stitution on the mode of ring opening of cyclopropene **6**. The distribution of the 1,3-cyclopentadienes obtained corresponds to preferential bond b cleavage and is closely related to the results encountered with cyclopropene **1**. In both of these cases, the major product (indene or cyclopentadiene) formed is derived from cleavage of the cyclopropene bond attached to the methyl group. This result can be understood in terms of the mechanisms outlined in Scheme I. If the carbene mechanism (path A) were correct, preferential formation of the more stabilized carbene **11** (phenyl substituted) might be expected. This is not the case. It should be pointed out, however, that theory predicts[4] that it is the 1,3-diradical singlet state rather than the methylene like singlet which results on opening of the cyclopropene ring. The initially produced 1,3-diradical state may then decay to the carbene which could undergo subsequent reactions characteristic of a singlet vinylcarbene. Thus, the preference for bond b cleavage could conceivably be attributed to inductive destabilization of the initially generated vinyl radical by the attached phenyl group. In support of this explanation, Battiste and co-workers[2b] have found that tetraphenylcyclopropene rearranges to 1,2,3-triphenylindene with an activation energy 7 kcal more than that required for the racemization of optically active 1,3-diethylcyclopropene.[2i] This rather large difference clearly implies that phenyl groups affect the C–C single bond energies in cyclopropenes in a striking unprecedented manner. Alternatively, the predominant scission of bond b may stem from the occurrence of path B. According to this mechanism, π–π bridging would be expected to give the most stable diradical (**12**) and thus lead to the preferential formation of the 2-phenyl substituted 1,3-cyclopentadiene **7**. A similar explanation would also account for the regioselectivity observed for indene formation with cyclopropenes **1** and **6**.

In order to help elucidate the correct pathway, the photochemistry of cyclopropenes **4b** and **4c** was carried out in methanol. These experiments, which were designed to trap a carbene intermediate, were unsuccessful and the only products isolated were 1,3-cyclopentadienes **5b** and **5c**. Failure to trap a carbene intermediate on irradiation in methanol does not necessarily eliminate this species as a reaction intermediate. The absence of methanol insertion products may be due to the facile intramolecular cyclization path available to the butadienyl carbene. Alternatively, a carbene intermediate may not be required if the photoreaction of **4b** proceeds through path B. Further studies on the scope and mechanism of this reaction are in progress and will be reported in due course.

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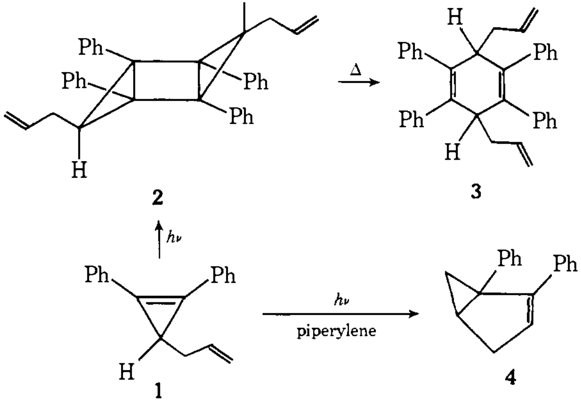
Photochemical Transformations of 3-Allyl Substituted Cyclopropenes[1]

Sir:

