

Figure 9. Plots of τ_A^{-1} as a function of $[H_2SO_4]$ for (a) the βRN^+H_3 -crown complex and (b) the αRN^+H_3 -crown complex.

at 300 K. The k_q' value in the α isomer is about 10 times greater than that for the β isomer, indicating that the intramolecular CT character in $(\alpha RNH_2-crown)^*$ is superior to that in $(\beta RNH_2-crown)^*$. These results for k_q' are consistent with those in free naphthylammonium ions.¹² The k_q' values at various temperature are also listed in Table V. It should be noted that proton-induced quenching k_q' occurs via electrophilic protonation at one of the carbon atoms of the aromatic ring.¹⁷ For 1-methoxynaphthalene (a model compound for k_q' experiments), it is known that protons mainly attack the 5 position of the naphthalene ring.¹⁷ The 5 position of the $(\alpha RNH_2-crown)^*$ complex is situated in the opposite site of 18-crown-6 of the complex, and protons can, therefore, attack the electronegative 5 position of the naphthalene ring of $(\alpha RNH_2-crown)^*$, whereas the amino group is effectively protected by the naphthyl group and 18-crown-6. A considerable steric effect on the protonation process is observed¹⁷ since protons behave as hydronium ions in the presence of water.⁴⁰ Recently,

(40) Protons exist in water as hydronium ions. However, protonation proceeds via proton transfer involving only the movement of a nucleus as has been stated by Bell: Bell, R. P. "The Proton in Chemistry"; Chapman and Hall: London, 1973.

it has been reported that protons produced by deprotonation in the excited state are trapped in water clusters.⁴¹ The protons trapped by several water molecules seem to be unexpectedly bulky, and they are subject to the steric effect on protonation to the substrate. The proton-transfer reaction of $(RN^+H_3-crown)^*$ is a one-way process since the rate for the back protonation is negligibly small compared to the other processes. Thus, it can be said that there is no prototropic equilibrium in the excited state of the $RN^+H_3-crown$ complex because of no reversible reaction k_2 .

Summary

(1) Complex formation of naphthylammonium ions with 18-crown-6 decreases markedly the proton dissociation rate k_1 in the excited singlet state, resulting in an increase of its lifetime.

(2) It is found that the excited naphthylamine-18-crown-6 complex $(RNH_2-crown)^*$ is produced by deprotonation of $(RN^+H_3-crown)^*$.

(3) The excited-state proton-transfer reaction of $(RN^+H_3-crown)^*$ is a one-way process, since the back protonation rate is negligibly small compared with those of the other decay processes. There is a large steric effect on protonation of the amino group of the excited neutral complex. Thus, there is no excited-state prototropic equilibrium in the $RN^+H_3-crown$ complexes.

(4) The excited-state proton-transfer reactions of the $RN^+H_3-crown$ complexes can be expressed as the reaction scheme containing proton-induced quenching k_q' .

(5) The association constants K_g in the ground state of the $RN^+H_3-crown$ complexes can be easily determined by means of the fluorescence titration method. There is a steric effect of the aromatic ring on K_g ; the K_g value for the $\beta RN^+H_3-crown$ complex is greater than that for the $\alpha RN^+H_3-crown$ complex.

(6) The Corey-Pauling-Koltun molecular model proposed by Izatt et al.² is strongly supported by the present work. The CPK molecular models were discussed using the K_g values and excited-state kinetic parameters.

Registry No. a, 84693-59-4; b, 84693-61-8.

(41) Huppert, D.; Kolodney, E.; Gutman, M.; Nachliel, E. *J. Am. Chem. Soc.* 1982, 104, 6946.

Cumulene Photochemistry: Photorearrangements of Tetraphenyl and Triphenyl C_3 Isomers

Michael W. Klett and Richard P. Johnson*

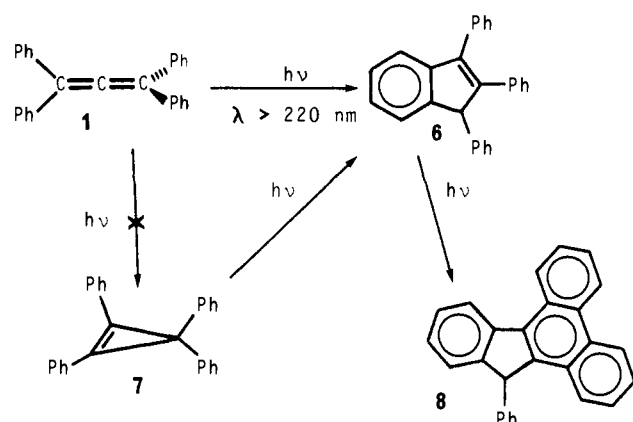
Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50011.
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Abstract: Photoreactions in aprotic solvents of tetraphenylallene (**1**), triphenylallene (**2**), 1,3,3- and 1,2,3-triphenylcyclopropenes, and related isomeric indenenes are described. Irradiation of tetraphenylallene (**1**) slowly yields 1,2,3-triphenylindene (**6**) as a primary product. Irradiation of triphenylallene (**2**) yields 1,3,3-triphenylcyclopropene (**10**; $\Phi = 0.004$), 1,3-diphenylindene (**9**; $\Phi = 0.019$), and 1,3,3-triphenylpropyne (**11**; $\Phi = 0.002$). A significant deuterium kinetic isotope effect is observed for these reactions. The common, but not exclusive, intermediacy of vinylcarbenes in cyclopropene and linear allene photochemistry is strongly indicated by product studies and independent generation experiments. Allenes are shown to be minor products of vinylcarbenes generated from photolysis of tosylhydrazone sodium salts and from cyclopropene photolysis. Ab initio configuration interaction calculations along pathways connecting allene with propyne and cyclopropene are described. In-plane hydrogen migration in singlet excited allene can lead to several excited-state minima. Internal conversion can result in the formation of vinylcarbenes, cyclopropene, or propyne, depending on the geometry at which this occurs.

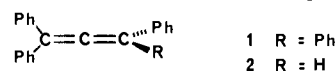
Despite prolonged interest in photoreactions of cyclopropenes,^{1,2} and numerous ethylene and 1,3-butadiene³ derivatives, allenenes

(1,2-propadienes) have received surprisingly little attention.⁴⁻⁶ Our interest in allene photochemistry was stimulated by the

Scheme I. Tetraphenylallene Photochemistry



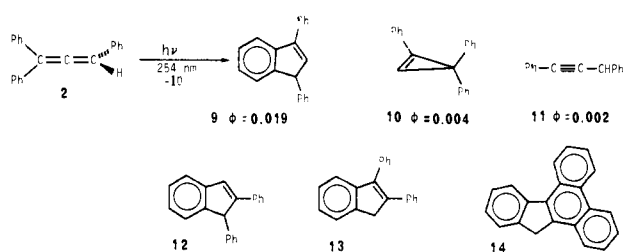
possibility of "sudden polarization"⁷ in planar allene excited states.⁸ During the past several years, we have explored a variety of experimental and theoretical aspects of the photoreactions of allenes.⁸⁻¹¹ Phenylallenes are among the oldest known and most widely studied of allenes; these seemed ideal candidates for exploratory photochemical studies. We report here the results of exploratory and mechanistic photochemical studies on tetraphenylallene (**1**) and triphenylallene (**2**) in aprotic solvents, and their interrelationship with reactions of vinylcarbenes, phenylcyclopropenes, and phenylindenes.¹⁰ Recent parallel studies on



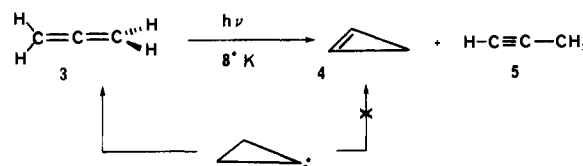
similar compounds are due to Steinmetz and co-workers.¹² One pertinent observation is that augmentation of the allenic chromophore by phenyl does not substantially alter its observed singlet photorearrangements.

Chapman was the first to report that irradiation of matrix-isolated allene at 8 K yielded cyclopropene and propyne.¹³ Although cyclopropylidene seems a reasonable intermediate in transformations to **4**, its photogeneration at 77 K afforded only allene.¹³ Recent ab initio studies show the barrier to 1,2-hydrogen shift in cyclopropylidene to be larger than that for the opening

Scheme II. Photoreactions of Triphenylallene



to allene.¹⁴ Irradiation of matrix-generated vinylcarbene was reported to yield **3-5**.¹³



Subsequent experiments have shown the allene \rightarrow cyclopropene + propyne photochemical conversions to be quite general reactions for both cyclic and acyclic allenes.^{6,9,10,12}

Exploratory Tetraphenylallene Photochemistry. Our studies began with tetraphenylallene (**1**). Direct irradiation of dilute cyclohexane solutions of **1**¹⁵ very slowly yielded 1,2,3-triphenylindene (**6**) and its known phenanthrene photoproduct **8**¹⁶ (Scheme I), along with several very minor unidentified products. Secondary **6** \rightarrow **8** conversion was substantially more rapid than primary reaction of **1**, and, even at <5% conversion, only small amounts of **6** were observable. Its intermediacy was verified by HPLC and 300-MHz ¹H NMR analyses at very low conversions. One very minor photoproduct in these reactions displayed an HPLC retention time (μ -Porasil) identical with both 1,1,3-triphenylindene (**6a**) and tetraphenylcyclopropene (**7**), known photochemical precursors to **6** and **8**.¹⁶ However, analysis by reverse-phase HPLC (*C*₁₈- μ -Porasil/CH₃OH-H₂O eluant) eliminated this possibility; preparative isolation showed this minor component to be a phenanthrene derivative (¹H NMR and UV), but a definitive structure could not be assigned. Thus, cyclopropene **7** does not appear to play a significant role as an intermediate between **1** and **6**. The quantum yield for the singlet reaction of **1** was not measured but is estimated to be <10⁻³, based upon comparison to **2**.

