

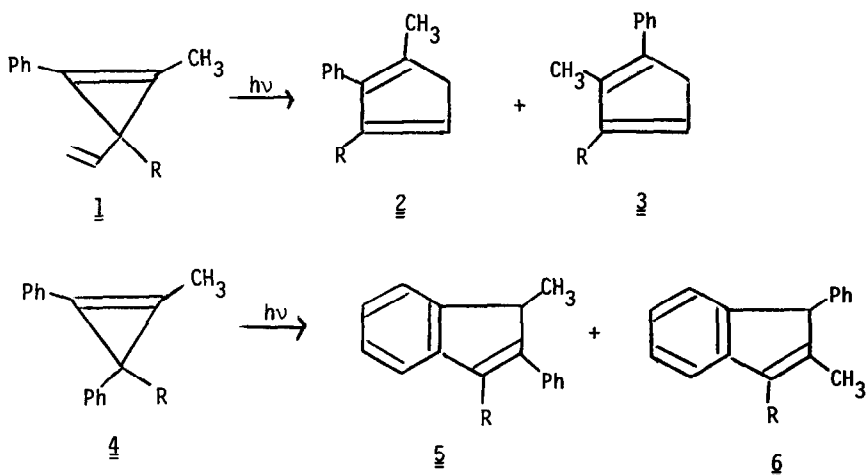
ON THE MECHANISM OF THE PHOTOCHEMICAL REARRANGEMENT
OF 3-PHENYL SUBSTITUTED CYCLOPROPENES TO INDENES

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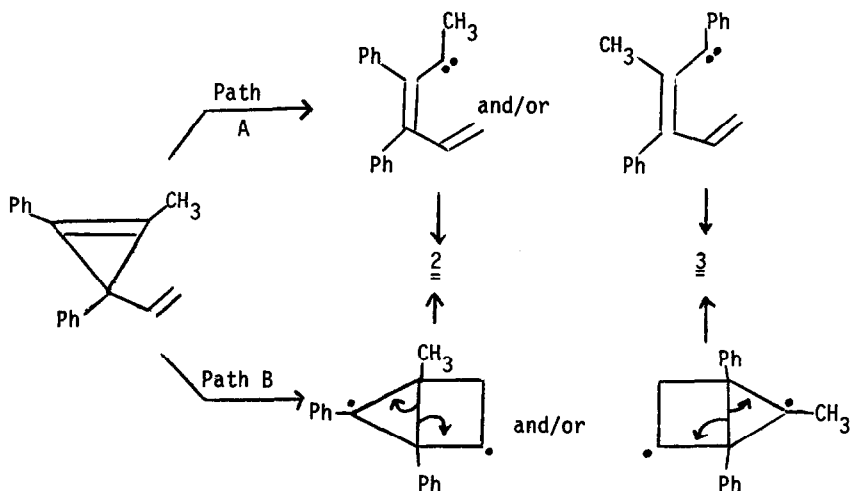
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During the course of our studies dealing with the photochemical transformations of small ring compounds, we uncovered an unusual substituent effect on the mode of ring opening of an unsymmetrically substituted cyclopropene.^{1,2} Thus, the major product obtained from the irradiation of 1 was derived from the preferential cleavage of the cyclopropene single bond which is methyl rather than phenyl substituted.^{3,4} Similarly, irradiation of methylphenylcyclopropene

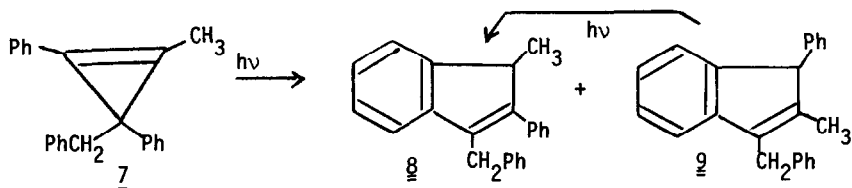


4 afforded a 4:1 mixture of indenes 5 and 6.⁵ Two fundamentally different mechanisms were proposed to account for product formation and are outlined in Scheme I. Path A involves cyclopropene ring opening to give a butadienyl carbene followed by electrocyclic closure. The alternate path (B) involves π - π bridging of the excited cyclopropene to give a diradical intermediate which subsequently cleaves to produce the 1,3-cyclopentadiene ring system. In this communication we wish to present evidence which suggests that path A, the carbene route, is the preferred process.