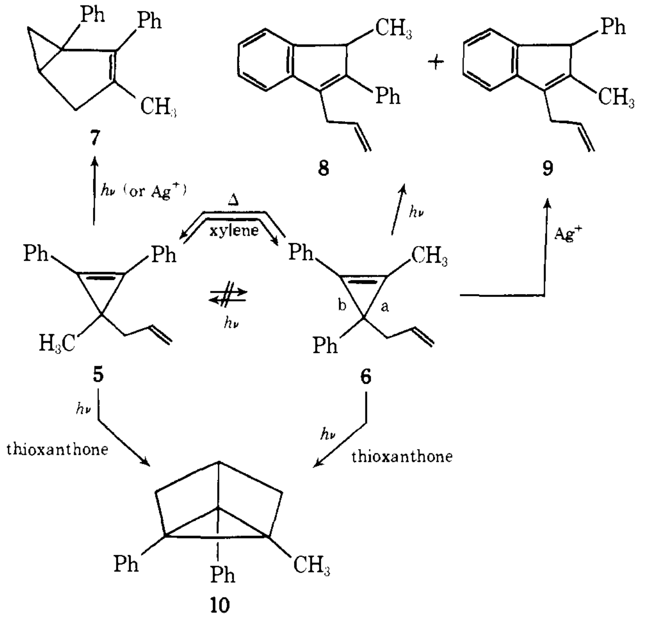
Studies of the thermal and photochemical reactions of cyclopropenes have played an important role in the development of our understanding of the mechanism by which carbon–carbon bonds may be broken and re-formed.[2] Recent calculations predict that the ring opening of cyclopropene should proceed to a diradical planar intermediate which may subsequently decay to a vinyl carbene.[3] This species can rotate back to the diradical state[2q,3] or undergo reactions characteristic of a singlet or triplet methylene. These include intramolecular hydrogen abstraction,[2m,q] insertion into a C–H bond,[2f] alkyl migration,[2f,o] and cyclization.[2c,g–i] Interestingly, none of the products reported correspond to addition of the carbene to a double bond.[4] It seemed to us that the intermediate vinyl carbene might undergo cycloaddition, provided an intramolecular trap were available. In this communication we describe the occurence of such a process and thus provide additional support for the intermediacy of a vinyl carbene in the photolysis of substituted cyclopropenes.

1,2-Diphenyl-3-allylcyclopropene[5] (**1**) was prepared in high yield by treating diphenylcyclopropenyl cation with allylmagnesium bromide according to the general procedure of Breslow and Dowd.[6] Irradiation of **1** in benzene or hexane with Pyrex filtered light[7] resulted in dimerization[8] and produced tricyclohexane **2**, mp 191–192 °C, in high yield. The assignment of structure **2** rests on its characteristic NMR, IR, and mass spectra,[5] its elemental analysis, and chemical behavior. Thus, photodimer **2** undergoes thermal rearrangement above 190 °C to an isomeric cyclohexadiene, **3**, mp 211–212 °C. Similar thermal rearrangements of related tricyclohexanes have been reported in the literature[8] and provide reasonable chemical analogy for this [2 + 2] retrogression reaction. Sensitization of **1** with benzophenone gave only **2**, in agreement



with the involvement of a triplet state in the dimerization process.[8] When the photolysis of **1** was carried out in the presence of a triplet quencher (i.e., piperylene),[9] a new product was formed (75%) whose structure is assigned as 1,2-diphenylbicyclo[3.1.0]hex-2-ene (**4**) on the basis of its straightforward spectral properties: NMR (100 MHz) τ 9.46 (t, 1 H, J = 4.0 Hz), 8.49 (ddd, 1 H, J = 9.0, 6.0 and 4.0 Hz), 8.23 (dd, 1 H, J = 9.0 and 4.0 Hz), 7.61 (dd, 1 H, J = 17.0 and 2.0 Hz), 7.21 (ddd, 1 H, J = 17.0, 6.0, and 2.0 Hz), 4.33 (broad s, 1 H) 2.70–3.0 (m, 10 H); UV (95% ethanol) λ_{max} 255 nm (ϵ 8000).