Triplet-sensitized irradiation of **1** with xanthone in benzene ($\lambda > 330 \text{ nm}$) led to nearly quantitative recovery of **1** and sensitizer. The triplet energy of **1** has been previously estimated from energy-transfer experiments by Ullman¹⁷ to be <57.4 kcal/mol; thus we conclude that energy transfer from xanthone (*E*_T = 74.2 kcal/mol) should be efficient, and triplets of **1** are simply unreactive.

Dilute solutions of allene **1** showed no detectable fluorescence emission at ambient temperature.

Exploratory Triphenylallene Photochemistry. With these results in hand, the photoreactions of triphenylallene (**2**) were explored. In this case, both hydrogen and phenyl migration are possible. Triphenylallene (**2**) was prepared by base treatment of triphenylpropyne¹⁸ and was rigorously purified. Initial direct irradiations at ambient temperature led to very complex mixtures which contained **9-14** (Scheme II) and several dimers.¹⁹ These compounds could be detected by HPLC and by 300-MHz ¹H NMR; all were isolated by chromatography of photoproduct

(1) Reviews: (a) Padwa, A. *Org. Photochem.* **1979**, *4*, 261. (b) Padwa, A. *Acc. Chem. Res.* **1979**, *12*, 310.

(2) Recent references: (a) Zimmerman, H. E.; Fleming, S. A. *J. Am. Chem. Soc.* **1983**, *105*, 622. (b) Zimmerman, H. E.; Bunce, R. A. *J. Org. Chem.* **1982**, *47*, 3377. (c) Zimmerman, H. E.; Kreil, D. J. *Ibid.* **1982**, *47*, 2060.

(3) Recent reviews: (a) Kropp, P. J. *Org. Photochem.* **1979**, *4*, 1. (b) Saltiel, J.; Charlton, J. L. "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; 1980; Wiley: New York, Vol. 3, pp 25-89. (c) See, for example: Kropp, P. J.; Tise, F. P. *J. Am. Chem. Soc.* **1981**, *103*, 7293.

(4) Brief review: Huntsman, W. D. In "The Chemistry of Ketenes, Allenes and Related Compounds"; Patai, S., Ed.; Wiley: New York, 1980; Part 2, pp 650-657.

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(b) Stierman, T. J.; Johnson, R. P. *J. Am. Chem. Soc.*, following paper in this issue. (c) Price, J. D.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 2187.

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(11) Klett, M. W.; Johnson, R. P. *Tetrahedron Lett.* **1983**, *24*, 1107.

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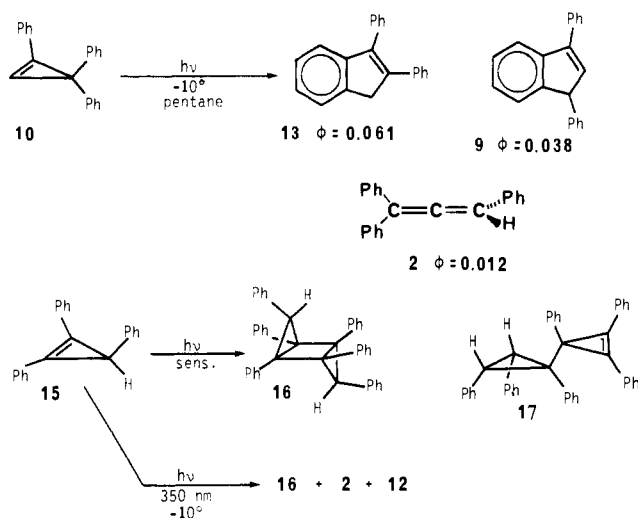
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(19) Triphenylallene undergoes relatively facile thermal dimerization: Capdevielle, P.; Rigaudy, J. *Tetrahedron* **1979**, *35*, 2093.

Scheme III. Triphenylcyclopropene Photochemistry



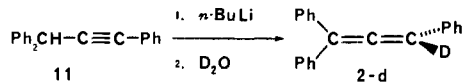
mixtures in sufficient purity for unambiguous identification by comparison to authentic samples. Cyclopropene **10** was prepared via a vinylcarbene precursor (vide infra). At high conversion (>50%), substantial secondary reaction had occurred, and the major isolated product was phenanthrene **14**, one of the ultimate photochemical "sinks" among triphenyl C_3 isomers.^{16b,20}

Low conversion runs (<5%) were conducted with 254-nm irradiation on dilute (10^{-3} M) solutions, maintained at -10°C . Analysis (HPLC, NMR) at varying conversions showed isomers **9–11** to be primary photoproducts, with **12–14** resulting from secondary reactions. Quantum yields for primary products were measured on an optical bench,²¹ with potassium ferrioxalate actinometry²² and product analysis by HPLC; results are summarized in Scheme II.

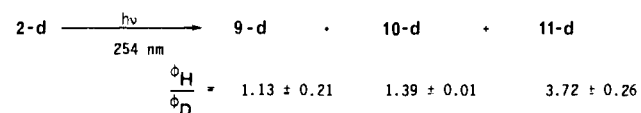
As with **1**, triplet sensitization of **2** (xanthone, benzene, $\lambda > 330$ nm) proved ineffective; sensitizer and allene were recovered.

Triphenylallene also proved nonfluorescent at ambient temperature.

Deuterium Kinetic Isotope Effects. Results for triphenylallene (**2**) suggested that hydrogen migration was a dominant reaction mode. To probe further the mechanism of these photoisomerizations, the effect of deuterium substitution was examined. 3-Deuteriotriphenylallene (**2-d**) was prepared from triphenylpropyne by treatment with *n*-BuLi/THF and subsequent quenching with D_2O .²³ Samples of **2** and **2-d** of identical con-

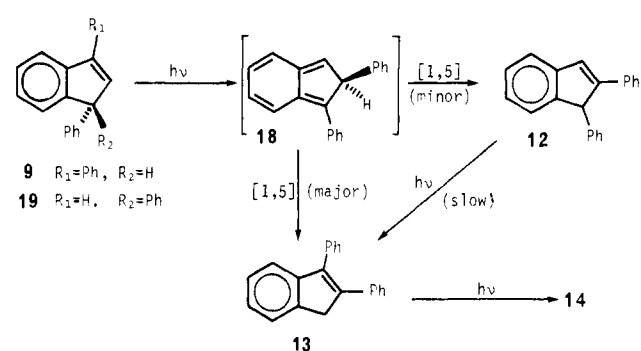


centration were then simultaneously irradiated at 254 nm to low conversion (1–2 min) in a merry-go-round apparatus with product analysis by HPLC, relative to an internal standard. Resultant values for Φ_H/Φ_D and the observed standard deviations are summarized below. The value measured for **9-d** is subject to the greatest experimental error due to rapid secondary conversion to **13**.^{16,20} The location of deuterium in products was determined



by ^1H and ^2H NMR to be on the vinyl position in **9-d** and **10-d** and the propargylic position in **11-d**.

Scheme IV. Diphenylindene Photoreactions

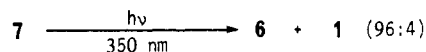


Cyclopropene Photochemistry. Direct irradiation of cyclopropene **10** yielded as primary photoproducts the expected indenes **9** and **13** (Scheme III), in addition to one unexpected product, allene **2**. These were identified by careful analysis of product mixtures and by isolation. Quantum yields again were measured in low-conversion runs; substantial secondary reactions occurred above 20–30% conversion.

Formation of allenes generally has not been reported in cyclopropene photochemistry.^{1,2} To establish the generality of this reaction, the photochemical behavior of several related phenylcyclopropenes was investigated or reinvestigated with careful analysis for allene photoproducts.

Photoreactions of 1,2,3-triphenylcyclopropene have been reported by several groups. DeBoer and Breslow initially reported "no reactions of quantum yield greater than 10^{-2} " on direct irradiation, but facile-sensitized reaction reportedly occurred to afford dimers **16** and **17**.²⁴ Subsequently, Dürr reported 1,2-diphenylindene (**12**), dimer **16**, and a different [2 + 2] dimer²⁵ but no **17**, a result which was later challenged by DeBoer.²⁶ Because we expected allene **2** as a photoproduct of **15**, we reexamined this. Direct irradiation of cold (-10°C) dilute pentane solutions at 350 nm (to eliminate secondary reaction) yielded a mixture of dimer **16**, triphenylallene, and 1,2-diphenylindene in a 18:1:6 ratio (NMR analysis). The **12:2** ratio proved invariant to conversion up to 83%. Dimer **17** could not be detected in the mixture. Thus, allene and indene are indeed formed, albeit inefficiently.