Scheme I

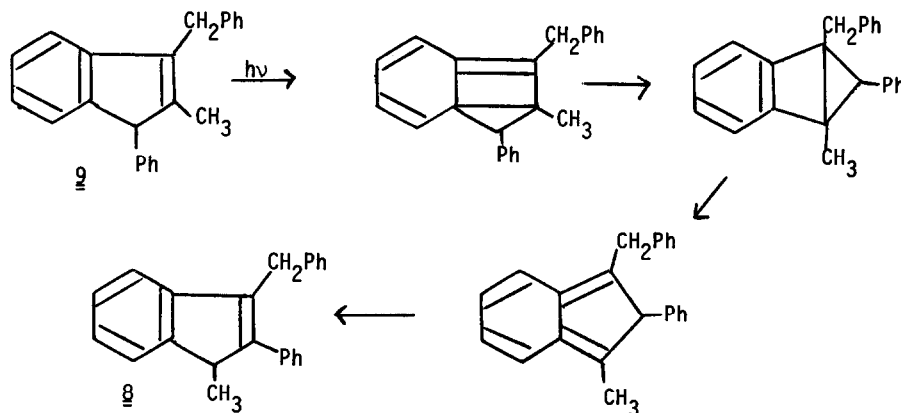


Irradiation of 1,3-diphenyl-2-benzyl-3-methylcyclopropene (**7**) in benzene for 1 hr under an argon atmosphere gave a 4:1 mixture of 1-methyl-2-phenyl-3-benzylindene (**8**) and 1-phenyl-2-methyl-3-benzylindene (**9**). The structures of these indenes were unambiguously confirmed by comparison with authentic samples prepared by treating 2-phenyl-3-methyl and 2-methyl-3-phenylindanone with benzylmagnesium bromide followed by dehydration of the resulting alcohol.⁶



A study of product distribution vs extent of irradiation established that the ratio of **8**:**9** varied as a function of time. At longer exposures, owing to a secondary photoreaction of **9**, the amount of **8** increased (ratio **8**:**9** = 10/1). This was independently demonstrated by the quantitative conversion of **9** to **8** in benzene under comparable photolytic conversions. When the irradiation of **7** was carried out for short periods of time (10 min, <10% conversion) the ratio of indenes (**8**:**9**) was 4:1. This result clearly indicates that **8** is a primary photoproduct. The mechanism of the photoisomerization of **9**→**8** can be rationalized by the following steps (1) an electrocyclic ring closure⁷ (2) a 1,3-sigmatropic shift (3) ring opening to an isoindene and (4) a 1,5-sigmatropic hydrogen shift.⁸ This process is analogous to that

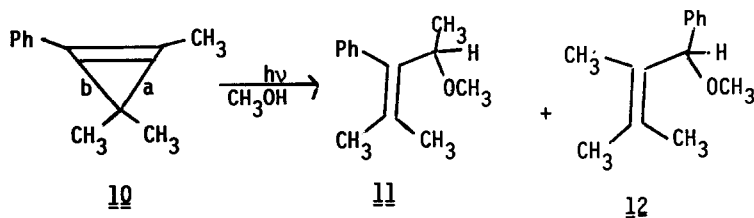
recently described by Morrison and Palensky⁹ for related substituted indenenes, except that in their case, the presence of an alkyl group at the 3-position completely quenched the rearrangement.



In order to help elucidate the correct mechanism for indene formation, the photochemistry of **7** was carried out in methanol. Under these conditions, no detectable quantities of **8** or **9** were present in the crude photolysate. Unfortunately, all attempts to separate the complex mixture of photoproducts were unsuccessful. Nevertheless, examination of the NMR spectrum of the crude photolysate clearly showed the presence of several methoxy ethers and a number of triphenyl-substituted pentadienes. The complete suppression of indene formation is consistent with the intervention of a vinylcarbene intermediate which is trapped by protonation in methanol to give an allyl cation. Subsequent loss of a proton or nucleophilic attack by methanol, could in principle, afford four different methoxy ethers and numerous cis and trans-pentadiene isomers. It should also be noted that the indenenes are stable toward irradiation in methanol and that the relative quantum yields for disappearance of **7** are the same in methanol and benzene.

Further support for the carbene mechanism was obtained from the irradiation of 1-phenyl-2,3,3-trimethylcyclopropene (**10**). The only products obtained from the irradiation of **10** in methanol are methoxy ethers **11** (78%) and **12** (9%). The identity of these compounds was established by comparison with independently synthesized samples.⁶ It is particularly worthy to note that the distribution of the methoxy ethers obtained corresponds to preferential bond

a cleavage and is closely related to the results encountered with cyclopropenes 1 and 4. In all of these cases, the major product is derived from cleavage of the cyclopropene bond attach-



ed to the methyl group. Even though cyclopropene 10 does not contain a π -bond at the 3-position, it still prefers to undergo bond a fragmentation. We conclude that the results are not in ready accord with the diradical mechanism B for indene formation.¹⁰ As was pointed out earlier,¹ the preference for bond a cleavage can be attributed to inductive destabilization of the initially generated vinyl radical by the attached phenyl group. Further studies on the scope and mechanism of this reaction are in progress and will be reported in due course.

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- (9) F. J. Palensky and H. A. Morrison, *J. Amer. Chem. Soc.*, 99, 3342 (1977).
- (10) Although the trapping of a carbene intermediate with 10 does not unequivocally eliminate Path B for cyclopropenes 1 and 4, it would be very fortuitous indeed to obtain the same ratio of bond cleaved products from the two different reaction pathways.