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CUMULENE PHOTOCHEMISTRY: PHENYL AND HYDROGEN MIGRATION IN PHENYLALLENE PHOTOREACTIONS

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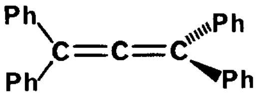
ABSTRACT: Photoreactions of tetra- and triphenylallene and 1,3,3-triphenylcyclopropene in hydrocarbon solvents are reported. Intermediacy of vinylcarbenes is supported by independent generation experiments.

Although cyclopropene photochemistry has been widely investigated,[1] isomeric allenes have received scant attention. As part of a comprehensive study of cumulene photoreactions, we have reported on photorearrangement of 1,2-cyclononadiene to an unusual bicyclic cyclopropene,[2] and on protic solvent photoadditions to phenylallenes.[3] We describe here the photorearrangements of tetraphenylallene (1), triphenylallene (2), and 1,3,3-triphenylcyclopropene (3) in hydrocarbon media. Our results further demonstrate the dynamic link between cyclopropene and allene photoreactions. In concert with a recent report by Steinmetz and co-workers on the 1,1-diphenyl-3-alkyl analogs of 2, vinylcarbenes are implicated as intermediates.[4]



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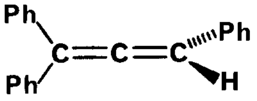

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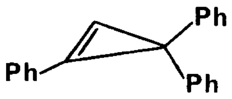

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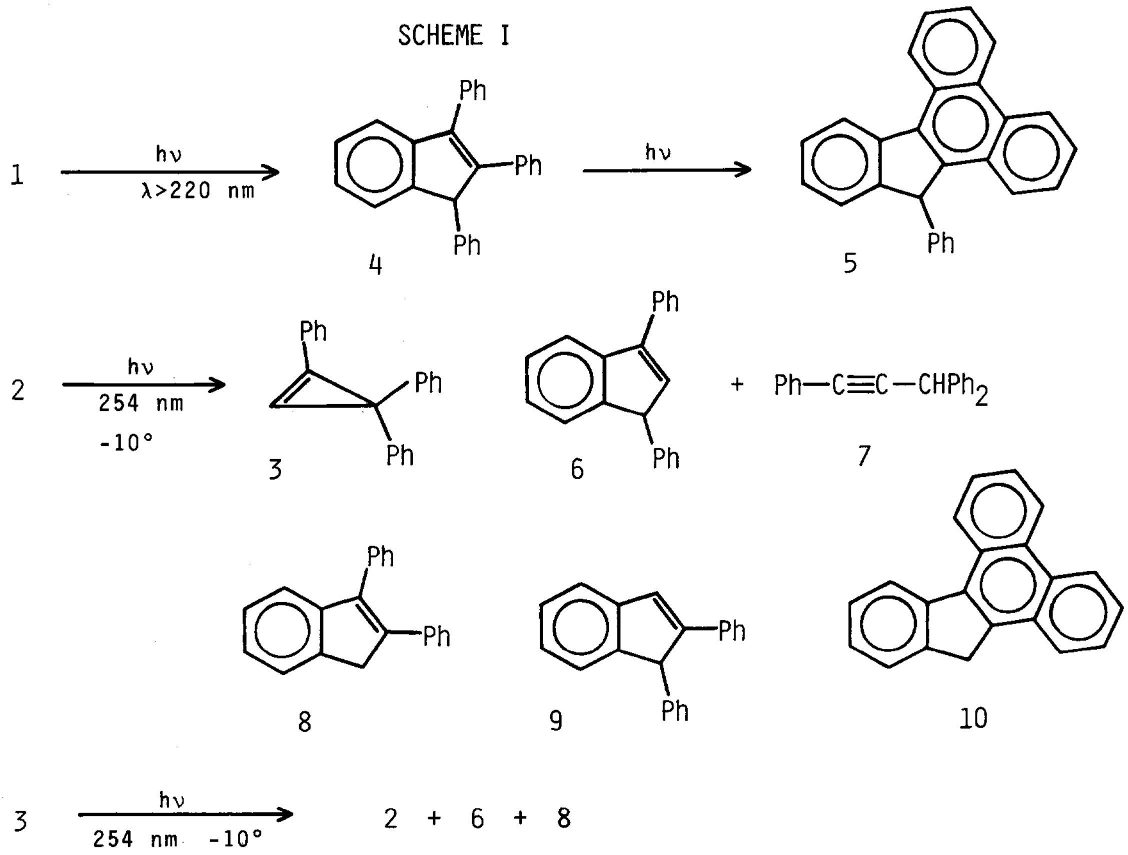
Irradiation (Vycor or Corex filter) of 1 in cyclohexane very slowly yielded (Scheme I) indene 4 and its photoproduct 5, identical to authentic samples,[5] as well as one very minor unidentified product.[6] Secondary 4 → 5 conversion is much more rapid than primary reaction and, even at low conversion (5-10%), predominantly 5 is isolated. Triplet sensitization (xanthone, benzene, $\lambda > 330$ nm) gave recovered 1 and sensitizer, thus this is a singlet reaction. Energy transfer from xanthone (E_T=74.2 kcal/mol) to 1 (E_T=57.4)[7] should be efficient.