In like manner, irradiation of tetraphenylcyclopropene, previously reported¹⁶ to give only indene **6**, was found by careful analysis to yield 4% tetraphenylallene. This presumably involves ring opening to the vinylcarbene and subsequent phenyl migration.



We conclude that the cyclopropene \rightarrow allene photoreaction is quite general as a minor pathway in cyclopropene photochemistry. Additional recent examples are due to Zimmerman and Kreil^{2c} and to our recent study of bicyclo[6.1.0]non-1(9)-ene.⁹ This strained bicyclic cyclopropene yields 22% 1,2-cyclononadiene.

Diphenylindene Photoreactions. Because of the abundant secondary processes observed in experiments with **2** and **10**, we sought to securely characterize the photochemistry of the isomeric diphenylindenes. Direct irradiation of pure 1,3-diphenylindene (**9**) led smoothly (Scheme IV) to isomers **12** ($\Phi = 0.011$) and **13** ($\Phi = 0.032$).²⁷ McCullough has reported²⁸ an identical product mixture from irradiation of isomer **19**, which argues for the common intermediacy of isoindene **18**. The photoconversion of **13** to phenanthrene **14** was originally reported by Padwa.²⁰

Irradiation of **12** slowly yielded **13** and **14** and a mixture of [2 + 2] dimers of **12**. Our experiments do not allow us to dis-

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(25) Dürr, H. *Liebigs Ann. Chem.* **1969**, *723*, 102.

(26) DeBoer, C. D.; Wadsworth, D. H.; Perkins, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 861.

(27) In a previous study on indene **9**, Padwa reported²⁰ only isomer **13**.

(28) Manning, C.; McClory, M. R.; McCullough, J. J. *J. Org. Chem.* **1981**, *46*, 919 and references therein.

Scheme V. Potential Vinylcarbene Intermediates

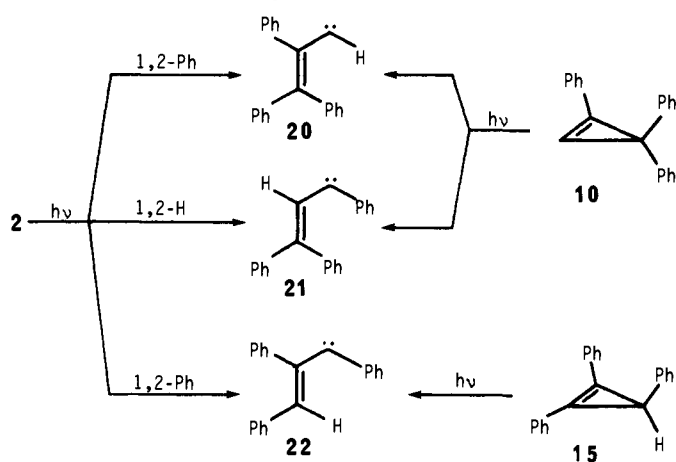


Table I. Hydrocarbon Products from Tosylhydrazones

vinyl-carbene	hydrocarbon prod (rel %) ^a						
	2	10	9	12	13	15	11
20	1.2	97.6			1.2		0
21	1.1	31.3	67.6				0
22	0.2			0.2		99.6	0

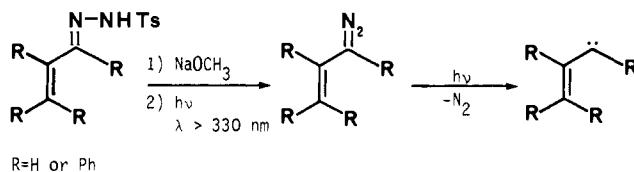
^aPyrazole products also are formed in some cases. See Experimental Section.

tinguish simple 1,2-hydrogen migration (to **18**) from the skeletal transformations which have been observed in alkylindenes by Morrison and co-workers.²⁹

The photochemistry of triphenylpropyne (**13**) was briefly explored. Major photoproducts were dimeric; no evidence for formation of isomers was observed. Similar behavior has been reported for phenylacetylenes.³⁰

Independent Triphenyl C₃ Vinylcarbene Generation. Experimental results for **2**, **10**, and **15** all suggested the common intermediacy of isomeric triphenylvinylcarbenes. Thus, triphenylallene (**2**) could, in principle, undergo 1,2-phenyl or 1,2-hydrogen migrations to yield vinylmethylenes **20–22** (Scheme V). Phenyl migration is well established in a variety of photoreactions,³¹ while 1,2-hydrogen migration in alkenes to give carbenes has ample precedent in simple alkene singlet photochemistry.^{3a,c} Cyclopropenes are well-known^{1,6} to undergo thermal and photochemical ring opening to vinylcarbenes; possibilities in the present context are shown in Scheme V.

Isolation of 1,3-diphenylindene (**9**) as a major photoproduct of **2** implied hydrogen migration to vinylcarbene **21**. However, a previous study on this vinylcarbene did not report cyclopropene **10** as a product.^{32a} Because the cyclopropene is a major photoproduct of **2**, competitive phenyl migration to vinylcarbene **20** seemed a potential source of **10**. To resolve this question, independent generation of vinylcarbenes **20–22** was carried out through photolysis of tosylhydrazone sodium salts in tetrahydrofuran. A transient pink coloration invariably appeared due to the diazo intermediate.^{32b} These reactions are presumed to yield the vinylcarbene singlet state, whereas vinylcarbenes probably are ground-state triplets. Irradiations were carried out with a uranium glass filter ($\lambda > 330$ nm), which precludes secondary hydrocarbon photoreactions. Yields of isolated hydrocarbon products are shown in Table I. Preparations of tosylhydrazones and their precursors



are detailed in the Experimental Section.

In surveying these results and their present significance, we note first that cyclopropene **10** is formed in exceptional efficiency (78% isolated yield) from carbene **20**, thus providing the first synthesis of this compound. Second, cyclopropene **10** and indene **9** are the major products of vinylcarbene **21**, which is consistent with its potential intermediacy in triphenylallene photoreactions. Cyclopropene **10** is quite photolabile, and we speculate that it was destroyed under the reaction conditions (Pyrex filter) employed in an earlier study.^{32a}

In both triphenylallene photolysis and in generation of vinylcarbene **21**, indene **9** is the predominant product, although indene/cyclopropene ratios (**9**:**10**) differ: 4.8:1 from irradiation of **2** and 2.2:1 from **21**. In view of the very different reaction conditions and modes of generation, we do not ascribe much significance to this difference.

Two final noteworthy points are the absence of triphenylpropyne (**11**) in these mixtures and the invariable isolation of a small yield of triphenylallene. Although the high-temperature interconversion of allene, propyne and cyclopropene is well established, and presumably involves vinylcarbenes,^{6,14} it seems generally believed that at lower temperatures, vinylcarbenes do not yield allenes.³³ The present experiments provide three examples of vinylcarbene to allene conversions, two through 1,2-phenyl shifts and one through hydrogen shift. The observation of similar results upon photolysis of cyclopropenes **3** and **8** provides argument that this is not an artifact of the mode of vinylcarbene generation. Indeed, it has been our observation that every cyclic⁹ or acyclic¹⁰ vinylcarbene which we have generated yields small amounts of allene, and we regard this as a general—if often kinetically uncompetitive—reaction. Thus, the generality of the cyclopropene \rightarrow allene photoconversion is most simply viewed as characteristic chemistry of the intermediate vinylcarbene.¹⁴

Reaction Mechanisms: Allene Photoreactions. The congruence of product identities, especially indenenes, from photolysis of triphenylallene, 1,3,3-triphenylcyclopropene, and appropriate tosylhydrazone sodium salts strongly implicates the common intermediacy of vinylcarbenes. An important exception is triphenylpropyne formation, which is uniquely observed for allene photoreactions. Cyclopropene and indene formation require a single hydrogen migration step, while propyne formation probably involves two separate steps. This is consistent with the observed kinetic isotope effects; i.e., k_H/k_D (propyne) $>$ k_H/k_D (cyclopropene) \approx k_H/k_D (indene).

Scheme VI shows a framework for our analysis of C₃H₄ reaction mechanisms. Central to this is bisected vinyl biradical **25**; this is related along C₂ reaction coordinates to allene and propyne through in-plane 1,2-H migrations, to cyclopropene through in-plane closure, and to vinylcarbenes through simple π -bond rotation. This geometry seems the most likely precursor to alkyne. Ab initio calculations (vide infra) support this possibility.