The photoreactions of the closely related methyl allyl-substituted diphenylcyclopropenes **5** and **6** were also studied in order to assess the generality of the above photocycloaddition reaction. Direct irradiation of **5** in benzene with Pyrex-filtered light afforded 1,2-diphenyl-3-methylbicyclo[3.1.0]hex-2-ene (**7**) in 65% yield as a crystalline solid, mp 44–45 °C. The NMR spectrum of **7** consists of a triplet at τ 9.24 (J = 4.0 Hz), a multiplet at 8.48, a doublet of doublets at 8.28 (J = 8.0 and 4.0 Hz), a methyl singlet at 8.20, a doublet at 7.64 (J = 17.0 Hz), a doublet of doublets 6.98 (J = 17.0 and 7.0 Hz), and a multiplet for the aromatic protons at 2.8–3.0 (10H); UV (95% ethanol) λ_{max} 256 nm (ϵ 11 000). Photolysis of cyclopropene **6** in benzene afforded a 4:1 mixture of 1-allyl-2-phenyl-3-methylindene (**8**), (80%), and 1-allyl-2-methyl-3-phenylindene (**9**) (20%). The structures of these indenes were confirmed by comparison with authentic samples prepared by treating 2-phenyl-3-methyl- and 2-methyl-3-phenylindanone with allylmagnesium bromide followed by dehydration of the resulting alcohols.[5]

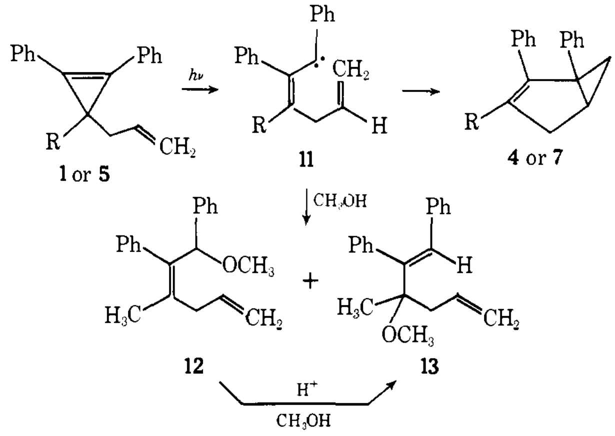


Although cyclopropenes **5** and **6** are thermally equilibrated upon heating in xylene, a control experiment showed that they were not interconverted by a Cope reaction under the photolytic conditions. Treatment of **5** with Ag$^+$ also gave bicyclohexene **7** in good yield whereas subjection of **6** to silver ion resulted in the exclusive formation of indene **9**.

Mention should be made here of the unusual effect of substituents on the photochemical ring opening of cyclopropene **6**. It is well known that phenyl substituents stabilize free radicals, and thereby lower carbon–carbon bond energies in saturated three-membered rings.[10] Were this effect to operate in the cyclopropene system, methylphenylcyclopropene **6** should undergo preferential cleavage at bond b. We note, however, that the major indene produced corresponds to cleavage of bond a. The source of this fourfold preference for bond a scission can be interpreted in one of two ways. One possibility involves inductive destabilization of the vinyl end of an initially produced diradical by the attached phenyl group. Alternatively, indene formation may proceed by a process involving π–π bridging on the excited cyclopropene with the adjacent 3-phenyl group to give a housane type diradical which then undergoes a Grob type fragmentation to produce the indene ring system. According to this mechanism, π–π bridging should result in the most stable diradical and thus ultimately lead to the preferential cleavage of bond a.[11]

The photochemical transformations encountered on direct irradiation of cyclopropenes **5** and **6** proceed through the singlet manifold since sensitization of both of these compounds with thioxanthone gave 1,2-diphenyl-6-methyltricyclo[2.2.0.0^{2,6}]hexane (**10**) as the exclusive photoproduct (NMR (270 MHz) τ 8.67 (s,3 H), 7.89 (d, 1 H, J = 8.0 Hz), 7.72 (d, 1 H, J = 8.0 Hz), 7.38 (dd, 1 H, J = 8.0 and 4.0 Hz), 7.21 (t, 1 H, J = 4.0 Hz), 7.17 (dd, 1 H, J = 8.0 and 4.0 Hz), 2.6–3.2 (m, 10 H)).[12] The formation of this tricyclic structure can be attributed to a novel intramolecular 2 + 2 cycloaddition. The implication of this observation is that there are severe steric constraints on the cyclopropene dimerization route. This is further indicated by the fact that related 1,2-diphenylcyclopropenes, where both 3-positions are substituted with groups larger than a hydrogen atom, do not dimerize.[8] As a consequence of this steric effect, the triplet states of tetrasubstituted cyclopropenes **5** and **6** prefer to undergo intramolecular [2 + 2] addition rather than bimolecular dimerization. This is in dramatic constrast to the case of trisubstituted cyclopropene **1**, where dimerization of the triplet state is the only path followed.[13]