Irradiation of 2 in pentane at -10° (to prevent thermal dimerization[8]) more rapidly afforded a mixture of 3, and 6 - 10. Products were characterized by a combination of column chromatographic isolation, HPLC (μ-Porasil; hexane elution) and 300 MHz NMR, with comparison to authentic samples in all cases.[9] Analyses at very low conversion (0.5-5%) showed that 3, 6 and 7 are primary (ratio 1:3:1 at *ca.* 1% conversion), 9 and 10 are secondary, and most, if not all, of 8 is secondary. Irradiation of pure 6 yielded 8 + 9, with 10 as a secondary product of 8.[10] Secondary photoreactions of 3 and 6 proved sufficiently rapid that, even at very low conversion (2-10%), substantial secondary photochemistry had occurred. As with 1, triplet sensitization (xanthone, benzene) was ineffective.

Photoreactions of pure cyclopropene 3 were next investigated. Direct irradiation (Scheme I) rapidly led to formation of 2, 6 and 8 (ratio 0.4:1.0:1.6) as primary photoproducts. Especially noteworthy here is the cyclopropene to allene conversion, which is quite rare[2,4] among known cyclopropene reactions.[1]

Vinylcarbenes are logical intermediates in reactions of 1 - 3; their product "fingerprints" from independent generation should resemble results from photolysis. The most straightforward mechanism for the 1 → 4 conversion is 1,2-phenyl migration to tetraphenylvinylcarbene.[5] Attempts to prepare a suitable precursor to this vinylcarbene have been unsuccessful; however, irradiation of tetraphenylcyclopropene does yield 4.[5]