One alternative hydrogen migration mechanism bears brief consideration; this is outlined in Scheme VII for **2-d**. Excited state π -bond twisting in S₁ may afford a "suddenly polarized" species **26**,⁸ which could close to singlet cyclopropylidene **27** or carbene **28**. In contrast to several previous studies, our calculations show a singlet ground state for cyclopropylidene.^{9b} 1,2-Deuterium shift in **27** or sequential 1,2-D and 1,2-H shifts in **28** would give the observed products. Perhaps the most cogent argument against this mechanism is that 1,2-D shift in singlet cyclopropylidene **27** would be expected to be uncompetitive with ring opening to **2-d**.¹⁴

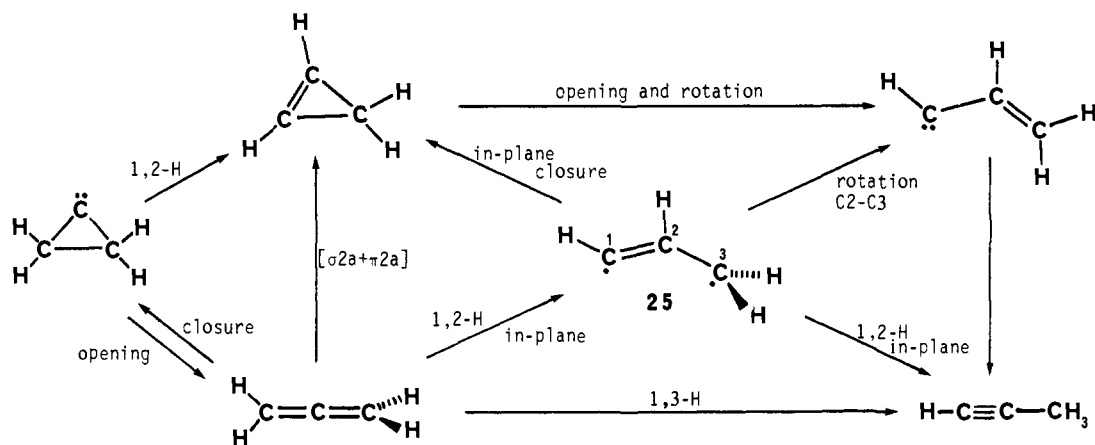
(33) For example, one early review states: "The conversion of a vinylcarbene into an allene has never been observed..." Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971; p 329.

(29) Morrison, H.; Giacherio, D.; Palensky, F. J. *J. Org. Chem.* **1982**, *47*, 1051.

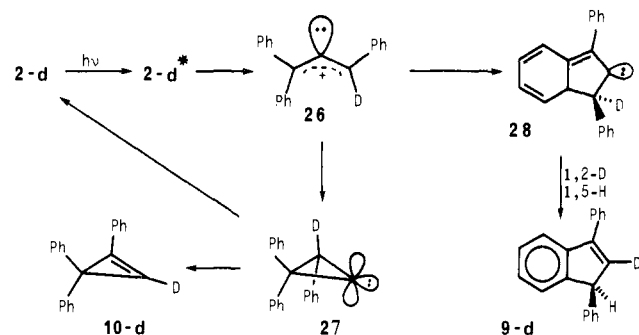
(30) Ota, K.; Murofushi, K.; Hoshi, T.; Inoue, H. *Tetrahedron Lett.* **1974**, 1431. Bryce-Smith, D.; Lodge, J. E. *J. Chem. Soc.* **1963**, 695. Bachi, G.; Perry, C. W.; Robb, E. W. *J. Org. Chem.* **1962**, *27*, 4106.

(31) See for example: (a) Zimmerman, H. E. *Tetrahedron* **1974**, *30*, 1617. Or ref 16a or 28. A di- π -methane rearrangement often is involved: (b) Zimmerman, H. E. "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, Essay 16, p 131.

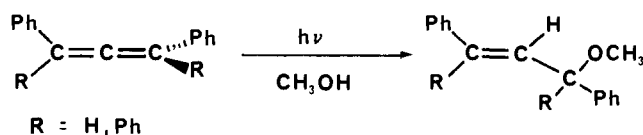
(32) (a) Dürr, H. *Chem. Ber.* **1970**, *103*, 369. (b) Nickon, A.; St. John Zurer, P. *J. Org. Chem.* **1981**, *46*, 4685.

Scheme VI. Potential Interconversions of C_3H_4 Intermediates

Scheme VII. Potential Reaction Mechanisms

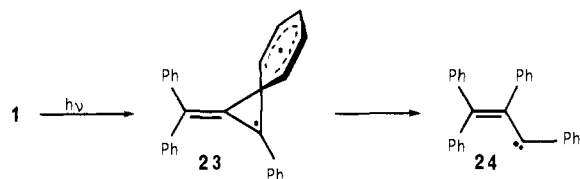


In addition, the similar small isotope effects observed for cyclopropene and indene formation argue for a common preceding step, as would occur in Scheme VI. In protic solvents (e.g., CH_3OH), efficient solvent addition occurs for **1** and **2**, while rearrangements are kinetically uncompetitive.¹¹ We have suggested that solvent addition occurs through protonation of a transient species such as **26**.^{8,11}



Hydrogen migration in phenylallenes occurs more efficiently than phenyl migration, a conclusion supported by the low reactivity of **1**, relative to **2**, and observation of exclusive hydrogen migration in **2**, within limits of detection. This is perhaps surprising, given the number of well-known photochemical phenyl migrations.³¹

A straightforward phenyl migration mechanism is shown below. Bridging and subsequent rotation about the bridged π bond would yield biradical **23**, which could open to planar vinylcarbene **24**.



We have been unsuccessful in attempts to prepare suitable precursors to independently generate **24**; thus its behavior could not be independently verified.

Inefficient reaction of **1** probably reflects both inefficient bridging and rapid competitive radiationless decay through π -bond rotation. Allenes are excellent "free-rotors",³⁴ as demonstrated

(34) Zimmerman, H. E.; Kamm, K. S.; Werthemann, D. P. *J. Am. Chem. Soc.* **1975**, *97*, 3718.

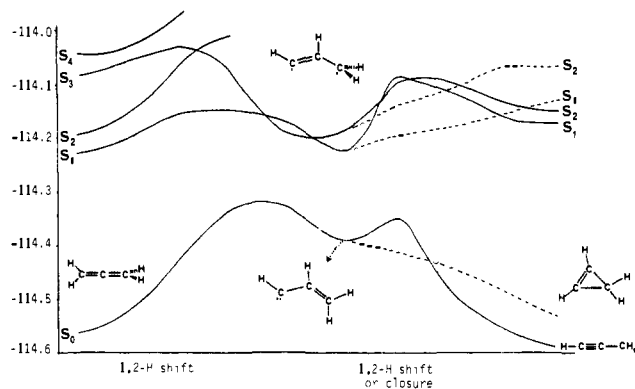


Figure 1. STO-3G CI potential surfaces.

by their lack of fluorescence and the observation of facile photoracemization with optically active allenenes.^{8,9b}

Theoretical Studies: C_s Potential Surfaces. Calculation of ground- and excited-state potential surfaces often provides substantial mechanistic insight. However, even for C_3H_4 , characterization of multidimensional surfaces is a formidable task, and we consider here only those C_s pathways outlined in Scheme VI. In recent studies, Yoshimine has mapped much of the ground-state surface.^{14a}

Minimal basis set (STO-3G) configuration interaction (CI) calculations were performed along C_s reaction coordinates connecting allene with propyne and cyclopropene. Experimental geometries were used for allene, cyclopropene, and propyne. Geometries at intermediate points were extrapolated or partially optimized at the CI level. The CI space (946 configurations) was generated from all single and double excitations from the six highest occupied MO's (closed-shell reference configuration) to the lowest seven virtuals.^{35a} Results of calculations are shown in Figure 1. Solid lines correlate states between allene, vinyl biradical **25** (Scheme VI), and propyne. Dashed lines correlate the vinyl biradical with cyclopropene. As a caveat, we note that these calculations are expected to be qualitatively useful in correlating valence states but should significantly overestimate barrier heights and excitation energies. Comparable level calculations have proved useful in understanding other aspects of C_3H_4 photochemistry.³⁶

Allene S_1 and S_2 valence states arise from in-phase and out-of-phase combination of out-of-plane excitations; i.e., $[\pi_x \rightarrow \pi_y^* \pm \pi_y \rightarrow \pi_x^*]$.⁸ Along a C_s reaction coordinate, these correlate with states of $^1A''$ symmetry, which are due to $\sigma \rightarrow \pi^*$ or $\pi \rightarrow$

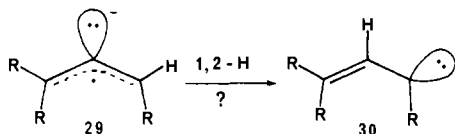
(35) (a) The program GAMESS was used for these calculations: Dupuis, M.; Spangler, D.; Wendoloski, J. J. NRCC Software Catalog 1, Program No. QG01 (GAMESS), Lawrence Berkeley Laboratory, University of California, Berkeley, CA, 1980. (b) Here, σ and π refer to local symmetry; i.e., σ is in the plane of hydrogen migration and π is out of plane.

(36) Sevin, A.; Arnaud-Danon, A. *J. Org. Chem.* **1981**, *46*, 2346.

σ^* excitations.^{35b} Thus, S_1 of allene formally correlates directly with the lowest $\sigma \rightarrow \pi^*$ state of cyclopropene. By contrast, S_3 and S_4 (neglecting Rydberg states) are due to in-plane excitations; i.e., $[\pi_x \rightarrow \pi_x^* \pm \pi_y \rightarrow \pi_y^*]$ and thus correlate with $^1A'$ states which are $\sigma \rightarrow \sigma^*$ or $\pi \rightarrow \pi^*$. Both A' and A'' states have minima along the C_s coordinate. Inspection of MO's shows orbital crossings for each hydrogen migration step.