The most reasonable explanation to account for the formation of bicyclohexenes **4** and **7** involves a sequence consisting of ring opening of the electronically excited singlet state to a vinyl carbene intermediate (**11**). Attack of the carbene carbon on the neighboring double bond generates the bicyclo[3.1.0]-hexene skeleton. Support for this postulate was obtained by carrying out the irradiation of **5** in a slightly basic methanolic solution. With this solvent system, the major products obtained are methoxy ethers **12** (60%) and **13** (40%). The identity of these compounds was established by comparison with independently synthesized samples.[14] This result is perfectly consistent with the intervention of a vinyl carbene intermediate which is trapped by methanol prior to intramolecular cycloaddition.[15] It should also be noted that bicyclohexene **7** is stable toward irradiation in methanol and that the relative quantum yields for disappearance of **5** are the same in methanol and benzene.



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(7) All of the incident light was absorbed by the diphenylcyclopropene ring in these irradiations; λ_{max} (95% ethanol) 337 and 319 nm (ϵ 21 000 and 2800).

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(9) It should be noted that the formation of **4** in the presence of piperylene has a much lower quantum yield than that for the formation of **2** in the direction irradiation of 1.

(10) (a) L. B. Rodewald and C. H. DePuy, *Tetrahedron Lett.*, 2951 (1964); (b) R. J. Crawford and T. R. Lynch, *Can. J. Chem.*, **46,** 1457 (1968).

(11) Further discussion of the regioselectivity of bond cleavage of unsymmetrical disubstituted cyclopropenes will be given in a forthcoming publication, see A. Padwa, T. Blacklock, D. Getman, and N. Hatanaka, unpublished results. Similar studies have also been carried by H. E. Zimmerman and S. M. Aasen, manuscript in press.

(12) For coupling constants in the tricyclo[2.2.0.0^{2,6}]hexane system, see C. Y. Ho and F. T. Bond, *J. Am. Chem. Soc.*, **96**, 7355 (1974).

(13) Our failure to detect reaction from the singlet state of cyclopropene **1** on direct irradiation can be reasonably attributed to a decrease in the rate of single bond cleavage relative to intersystem crossing. Introduction of an alkyl or phenyl substitutent on the 3-position of the cyclopropene will increase the rate of singlet ring opening relative to intersystem crossing. For a related substituent effect in ketone photochemistry, see P. S. Engel, M. A. Schexnayder, H. Ziffer, and J. I. Seeman, *J. Am. Chem. Soc.*, **96,** 924 (1974).

(14) Methoxy ether **13** was prepared by treating 3,4-diphenyl-3-buten-2-one with allyl magnesium bromide followed by reaction with sodium hydride and methyl iodide. Treatment of ether **12** with acidic methanol gave structure **13**,[5]

(15) An alternate mechanism involving protonation of the excited cyclopropene double bond, followed by a cyclopropyl → allyl cation rearrangement and methanol trapping has been suggested by one of the referees and cannot necessarily be eliminated at this time.

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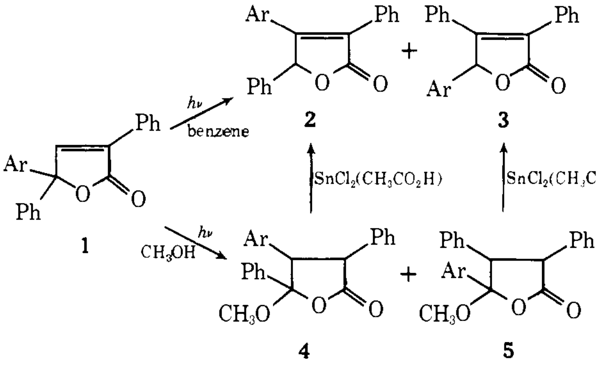
Solvent Control of Migratory Aptitudes in the Photochemical Rearrangement of 2(5*H*)-Furanones[1]

