effect ($<$ 1%) was seen. Thus, hydrogen transfer does not occur in the product determining step. The following mechanism rationalizes this unusual observation:



The addition of triplet $I^{*(3)}$ to I proceeds so as to put the hydrogens in the hindered endo positions (this is confirmed by the failure of the more hindered 3-methyl-1,2,3-triphenylcyclopropene to form either a dimer or a mixed dimer with I under these conditions). Two isomeric adducts, A and B, are formed in roughly equal (60/40) amounts. In the "chair" conformation, A can close to tricyclohexane II, while B would have to assume the "boat" conformation in order to close to a tricyclohexane. (The "boat" isomer of tricyclohexane II is not seen in the products.) However, hydrogen transfer can occur in B via a chairlike conformation, but hydrogen transfer in A would require a "boat" conformation. Thus, each diradical, A and B, has only one likely fate, and the product has been determined before hydrogen transfer.

It was of interest to determine whether the triphenylcyclopropene triplet would add to other substrates. Equimolar mixtures of 1,2,3-triphenylcyclopropene (I) and a second substrate (*cis*-stilbene, diphenylacetylene, phenylacetylene, 3-methyl-1,2,3-triphenylcyclopropene, and 1,2-diphenyl-3-carbomethoxycyclopropene) with various sensitizers were irradiated. The solvent was benzene and the concentration of both the triphenylcyclopropene and the second substrate was 0.04 M. Only products II and III were observed, with no sign of any cross adducts, except in the case of 1,2-diphenyl-3-carbomethoxycyclopropene, where several unidentified new peaks were seen in the NMR which could not be assigned to products from the dimerization of either substrate alone. Moreover, the quantum yield for the dimerization of triphenylcyclopropene was not lowered by the presence of phenylacetylene or diphenylacetylene. The presence of *cis*-stilbene lowered the quantum yield of the dimerization to less than $10^{-2}$; this can be explained if energy transfer from the sensitizer to *cis*-stilbene is faster than transfer to triphenylcyclopropene and/or if tirphenylcyclopropene triplets transfer energy to *cis*-stilbene. Both of these possibilities would suggest that 1,2,3-triphenylcyclopropene has a higher triplet energy than *cis*-stilbene.

The quantum yields for the total production of dimers of triphenylcyclopropene with various sensitizers were measured. The results are shown in Table I.

TABLE I

| Sensitizer | Triplet Energy | Con. Starting Mat. | $\phi^*$ |
|---|---|---|---|
| Benzophenone | 68.5 kcal/mole | 0.04 M | 0.5 ± .05 |
| Michler's Ketone | 61.0 | 0.04 M | 0.7 |
| 2-Acetonaphthone | 59.3 | 0.04 M | 0.4 |
| Chrysene | 56.6 | 0.04 M | 0.2 |
| Fluorenone | 53.3 | 0.04 M | 0.5 |
| Benzil | 50.9 | 0.04 M | 0.5 |
| 1,2-Benzanthracene | 47.2 | .04 M | 0.3 |

TABLE I (CONT'D)

| Sensitizer | Triplet Energy | Con. Starting Mat. | $\emptyset^*$ |
|---|---|---|---|
| Acridine | 45.3 kcal/mole | 0.04 M | 0.2 |
| Anthracene | 42.7 | 0.04 M | less than $10^{-2}$ |

*Corrected for the different intersystem crossing ratios of the sensitizers.

Table I shows that there is some variation in the quantum yield which does not depend on the energy of the sensitizer triplet. This variation is possibly of steric origin. Such variations are often seen[5] when the triplet energy of the sensitizer is less than that of the acceptor, i.e. when the energy transfer process is endothermic. Some of the variation may be due to internal filtering of light by the 1,2,3-triphenylcyclopropene, since it has a small absorbance at 3650 Å ($A\approx.1$) at these concentrations.

The variation of the quantum yield with concentration of 1,2,3-triphenylcyclopropene was also measured, using fluorenone as the sensitizer. The results were treated to the ususal kinetic analysis[4] and the rate of energy transfer from the sensitizer triplets to triphenylcyclopropene calculated. The rate of energy transfer from fluorenone triplets to cis-stilbene has been directly measured[6] and is found to be nearly diffusion controlled ($k = 1 \times 10^9$). We find that triplet energy transfer from fluorenone triplets to 1,2,3-triphenylcyclopropene is about $10^3$ times slower than transfer to cis-stilbene (triplet energy = 57 kcal/mole[4]).

The most economical explanation of the lower rate of energy transfer to triphenylcyclopropene than to cis-stilbene is again that the triplet energy of 1,2,3-triphenylcyclopropene is higher than that of cis-stilbene. This is in the direction expected since the double bond in triphenylcyclopropene is shorter (stronger) than that in cis-stilbene. We have unsuccessfully attempted to determine the triplet energy of I by absorption spectroscopy in ethyl iodide. Phosphorescence from I at 77°K is also weak, but an emission of energy = 72 kcal/mole is tentatively assigned to the 0-0 band of I.

This is consistent with the kinetic data, since in other known systems[6,7] a $10^3$ decrease below the diffusion controlled rate of triplet energy transfer is associated with an approximately 10-15 kcal/mole endothermicity.

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