In-plane hydrogen migration leads over a small barrier—undoubtedly exaggerated by our calculations—to either of two excited minima. The first of these corresponds to the expected pericyclic minimum for concerted $[\sigma 2a + \pi 2a]$ formation of cyclopropene. Internal conversion at this geometry might lead to cyclopropene or, through π -bond rotation, to intermediate vinylcarbene. Molecular constraints, such as exist in a cyclic allene, might prevent rotation, and yield cyclopropene directly, in an effectively concerted reaction. We have not explored out-of-plane hydrogen migration paths and thus cannot rule these out. However, the in-plane path provides the most straightforward route to cyclopropene and propyne.

The second minimum seems more closely poised above the ground transition state to propyne, and the second hydrogen migration may occur on a ground-state surface, over a small barrier or during the crossing back to ground state. At this point on the ground-state surface, hydrogen shift and π -bond rotation to vinylcarbene are competitive. The precise molecular dynamics will be highly structure-dependent, and Figure 1 is, at best, a crude model for reaction of phenylallene **2**. High-temperature ($>200^\circ\text{C}$) interconversion of allene and propyne is well documented.⁶ Deuterium labeling and kinetic studies have provided argument for the intermediacy of cyclopropene.³⁷ The major process competing with hydrogen migration in **2** will be simple π -bond rotation in vertically excited allene. Low efficiencies for reaction of **1** and **2** and lack of observable fluorescence argue that these molecules are efficient free rotors.³⁴ Such π -bond rotation leads to strongly polarized species,⁸ which may be trapped in polar solvents.¹¹ It is conceivable that in-plane hydrogen migration (**29** \rightarrow **30**) might offer a path to vinylcarbene. This would be ex-



thermic by >20 kcal/mol^{14,8} but seems a rather unusual mechanism. Some support is found in ab initio calculations by Evleth and Sevin, which show that in-plane 1,2-hydrogen migration in twisted (C_s) ethylene can lead to ethylidene, through an adiabatic process.³⁸ However, since **29** is already an excited surface minimum, it seems unlikely that this hydrogen shift could compete with internal conversion to the ground state.⁸

Steinmetz has suggested an excited singlet ($^1A''$) vinylcarbene, potentially in a specific syn conformation, as the precursor to alkynes.⁶ We believe this state-selective chemistry to be highly unlikely, since the low-lying singlet electronic states of the syn-anti isomers of vinylcarbene probably are quite close in energy and easily equilibrated in solution. Theoretical studies suggest that the upper vinylcarbene state ($^1A''$ in C_s symmetry) might not correspond to a discrete intermediate.^{14b}

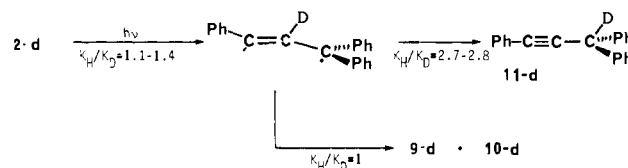
Thus, we envision two mechanistic extremes as the most likely route from vertically excited allene to products: (a) in-plane hydrogen migrations along a C_s reaction coordinate, which can readily afford both cyclopropene and propyne, or (b) hydrogen migration and rotation to discrete vinylcarbene intermediates, precursors to cyclopropene, and indene products.

Discussion

Kinetic Isotope Effects. Although the effect of deuterium on excited-state lifetimes is well-known, relatively little is known about kinetic isotope effects in photoreactions.³⁹ In the mechanism

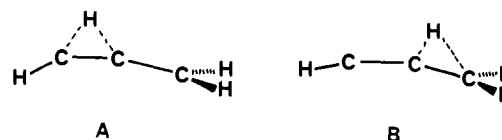
described above for **2**, we assume a common excited state 1,2-H (D) shift leading to all products, with a second H (D) shift affording propyne. Consistent with this is the observation that values for **9** and **10** (1.13 and 1.39) are similar within our estimated experimental error, while that observed for **11** is much larger (3.72). Steinmetz has observed similar values for 1,1-diphenyl-3-alkylallenes.⁴⁰ In related studies on 1,2-cyclononadiene, we have determined $k_H/k_D = 1.30 \pm 0.06$ for cyclopropene formation.^{9b}

If we assume the isotope effects for each hydrogen migration step to be approximately multiplicative, we arrive at the scheme shown below. In principle, this scheme should lead to a reverse



isotope effect in formation of **9-d** and **10-d**; however, since **11-d** is only a minor product, the magnitude is too small to be observable.

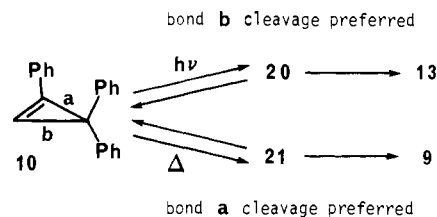
Kinetic isotope effects of the magnitude observed here normally are ascribed to strongly bent transition states, with C-H-C angles of 60 – 90° . On the basis of the classic More-O'Ferrall relationship,⁴¹ the observed k_H/k_D values are not inconsistent with the approximate geometries predicted from our ab initio calculations. The transition state for the first 1,2-H shift (A) is predicted to be symmetrical while that for propyne formation (B) is quite early and unsymmetrical, due to its greater exothermicity. Theoretical



studies by Yoshimine¹⁴ show geometry B to be a transition state on the ground-state pathway from allene to propyne. In the photoreaction, this provides an approach of ground- and excited-state surfaces, and the second hydrogen migration may occur simultaneously with internal conversion from S_1 to S_0 . Thus, the observed isotope effect probably is not due to a simple ground-state process. Although we have no evidence to support this, it seems possible that 1,2-hydrogen migration in **2** and other allenes may involve substantial tunneling.

Regioselectivity in Cyclopropene Cleavage. Phenylcyclopropenes generally exhibit opposite regioselectivity in thermal and photochemical ring opening.¹ Thus, as expected, thermolysis of cyclopropene **10** at 85 – 200°C yielded **9** and **13** in a 3:1 ratio. This implies a preference for thermal opening to vinylcarbene **21**.

Photolysis of **10** yields **9** and **13** in a ca. 1:1.8 ratio. To estimate the true regioselectivity in photochemical opening, we note that independently generated **20** (Table I) yields mostly cyclopropene **10** (**10**:**13** ratio 81:1), while **21** shows a preference for indene **9**



(**10**:**9** ratio 1:2.2). If we assume similar behavior on photolysis

(39) For example: (a) Kropp, P. J.; Fravel, H. G., Jr.; Fields, T. R. *J. Am. Chem. Soc.* **1976**, *98*, 840. (b) Paquette, L. A.; Bay, E. *J. Org. Chem.* **1982**, *47*, 4599. (c) Hemetsberger, H.; Neustern, F.-U. *Tetrahedron* **1982**, *38*, 1175. (d) Padwa, A.; Chou, C. S.; Rosenthal, R. J.; Rubin, B. *J. Am. Chem. Soc.* **1974**, *96*, 6773 and references therein.

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(41) More-O'Ferrall, R. A. *J. Chem. Soc. B* **1970**, 785.

(37) Hopf, H.; Priebe, H.; Walsh, R. *J. Am. Chem. Soc.* **1980**, *102*, 1210.

(38) Evleth, E. M.; Sevin, A. *J. Am. Chem. Soc.* **1981**, *103*, 7414.

of **10**, then a strong preference for photochemical opening to **20** is indicated.

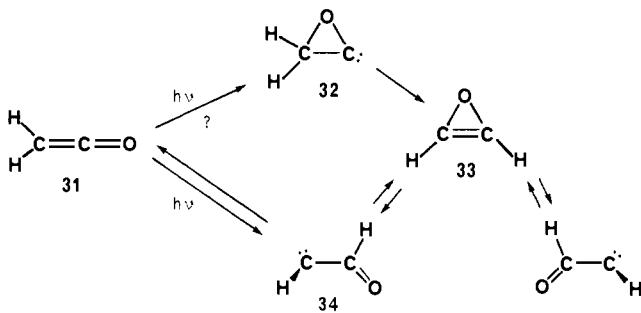
For similar compounds, both Padwa^{1a} and Zimmerman^{2b} have argued that ground-state selectivity follows the relative stabilities of incipient vinylcarbenes, while excited-state selectivity is a consequence of a closer approach of ground- and excited-state surfaces along the reaction coordinate toward the less stable carbene. An alternative possibility is that ground- and excited-state bond orders for the two cyclopropene σ bonds are reversed; we are currently exploring this through molecular orbital calculations. It is significant that the lowest singlet excited state of cyclopropene is predicted (Figure 1) to be $\sigma \rightarrow \pi^*$.³⁶

Conclusions

Singlet photorearrangement of simple alkenes to carbenes via 1,2-hydrogen or alkyl shifts is a well-known process.^{3a,c} Kropp has advocated the intermediacy of Rydberg states ($\pi \rightarrow 3s$),^{3a} although evidence for this is inconclusive. In allenes, current evidence indicates the lowest excited state to be valence ($\pi \rightarrow \pi^*$).^{8,42,43} 1,2-Shifts can lead to vinylcarbenes as discrete intermediates or along closely related pathways which lead directly to cyclopropene and propyne. Present evidence suggests that the mechanism is quite dependent upon structure. For the linear phenylallenes described here¹⁰ and those studied by Steinmetz,¹² vinylcarbenes are likely precursors to cyclopropene and indene photoproducts, whereas in 1,2-cyclononadiene, ring constraints may favor an effectively concerted process.⁹ Ab initio calculations show that hydrogen migration in S_1 of allene can lead to points on the excited-state surface which, through internal conversion or rotation, provide routes to vinylcarbenes, cyclopropene, or propyne. The exact pathway and partitioning among these various outcomes will be highly structure-dependent. Along the route to propyne, we believe the first 1,2-H shift to occur in the excited state and the second after (or perhaps during) crossing to the ground state.

