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(12) At −60 °C the intermediate **2a** is evidenced by the following ^{1}H NMR spectrum: δ ($CDCl_3$) 6.23–6.33 (m, 2 H), 5.99 (s, 1 H), 5.03 (m, 1 H), 4.78 (m, 1 H), 2.00 (d ($J \approx 8.5$ Hz) of m, 1 H) and 1.74 (d)$J \approx 8.5$ Hz) of m, 1 H).

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The Photochemistry of Vinylcyclopropenes; a New and General Cyclopentadiene Synthesis. Exploratory and Mechanistic Organic Photochemistry[1]

Sir:

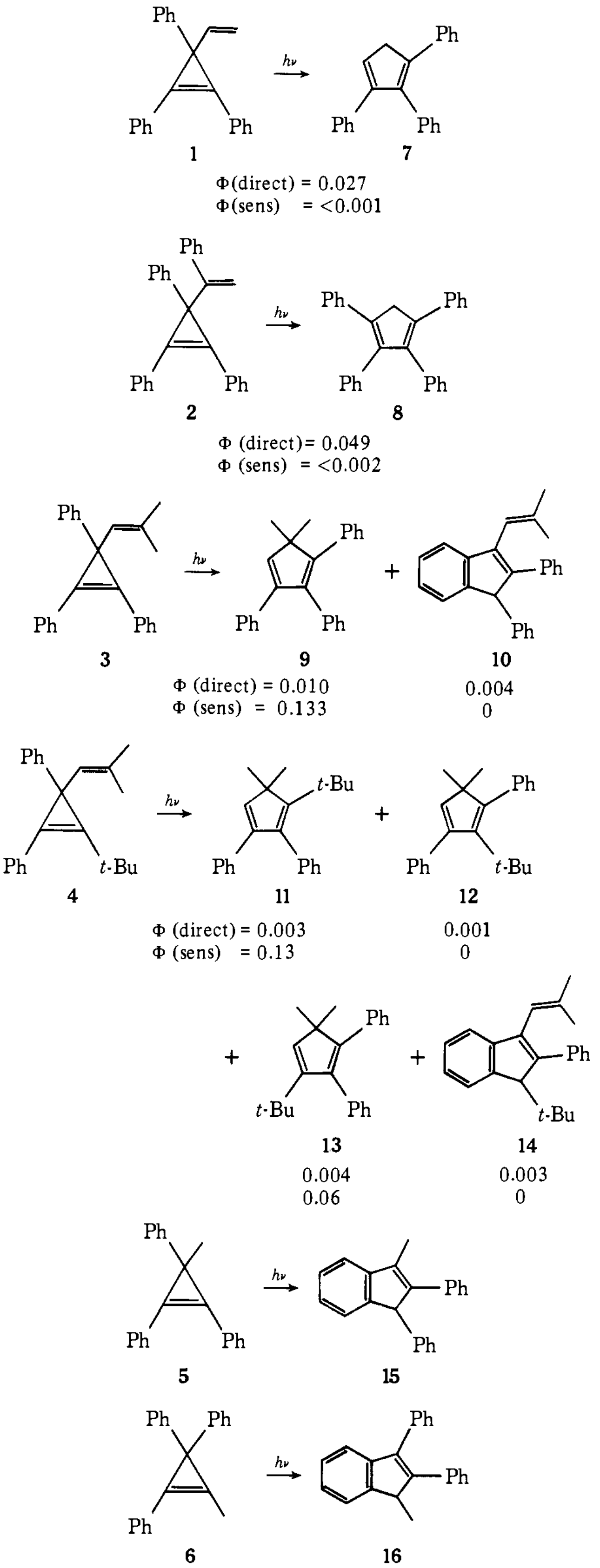
While 3-arylcyclopropenes have been photolyzed,[2] the photochemistry of 3-vinylcyclopropenes has remained uninvestigated. Presently we report: (a) the smooth formation of cyclopentadienes from the photolysis of these reactants, (b) competing with this, an unusual degenerate di-π-methane rearrangement, (c) a trend of quantum efficiencies as a function of structure, (d) a multiplicity dependence favoring singlet or triplet as a function of structure, (e) preliminary evidence indicating a diradical rather than a carbene mechanism, and (f) information suggesting that the rearrangement is mechanistically related to the previously known[2] formation of indenes from 3-arylcyclopropenes.