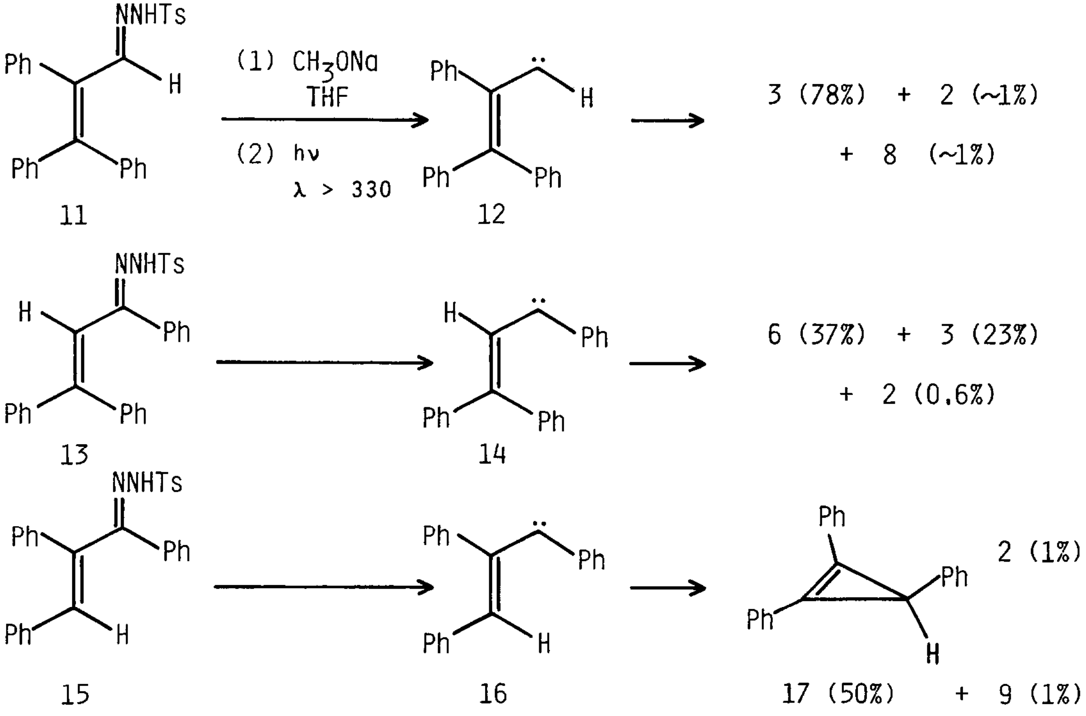
SCHEME I



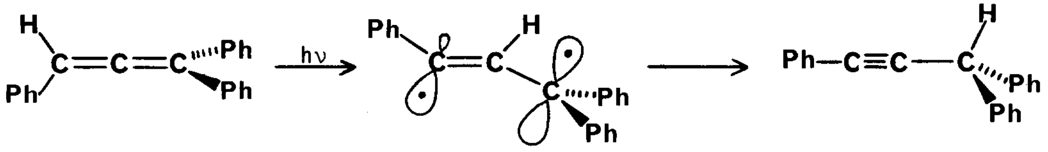
Phenyl or hydrogen migration in triphenylallene can yield isomeric vinylcarbenes 12, 14, or 16, while cyclopropene 3 can open to either 12 or 14. To establish their potential intermediacy, we have carefully examined independent vinylcarbene generation from photolysis of tosylhydrazone precursors. Results are summarized in Scheme II.[11] Vinylcarbenes 12 and 16 yielded predominantly cyclopropenes, while 14 gave significant amounts of both 6 and 3. Significantly, alkyne 7 was not observed, while allene 2 was reproducibly a minor product in each case. Formation of 3 was not reported in a previous study of 14.[11]

The product distribution from 2 is thus consistent with preferential hydrogen migration to 14. Phenyl migration may be a minor competitive pathway, but this cannot be established without isotopic labelling experiments. For cyclopropene 3, the observed product distribution, especially the large percentage of 8, suggests predominant opening to 12, from which reclosure would be rapid. The regioselectivity of this opening accords with many previous examples of formation of the less stable vinylcarbene.[1c]

SCHEME II



Propyne 7 clearly results from a very different mechanism. We envisage hydrogen migration along a C_s reaction coordinate, passing through bisected vinylbiradical 18 (ground or excited state). A second hydrogen migration leads to alkyne, while rotation or internal conversion provides entry onto the vinylcarbene surfaces.[12]



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In conclusion, we have observed evidence for phenyl migration in 1, and preferential hydrogen migration in 2. These reactions are not observed in protic solvents[3] because they cannot compete with more rapid solvent addition. Results for 2 and 3 further demonstrate the interrelationship of cyclopropene and allene photochemistry. Vinylcarbenes are likely to be common intermediates, at least for the acyclic systems described here.

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References and Notes

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(6) This substance has an HPLC retention time identical to tetraphenylcyclopropene, however preparative HPLC isolation showed this to be a phenanthrene derivative. Structure elucidation is in progress.

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