Isotope effects observed here and in reactions of 1,2-cyclononadiene^{9b} have little precedent, but the immediate interpretation seems little different from that which usually is given for ground-state processes. Unfortunately, allene **2** is nonfluorescent; thus it is not possible to measure the effect of deuterium on the singlet lifetime or absolute rates for rearrangement.

In conclusion, we note that photoreactions of allene have some interesting, and perhaps surprising, parallels in those of ketene.^{44,45} In addition to the well-known photodissociation, Russell and Rowland observed carbon scrambling in irradiated ketene. This was suggested to occur as a result of closure to oxacyclopropylidene (**32**), 1,2-hydrogen shift to oxirene (**33**), and equilibration through formylmethylenes.⁴⁵ However, ab initio calculations predict⁴⁶



a large barrier for 1,2-H shift in **32**, relative to that for ring opening. To account for the observed photochemical scrambling, Radom has suggested a 1,2-H shift to formylmethylene (**34**) in

a ketene excited state.⁴⁶ This behavior is paralleled in reactions of allene.

We are continuing to explore a variety of allene photoreactions.

Experimental Section

General. ¹H NMR were measured on a Nicolet 300-MHz spectrometer, with CDCl₃ as solvent. ¹³C NMR spectra were determined on Jeolco FX-90Q or Nicolet 300-MHz spectrometers. HPLC analyses employed a Waters Assoc. unit, with detection at 254 nm. A Hewlett-Packard Model 3390A integrator was used to measure peak HPLC areas for quantum yield determinations. Fluorescence experiments were performed with a SPEX Fluorolog 2, using cyclohexane as solvent. No fluorescence was detected for **1** or **2**. Melting points are uncorrected.

Preparative photochemical experiments employed a standard immersion-well apparatus, equipped with 450-W Canrad-Hanovia lamp and sleeve filters, or a Rayonett RPR-100 reactor. For subambient temperature irradiations in the Rayonett, quartz or Pyrex vessels with external Dewar jackets were constructed. Temperature was controlled with an internal cooling coil and a Lauda RC3 refrigerated recirculating bath.

Quantum yield measurements were made on an optical bench which is similar to that described by Zimmerman and co-workers.²¹ This consists of a 200-W high-pressure Hg lamp, a Bausch & Lomb high-intensity monochromator, a beam splitter, and an integrating electronic actinometer, which is calibrated vs. potassium ferrioxalate. Monochromator entrance and exit slits were set at 3.4 and 1.9 nm, respectively, to give a band-pass of 12.4 nm.

In all photochemical experiments, spectroquality solvents were used. Argon was bubbled through solutions prior to and during irradiation.

Tetraphenylallene (1) was prepared by the method of Tadros, Salka, and Helmy: mp 166.5–167 °C [lit.¹⁵ mp 165 °C]; ¹H NMR (CDCl₃) δ 7.25–7.37 (m, 12 H), 7.38–7.44 (m, 8 H). **Tetraphenylcyclopropene (7)** was prepared by the method of Stoffer and Bohanon: mp 177–178 °C [lit.^{16b} mp 176–177 °C]; ¹H NMR (CDCl₃) δ 7.15–7.26 (m, 6 H), 7.34–7.45 (m, 10 H), 7.52 (d, 4 H, $J = 7.5$ Hz). **1,2,3-Triphenylindene (6)** was prepared by the method of Hodgkins and Hughes: mp 133–134 °C [lit.⁴⁷ mp 132–134 °C]; ¹H NMR (CDCl₃) δ 5.11 (s, 1 H), 7.04–7.19 (m, 15 H), 7.25 (d, 2 H, $J = 8.0$ Hz), 7.42 (d, 2 H, $J = 4.5$ Hz). **1,1,3-Triphenylindene (6a)** was prepared by the method of Vorander and Siebert: mp 139–140 °C [lit.⁴⁸ mp 135–136 °C]; ¹H NMR (CDCl₃) δ 6.82 (s, 1 H), 7.21–7.30 (m, 12 H), 7.39–7.57 (m, 4 H), 7.56 (d, 1 H, $J = 7.3$ Hz), 7.64 (d, 2 H, $J = 7.0$ Hz). **Phenylindeno-phenanthrene (8)** was obtained by irradiation of **6**: mp 200.5–201 °C [lit.⁴⁹ mp 213–215 °C]; ¹H NMR (CDCl₃) δ 5.40 (s, 1 H), 7.13–7.25 (m, 6 H), 7.39–7.57 (m, 3 H), 7.59 (t, 1 H, $J = 7.7$ Hz), 7.74–7.82 (m, 3 H), 8.43 (d, 1 H, $J = 7.7$ Hz), 8.73 (d, 1 H, $J = 8.5$ Hz), 8.86 (d, 1 H, $J = 7.7$ Hz), 8.96 (d, 1 H, $J = 7.8$ Hz). **Triphenylallene (2)** was prepared by the method of Jacobs, Danker, and Singer: mp 77.5–79 °C [lit.¹⁸ mp 77.5–79 °C]; ¹H NMR (CDCl₃) δ 6.70 (s, 1 H), 7.2–7.4 (m, 15 H). **1,3,3-Triphenylpropyne (11)** was prepared by the method of Wieland and Kloss: mp 79–80 °C [lit.⁵⁰ mp 79 °C]; ¹H NMR (CDCl₃) δ 5.21 (s, 1 H), 7.2–7.3 (m, 6 H), 7.4–7.5 (m, 9 H). **1,3-Diphenylindene (9)** was prepared by the method of Greibrokk: mp 84.5–85.5 °C [lit.⁵¹ mp 68–69 °C]; ¹H NMR (CDCl₃) δ 4.70 (d, 1 H, $J = 2.0$ Hz), 6.34 (d, 1 H), 7.16–7.46 (m, 11 H), 7.58 (d, 1 H, $J = 8.4$ Hz), 7.64 (d, 2 H, $J = 0.98$ Hz). **2,3-Diphenylindene (13)** was prepared by the method of McCullough: mp 108–109 °C [lit.⁵² mp 108–109 °C]; ¹H NMR (CDCl₃) δ 3.92 (s, 11 H), 7.11–7.29 (m, 8 H), 7.34–7.41 (m, 5 H), 7.21 (d, 1 H, $J = 7.0$ Hz). **1,2-Diphenylindene (12)** was prepared by the method of Pettit and Wilson: mp 177–179 °C [lit.⁵³ mp 175–177 °C]; ¹H NMR (CDCl₃) δ 4.97 (s, 1 H), 7.10–7.27 (m, 11 H), 7.36 (s, 1 H, vinyl), 7.41 (d, 1 H, $J = 2.4$ Hz), 7.50 (d, 2 H, $J = 7.4$ Hz). **1,2,3-Triphenylcyclopropene (15)** was prepared by the method of Breslow and Chang: mp 112–113 °C [lit.⁵⁴ mp 112–113 °C]; ¹H NMR (CDCl₃) δ 3.26 (s, 1 H), 7.11–7.16 (m, 1 H), 7.22–7.24 (m, 4 H), 7.33 (t, 2 H, $J = 7.2$ Hz), 7.42 (t, 4 H, $J = 7.5$ Hz), 7.68 (d, 4 H, $J = 7.5$ Hz). **Indenophenanthrene (14)** was prepared by irradiation of **13**: mp 158–159 °C [lit.²⁰ mp 158–159 °C]; ¹H NMR (CDCl₃) δ 4.29 (s, 2 H), 7.37 (t, 1 H, $J = 7.4$ Hz), 7.51 (t, 1 H, $J = 7.8$ Hz), 7.65–7.79 (m, 5 H), 8.11 (d, 1 H, $J = 2.8$ Hz), 8.13 (d, 1 H, $J = 3.3$ Hz), 8.42 (d, 1 H, $J = 7.8$ Hz), 8.74 (d, 1 H, $J = 3.3$ Hz), 8.76 (d, 1 H, $J = 3.4$ Hz), 8.84 (br d, 1 H, $J = 7.7$ Hz), 8.88 (br d, 1 H, $J = 8.0$ Hz).

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(51) Greibrokk, T. *Acta. Chem. Scand.* **1973**, *27*, 2252.

(52) McCullough, J. J. *Can. J. Chem.* **1968**, *46*, 43.

(53) Pettit, W. A.; Wilson, J. W. *J. Am. Chem. Soc.* **1977**, *99*, 6372.

(54) Breslow, R. Chang, H. W. *J. Am. Chem. Soc.* **1961**, *83*, 2374.