Thus we have irradiated[3] the four 3-vinylcyclopropenes, **1–4**, and the two 3-arylcyclopropenes **5** and **6** (note Chart I). Interestingly, although indenes are a priori products from the 3-vinyl-3-arylcyclopropenes **1–4**, cyclopentadienes were found exclusively in the cases of cyclopropenes **1** and **2** and as major products (note Chart I) from cyclopropenes **3** and **4**. The photolysis proved sufficiently facile and free of by-products such that the reaction is of considerable synthetic utility. For example, irradiation of 500 mg of vinylcyclopropene **1** for 3.25 h with a 450-W lamp afforded 436 mg (87%) of 1,2,3-triphenyl-1,3-cyclopentadiene (**7**).

Two mechanisms seem plausible. Path A (note Chart II) involves π–π bridging of the excited state to afford the housane diradical **17**. This, in turn, undergoes Grob fragmentation, typical[4] of 1,4-diradicals, to give cyclopentadiene product.

A second reasonable mechanism involves cyclopropene ring opening with formation of carbene **18** followed by electrocyclic closure affording cyclopentadiene product. This is depicted in Chart II as path B. There is, indeed, evidence for formation of carbenes from cyclopropenes both thermally[6] and photochemically.[7]

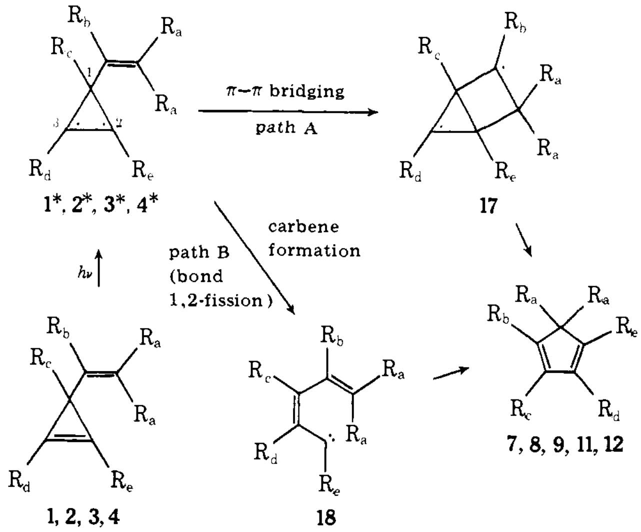
Chart I. Vinyl and Aryl Cyclopropene Reactions



Both mechanisms lead to the same skeletal change as can be seen from Chart II.

The formation of indenes from 3-arylcyclopropenes (note examples **5** and **6** in Chart I) can be formulated in exactly

Chart II. Two a Priori Mechanisms for Cyclopentadiene Formation



parallel fashion using either of the two mechanisms.[8]

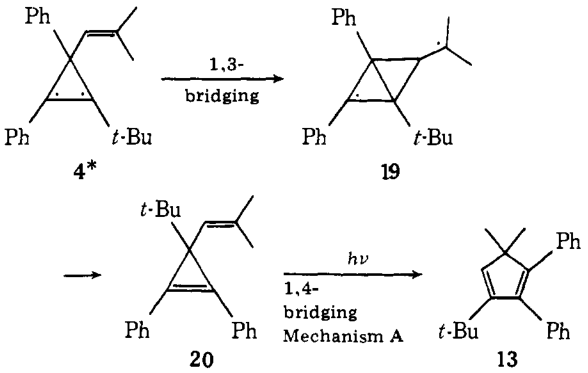
There is preliminary evidence suggesting that mechanism A, the diradical route, is utilized. A first point to be noted is that phenyl substitution as R_b (note Chart II) leads to an enhancement of the reaction efficiency (i.e., $\phi = 0.027$ for **1** vs. $\phi = 0.049$ for **2**). While quantum yields are not necessarily directly related to excited state rate constants,[5] strongly suggestive evidence is provided for a facilitating effect. We note in Chart II that in mechanism A, R_b is at a center bearing odd electron density in diradical **17** and that bridging to give the housane diradical (i.e., **17**) should therefore be facilitated. Conversely, in mechanism B there is no obvious reason why such phenyl substitution should enhance the efficiency of the carbene process.