Sir:

During the course of our studies dealing with the photochemical rearrangement of 5,5-diaryl-2(5*H*)-furanones,[2] we uncovered a striking and rare[3] crossover in the competitive migratory aptitudes[4] of aryl groups which arises from a solvent alteration. We report here the results of this study which show that, in certain instances, excited-state migratory aptitudes can be controlled by stabilization of the nonmigrating aryl group.

We had previously studied the photochemical rearrangement of 5-(4′-anisyl) (**1a**) and 5-(4′-cyanophenyl)-3,5-diphenyl-2(5*H*)-furanone (**1b**) in benzene.[2] In both cases, rearrangement is a triplet derived reaction and the substituted aryl group was found to migrate in preference to the unsubstituted phenyl group. The rate constants of aryl group migration for furanones **1a–1c** were estimated from quenching studies using piperylene as a quencher. These were found to be 0.18×10^{10}, 1.3×10^{10}, and 0.9×10^{10} s^{-1} for migration of phenyl,[5] *p*-anisyl, and *p*-cyanophenyl in benzene[6,7] (Table I). Thus, *p*-An and *p*-CNPh are more reactive migrating groups than phenyl by factors of 7.2 and 5.0, respectively. Zimmerman and Levin[4,8] found that a nonmigrating *p*-CNPh group increased the rate constant for phenyl migration in 4,4-diarylcyclohexenones by a factor of 1.3. We found that, relative to phenyl migration with nonmigrating phenyl, the rate of phenyl migration is accelerated 1.4-fold by nonmigrating *p*-CNPh and decreased 2.0-fold by a nonmigrating *p*-An group when benzene is used as the solvent.



1a, Ar = p-$CH_3OC_6H_4$
1b, Ar = p-CNC_6H_4
1c, Ar = C_6H_5
1d, Ar = m-$CH_3OC_6H_4$
1e, Ar = p-$CH_3C_6H_4$

Irradiation of furanones **1a–e** in methanol gave lactones **4** and **5**. The structures of **4** and **5** were established by treatment with stannous chloride in refluxing acetic acid to give furanones **2** and **3**, respectively. Compounds **2a–e** and **3a–e** were identified by comparison with authentic samples prepared by independent syntheses.[9] Table I lists quantum yields, rate data, and migratory aptitudes for compounds **1a–c** in both benzene and methanol. Although no quantitative studies were performed on the related furanones **1d** and **1e**, product ratios were measured in benzene and methanol. Rearrangement of furanone **1d** in benzene indicated the *m*-anisyl had migrated with slight preference over phenyl (ratio **2d**/**3d** = 1.5/1). When methanol was used as the solvent, both groups had migrated with the same ease (i.e., ratio **4d**/**5d** = 0.95). With *p*-toluyl furanone **1e,** irradiation in benzene afforded lactones **2e** and **3e** (ratio 3.5/1), whereas photolysis in methanol resulted in preferential phenyl migration (ratio **4e**/**5e** = 0.81).

The striking feature of these rearrangements is that a substantial crossover in migratory aptitude occurs upon changing the solvent from benzene to methanol. The reversal of the migratory aptitude of *p*-anisyl vs. phenyl when the reaction of **1a** is carried out in methanol is of special interest. The quantum yield for the reaction of **1a** in methanol is much lower than for the reaction in benzene. The triplet sensitized reaction in methanol, however, is quite efficient (Φ = 0.40). The product distribution for the sensitized reaction was found to be virtually identical with that for the direct irradiation. These results indicate either that the product distribution for rearrangement in the singlet manifold is identical with that for the triplet, or, more plausibly, that rearrangement occurs only in the triplet manifold. Assuming the latter, the efficiency of intersystem