3-Deuteriotriphenylallene (2-d). Triphenylpropyne (1.00 g, 3.73 mmol) in dry THF was treated with *n*-butyllithium (4.42 mmol) at 0 °C. The resultant red solution was quenched with D₂O (2.0 mL). Conventional workup, silica gel chromatography, and recrystallization from pentane yielded 560 mg (56%) of pure 2-d, mp 76–78 °C. The ¹H NMR showed no vinyl resonance. HPLC showed no detectable propyne. MS, *m/e* 269.131 58 (ca. 269.131 48).

2,3,3-Triphenylpropenal (35). A slurry of 2,3,3-triphenylpropenal⁵⁵ (4.00 g, 14.0 mmol) and excess activated MnO₂ in benzene (200 mL) was stirred under nitrogen for 4 h. The mixture was filtered through Celite, and the solvent was evaporated to yield a yellow residue. Recrystallization from ethanol afforded 3.86 g (97%) of 35 as slightly yellow crystals: mp 175–177 °C [lit.⁵⁶ mp 177–178 °C]; ¹H NMR δ 6.9–7.6 (m, 15 H), 9.78 (s, 1 H).

1,2,3-Triphenylpropenone (36). 2,3-Diphenylpropenoic acid⁵⁷ (7.00 g, 31.2 mmol) was added portionwise at 0 °C to phenyllithium (64.8 mmol). After 0.5 h, conventional workup yielded a brown oil. This was taken up in ether and triturated with hexane to separate a brown tar. Upon standing, the propenone crystallized from the mother liquor: mp 99–100 °C [lit.⁵⁸ mp 100 °C].

1,3,3-Triphenylpropenone (37) was prepared by the method of Clemo, Raper, and Robson: mp 86–87 °C [lit.⁵⁹ mp 85–87 °C].

2,3,3-Triphenylpropenal Tosylhydrazone (38). Propenal 35 (5.00 g, 17.6 mmol) and *p*-toluenesulfonylhydrazide (4.47 g, 24.0 mmol) in methanol (50 mL) was treated with H₂SO₄ (3 drops) and refluxed for 20 min. The mixture was cooled in ice, and 3.80 g (80%) of 38 was collected. Recrystallization from ethanol gave white crystals: mp 141–142 °C; ¹H NMR (CDCl₃) δ 2.46 (s, 3 H), 6.81–7.62 (m, 21 H); IR (KBr) 3200, 3045, 3022, 2820, 1595, 1486, 1440, 1360, MS, 1164, 1050, 935, 885, 775, 765, and 695 cm⁻¹; MS, no M⁺, *m/e* 296.131 20 (*m*-tosyl H; ca. 296.131 35).

1,2,3-Triphenylpropenone tosylhydrazone (39) was prepared as described by Dürr: mp 169–171 °C [lit.³² mp 171–172 °C].

1,3,3-Triphenylpropenone tosylhydrazone (40) was prepared as described by Dürr: mp 172–173 °C [lit.³² mp 173–174 °C].

Direct Irradiation of Tetraphenylallene (1). Allene 1 (288 mg) in cyclohexane (180 mL) was irradiated through a Vycor filter ($\lambda > 220$ nm) for 17.5 h. The solution was concentrated in vacuo and chromatographed over silica gel (2.0 × 75 cm). Elution was with 1% ether–hexane in 50-mL fractions: 1–5, nil; 6–9, 186 mg of 1; 10–11, 37 mg of 8; mass balance 80%.

In other experiments at lower conversion and at 254 nm, reaction was followed by HPLC (μ -Porasil, hexane elution) and 300-MHz NMR. Both 8 and its precursor 6 were consistently observed. Several very minor products could not be isolated in sufficient quantity for identification. 1,1,3-Triphenylindene (6a) was shown not to be present.

Sensitized Irradiation of Tetraphenylallene (1). Allene 1 (405 mg) and xanthone (1.18 g) in benzene (150 mL) were irradiated through a uranium ($\lambda > 330$ nm) filter for 18 h. Concentration and chromatography over silica gel gave 393 mg (97%) of unreacted 1 and 1.16 g (98%) of sensitizer.

Direct Irradiation of Tetraphenylcyclopropene (7). Cyclopropene 7 (100 mg) in cyclohexane (100 mL) was irradiated with 350-nm lamps in the Rayonett apparatus. After 15 min, 6 and 1 were observed (HPLC analysis; μ -Porasil) in a ratio of 26:1. Continued irradiation yielded increasing amounts of phenanthrene 8. Concentration and repetitive preparative TLC (silica plates) yielded pure samples of 1, 6, and 8, identical with authentic material.

Direct Irradiation of Triphenylallene (2). Allene 2 (250 mg) in pentane (200 mL) at -10 °C was irradiated with 254-nm lamps for 2 h. The solution was concentrated in vacuo and chromatographed over silica gel (2 × 65 cm). Fractions were analyzed by 300-MHz NMR and HPLC, with comparison to authentic samples in all cases. Elution was with hexane in 50-mL fractions: 1–8, nil; 9–14, 122 mg of essentially pure triphenylallene (2); 15–20, 79 mg of a mixture of 2, 10, 9, 13, and 14, ratio 3.0:0.5:1.3:1.0:0.1; 21–24, 16 mg of a mixture of 10, 9, 13, and 14, ratio 0.6:1.2:1.0:0.2; 25–28, 8 mg of 11, 10, 9, and 13, ratio 1:2.6:1.4:1.0; 29–31, 5 mg of 11 and 10, ratio 1:0.4; 32–35, 5 mg of 10, 11, and 12, ratio 0.1:1.0:35; 36–40, 3 mg of 11 and 12, ratio 1:2.1; 49–61, 2 mg of pure 1,2-diphenylindene (12); mass balance 97%.

Fractions 21–28 were rechromatographed (1.2 × 80 cm). Elution with hexane in 20-mL fractions yielded the following: 1–10, nil; 11–13, 5 mg of 2; 14–18, 23 mg of overlap; 19, 2 mg of pure 1,3,3-triphenylcyclo-

propene (10); 20–22, 8 mg of overlap; 23–26, 7 mg of pure 1,3,3-triphenylpropyne (2).

In other experiments at lower conversion, reaction was followed by HPLC (μ -Porasil, hexane elution) and 300-MHz NMR. Triphenylcyclopropene (10), 1,3-diphenylindene (9), and 1,3,3-triphenylpropyne were observed to be primary, with the remaining products secondary.

Sensitized Irradiation of Triphenylallene (2). Allene 2 (442 mg) and xanthone (1.20 g) in benzene (150 mL) was cooled to 10 °C and irradiated through uranium for 24 h. Concentration at reduced pressure and chromatography yielded 450 mg (102%) of unreacted 2 and 1.18 g (97%) of recovered sensitizer.

Direct Irradiation of 1,3,3-Triphenylcyclopropene (10). Cyclopropene 10 (128 mg) in pentane (200 mL) at -10 °C was irradiated at 254 nm for 16 min. Chromatography over silica gel (2.1 × 74 cm) with hexane in 25-mL fractions yielded the following: 1–47, nil; 48–56, 5 mg of predominantly triphenylallene (2); 57–60, 6 mg of 2, 9, 13, and 14, ratio 1:2.8:1.5; 61–63, 13 mg of 9, 13, and 14, ratio 1:2.5:0.1; 64–76, 48 mg of 9, 13, 14, and 10, ratio 1:2:0.1:9; 77–102, 30 mg of pure 10; 103–112, 2 mg of pure 12; mass balance 81%.

Other experiments monitored by HPLC and 300-MHz NMR showed 2, 9, and 13 to be primary (ratio 0.38:1.0:1.6 at 4% conversion).

Direct Irradiation of 1,2,3-Triphenylcyclopropene (15). Cyclopropene 15 (152 mg) in pentane (200 mL) at -10 °C was irradiated at 350 nm for 9 h. The solvent was decanted from a white precipitate which had formed during irradiation. Chromatography over silica gel (1.8 × 45 cm) with hexane in 100-mL fractions yielded the following: 1–5, nil; 6, 5 mg of a mixture of triphenylallene (2) and 15, ratio 1:1; 7–10, 25 mg of a mixture of 2 and 15, ratio 1:16; 11–16, 27 mg of pure 1,2-diphenylindene (12); 17, 5% ether–hexane, nil; 18–21, 5% ether–hexane, 46 mg of oligomeric material, from which 4 mg of 16 was obtained by trituration with hexane. The precipitate in the reaction vessel was removed with CH₂Cl₂ to yield another 38 mg of dimer 16; mass balance 93%.

The dimer 16 was recrystallized from hexane. It melted at 214 °C and then was crystallized between 216 and 220 °C [lit.²⁴ mp 330–350 °C with phase change ~200 °C]; ¹H NMR (CDCl₃) δ 4.10 (s, 1 H), 6.7–7.1 (m, 5 H), 7.26 (s, 10 H).

Direct Irradiation of 1,3-Diphenylindene (9). Indene 9 (200 mg) in pentane (200 mL) at 0 °C was irradiated at 254 nm for 2.5 h. The solution was concentrated in vacuo and chromatographed over silica gel (1.8 × 48 cm) with hexane in 100-mL fractions: 1–5, nil; 6–10, 152 mg of 9, 13, and 14, ratio 0.16:1.0:3.6; 11, 5 mg of 13 and 14, ratio 0.15:1.0; 12–17, 29 mg of 12; mass balance 93%.