Another source of evidence is the regioselectivity observed in the reactions where R_d and R_e are different. Both in the case of vinylcyclopropene **4**, having phenyl and *tert*-butyl as R_d and R_e, as well as with triphenylcyclopropene **6**, having phenyl and methyl as these groups, there is a preference for formation of one of two possible product isomers. Thus, from vinylcyclopropene **4**, 1-*tert*-butyl-2,3-diphenyl-5,5-dimethylcyclopentadiene (**11**) is preferred over its 2-*tert*-butyl isomer **12.** This indicates that the phenyl group prefers to be R_d while *tert*-butyl is R_e. The same is true in the case of indene formation from cyclopropene **6**, except that here phenyl prefers to be R_d while methyl is R_e. Reference to Chart II again reveals that R_d is in a position in the housane diradical **17** where it can delocalize odd electron density, and we can understand the preference for this group being phenyl in terms of mechanism A. Conversely, if the carbene mechanism were correct, one would expect preferential formation of the more stabilized carbene (i.e., phenyl at the carbene center), and R_e would preferentially be phenyl in the two cases. We conclude that the results are not in ready accord with the carbene mechanism B.[8c]

Another point of interest is that the vinylcyclopropenes with isopropylidene groups (i.e., **3** and **4** where R_a = Me) react with lower direct irradiation efficiencies than those where R_a is hydrogen. This fits the diradical mechanism A in which the vinyl group must approach the excited cyclopropene π bond and steric hindrance makes this more difficult.

The reaction multiplicity of those cases where the isopropylidene group is absent (i.e., where R_a = H) proved to be singlet; sensitization with xanthone led to no reaction despite favorable energetics. However, the isopropylidene examples react by both singlet and triplet excited states, and the triplet process is remarkably efficient (note Chart I). Differing product distributions in direct and sensitized runs exclude intersystem crossing in the direct irradiations. The isopropylidene cyclopropene triplet reaction may derive from less than facile free rotor decay[9] with this bulky potential free rotor. In the cyclopropene photochemistry leading to indenes studied by Griffin[2a] the evidence favored a singlet reactant, and this is in agreement with our evidence.

Finally, an unusual product, namely 1,2-diphenyl-3-*tert*-butyl-5,5-dimethylcyclopentadiene (**13**) was encountered both in the direct and sensitized irradiations of vinylcyclopropene **4**. This product is understood as arising from an incipient di-π-methane rearrangement to give diradical **19** which affords isomeric cyclopropene **20** (note eq 1). This cyclopropene, utilizing mechanism A, should then afford the observed anomalous product **13.** That this cyclopropene was not spectroscopically detectable suggests that it is consumed as it is formed.



(1)

Hence, the vinylcyclopropene rearrangement seems to be a very general one. We are further investigating its synthetic and mechanistic ramifications.

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References and Notes

(1) (a) This is Paper 104 of our Mechanistic and Exploratory Organic Photochemistry series; (b) for Paper 103 note H. E. Zimmerman, L. C. Roberts, and R. Arnold, *J. Org. Chem.*, in press.

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clopentadiene formation leads to complex kinetic arguments which are delayed for our full paper. Also complicating matters in the carbene mechanism is the possibility of cis and trans carbenes.

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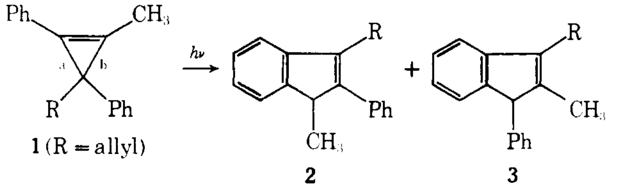
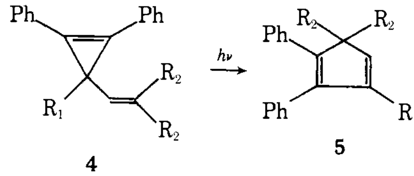
Regioselectivity of Bond Cleavage in the Photochemical Rearrangement of 3-Vinylcyclopropenes[1]

Sir:

Vinylcarbenes have frequently been proposed as intermediates in the thermal and photochemical reactions of cyclopropenes.[2] Extended Huckel calculations carried out on the parent vinylcarbene system suggest a triplet diradical type structure for the ground state of this system.[3] More recent calculations by Davis, Goddard, and Bergman[4] predict that the ring opening reaction of cyclopropene first proceeds to a diradical planar intermediate which subsequently decays to a carbene. As part of a continuing study dealing with the thermal and photochemical reactions of cyclopropenes, we recently encountered an unusual substituent effect on the mode of ring opening of an unsymmetrical diarylcyclopropene.[5] Thus, irradiation of methylcyclopropene **1** afforded a 4:1 mixture of indenes **2** and **3**.[6] It is well known that phenyl substituents stabilize free radicals, and thereby lower carbon-carbon bond energies in saturated three-membered rings.[7] Were this effect to operate in the cyclopropene system, methylphenylcyclopropene **1** should undergo preferential cleavage at bond a. We note, however, that the major indene produced corresponds to cleavage of bond b. In this communication we suggest an explanation to account for this unusual regioselectivity as well as a description of the formation of cyclopentadienes from the irradiation of 3-vinylcyclopropenes.[8]

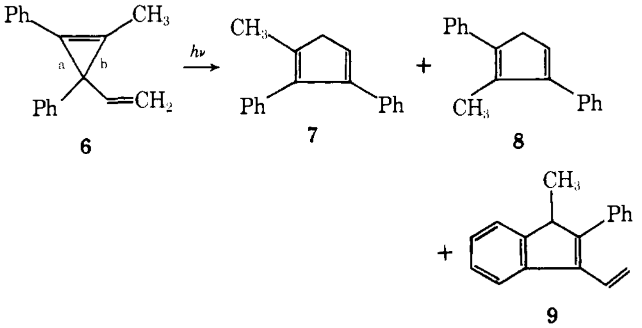


A number of 3-vinyl substituted diarylcyclopropenes were prepared by treating variously substituted cyclopropenyl cations with vinyl Grignard reagents and separating the mixture of isomers formed by column chromatography. Although indenes are generally formed from the irradiation of 3-aryl substituted cyclopropenes,[2b,d,e] the photolysis of **4a** resulted in the exclusive formation of cyclopentadiene **5a**. Similar rearrangements were also found to occur with cyclopropenes **4b-d**.[9]



a, $R_1 = Ph$; $R_2 = H$
b, $R_1 = R_2 = H$
c, $R_1 = CH_3$; $R_2 = H$
d, $R_1 = R_2 = CH_3$

Subjection of cyclopropene **6** to similar photolysis conditions gave a mixture of 1-methyl-2,3-diphenyl (**7**) and 2-methyl-1,3-diphenyl-1,3-cyclopentadiene (**8**) as well as 1-vinyl-2-phenyl-3-methylindene (**9**) in good yield. With this system the formation of the isomeric 1-vinyl-2-methyl-3-phenylindene was not observed. The structures of these compounds were based on their spectroscopic and analytical properties and were further confirmed by the Diels-Alder reactions of **7** and **8** with dimethyl acetylenedicarboxylate. The major products obtained correspond to the preferential cleavage of bond b (ratio **7**/**8** = 2.5/1).



The mechanism by which these 3-vinyl substituted cyclopropenes undergo rearrangement and the identification of the excited state responsible for the reaction are of considerable interest. Two fundamentally different mechanisms seem possible and are presented in Scheme I. Path A involves cyclopropene ring opening to give a butadienyl carbene followed by electrocyclic ring closure. This route bears a strong similarity to mechanisms previously suggested to rationalize the products derived from substituted cyclopropenes on electronic excitation.[2,5] 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. The bridging and cleavage steps are related to the first two formal steps of a di-π-methane rearrangement.[10]

The excited state responsible for photoreaction of the 3-vinyl substitued cyclopropenes is a π-π* singlet, since sensitization with thioxanthone led to no reaction with cyclopropenes **4a** and **4c** and gave a 2 + 2 dimer with **4b**. This is consistent with DeBoer's earlier observation that the intersystem crossing efficiencies of diphenylcyclopropenes are close to zero.[11]

Mention should be made here of the unusual effect of sub-

Scheme I