Direct Irradiation of 1,2-Diphenylindene (12). Indene 12 (100 mg) in pentane (200 mL) at 0 °C was irradiated at 254 nm for 10.5 h. The solution was concentrated in vacuo and chromatographed over silica (1.8 × 48 cm) in 100-mL fractions: 1–4, hexane, nil; 5–8, hexane, 4 mg of 14; 9–16, hexane, 47 mg of 12; 17, 5% ether–hexane, nil; 18–19; 5% ether–hexane, 34 mg of dimers; mass balance 85%.

Photolysis of 2,3,3-Triphenylpropenal Tosylhydrazone Sodium Salt. Sodium methoxide (2.30 g, 42.6 mmol) was added to 38 (4.80 g, 10.6 mmol) in dry THF (280 mL), and the solution was irradiated through a uranium filter for 3.3 h. The photolysis mixture was filtered through Celite and concentrated in vacuo. Chromatography was over silica gel (2.8 × 54 cm) in 200-mL fractions: 1–3, hexane, nil; 4–5, hexane, 703 mg of 2, 13, and 10, ratio 1:1:40; 6, hexane, 581 mg of 2, 13, and 10, ratio 1:0.5:62; 7–10, hexane, 899 mg of pure 10; 11–15, 0.5% ether–hexane, 129 mg of pure 10; 16, 0.5% ether–hexane, nil; 17–19, 0.5% ether–hexane, 131 mg of hexatriene dimers; 20–23, 1.0% ether–hexane, 105 mg of 2,3-diphenylindene; mass balance 87%.

1,3,3-Triphenylcyclopropene (10) was recrystallized from pentane: mp 88–89 °C; ¹H NMR (CDCl₃) δ 7.16–7.38 (m, 13 H), 7.51 (s, 1 H, vinyl), 7.62 (d, 2 H, *J* = 7.3 Hz); ¹³C NMR (CDCl₃) δ 146.2, 131.0, 129.5, 129.3, 128.8, 128.1, 127.7, 127.2, 125.7, 122.6, 106.5, 35.2; IR (KBr) 3120, 3080, 3055, 3020, 1758, 1595, 1488, 1442, 780, 756 and 695 cm⁻¹; UV (cyclohexane) λ_{max} 258 (ϵ 18 000); MS, *m/e* 268.124 92 (ca. 268.125 20).

Photolysis of 1,2,3-Triphenylpropenone Tosylhydrazone Sodium Salt. Sodium methoxide (1.10 g, 20.4 mmol) was added to 39 (2.20 g, 4.87 mmol) in dry THF (280 mL). The mixture was irradiated for 0.5 h, concentrated in vacuo, and filtered through silica with hexane to afford 675 mg of 2, 15, and 12, ratio 0.2:99.6:0.2, by ¹H NMR analysis. Hot ethyl acetate washing of the silica gel afforded 434 mg of 3,4,5-triphenylpyrazole;³² mass balance 102%.

Photolysis of 1,3,3-Triphenylpropenone Tosylhydrazone Sodium Salt. Sodium methoxide (1.00 g, 18.5 mmol) was added to 40 (1.95 g, 4.31 mmol) in dry THF (280 mL), and the solution was irradiated through a uranium filter for 1.5 h. The photolysis mixture was filtered through Celite and concentrated in vacuo. Chromatography was over silica gel (2.8 × 54 cm) in 100-mL fractions: 1–10, hexane, nil; 11–12, hexane, 45 mg of 2 and 9, ratio 1:10; 13–14, hexane, 169 mg of 2, 9, and 10, ratio

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1:96:3; 15-18, hexane, 298 mg of **9** and **10**, ratio 7:3; 19-24, hexane, 129 mg of **9** and **10**, ratio 4:6; 25-26, hexane, 23 mg of **9** and **10**, ratio 1:4; 27-30, 12 mg of **10**; 31-38, 1% ether-hexane, nil; 39-42, 1% ether-hexane, 210 mg of oligomeric material; 43-44, 5.0% ether-hexane, nil; 45-52, 5% ether-hexane, 17 mg of oligomeric material; 53-60, 10% ether-hexane, 45 mg of hexatriene dimers; 61-62, 10% ether-hexane, nil; 63-69, 10% ether-hexane, 62 mg of **40**.

Direct Irradiation of 3-Deuteriotriphenylallene (2d). Allene **2d** (100 mg) in pentane (200 mL) was cooled to -10 °C, irradiated with 254-nm lamps for 1.0 h, and then was concentrated in vacuo. ¹H NMR analysis showed singlets at δ 4.70 (allylic proton of **9**) and broad singlets at 4.25, 3.90, and 4.97 (corresponding to **13**, **14**, and **12**, respectively). No signals at δ 5.21 (propyne) or 6.67 (vinyl proton of **9**) were observed.

Measurement of Deuterium Isotope Effect. Quartz tubes containing identical pentane solutions of **2** and **2d** (10.0 mg each) were purged with N₂, cooled to -20 °C, and irradiated in a Rayonett merry-go-round apparatus for 1-2 min. Internal standard was added, and the mixture was analyzed by HPLC. Three separate runs at 0.5-1% conversion yielded (HPLC analysis) the following results for k_H/k_D (standard deviations shown): 1,3-diphenylindene (**9**), 1.13 \pm 0.21; 1,3,3-triphenylcyclopropene (**10**), 1.39 \pm 0.01; 1,3,3-triphenylpropyne (**11**), 3.72 \pm 0.26.

Quantum Yield Determination for Triphenylallene (2). A 1.54 \times 10⁻³ M isooctane solution of **2** (50 mL) in a quartz cell was irradiated on the optical bench²¹ for periods of 40 min to 3 h. Internal standard was added, and the mixture was analyzed by HPLC. Four separate runs at 0.1%-1.0% conversion yielded the following quantum yields for product formation: cyclopropene (**10**), 0.004 \pm 0.0006; 1,3-diphenylindene (**9**), 0.019 \pm 0.004; 1,3,3-triphenylpropyne (**11**), 0.002 \pm 0.0005.

Quantum Yield Determination for 1,3,3-Triphenylcyclopropene (10). A quartz cell containing **10** (30 mg) and isooctane (50 mL) was irradiated on the optical bench for 7.5-14 h. Internal standard was added, and the solution was concentrated in vacuo. The product was analyzed by 300-MHz NMR integration. Five separate runs at 1-10% conversion yielded the following quantum efficiencies for products: triphenylallene

(**2**), 0.012 \pm 0.003; 2,3-diphenylindene (**13**), 0.061 \pm 0.01; 1,3-diphenylindene (**9**), 0.034 \pm 0.006.

Quantum Yield Determination for 1,3-Diphenylindene (9). A quartz cell containing **9** (25 mg) and isooctane (50 mL) was irradiated on the optical bench for 2-9 h. Internal standard was added, and the solution was concentrated in vacuo. Products were analyzed by 300-MHz NMR integration. Five separate runs at 0.5-20% conversion yielded the following quantum efficiencies for product formation: 2,3-diphenylindene (**13**), 0.12 \pm 0.01; 1,2-diphenylindene (**12**), 0.031 \pm 0.004.

Thermolysis of 1,3,3-Triphenylcyclopropene (10). Samples of cyclopropene **10** (16 mg) in toluene (10 mL) were degassed with three freeze-pump-thaw cycles, sealed, and then thermolyzed at constant temperature. Internal standard was added, and solution was concentrated in vacuo. Products were analyzed by 300-MHz NMR integration. Three separate runs yielded the following results:

temp, °C	time, h	% 9	% 13	conversion
196	1	78	22	100%
132	0.5	78	22	100%
85	0.5	75	25	6%

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Cumulene Photochemistry: Singlet and Triplet Photorearrangements of 1,2-Cyclononadiene

Thomas J. Stierman and Richard P. Johnson*

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50011.
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Abstract: Direct solution-phase irradiation of 1,2-cyclononadiene (**1**) yields bicyclo[6.1.0]non-1(9)-ene (**6**), tricyclo[4.3.0.0^{2,9}]nonane (**3**), and cyclononyne (**7**) as primary photoproducts in a 94:3:3 ratio. Monodeuterated **1** shows a kinetic isotope effect of $k_H/k_D = 1.30 \pm 0.06$ for the formation of **6**, which implies that hydrogen, rather than carbon, is migrating. Optically active **1** is rapidly photoracemized; the relative rate of racemization to isomerization to **6** is determined to be 70. Irradiation of **1** in methanol yields **6**, **7**, **3**, and *cis*-3-methoxycyclononene in a 90:2:3:3 ratio. Independent generation of vinylcarbenes potentially related to **1** and **6** was carried out through photolysis of tosylhydrazone sodium salts. These experiments provide argument that vinylcarbenes are not involved in solution-phase photoreactions of **1**, and a concerted rearrangement mechanism is proposed. Vapor-phase irradiation of **1** at 185 nm yields complex product mixtures. Among the major products is 1,3,8-nonatriene, the apparent product of β -homolytic cleavage. Benzene-sensitized vapor-phase irradiation of **1** yields the previously reported tricyclo[4.3.0.0^{2,9}]nonane (**3**, 89%), in addition to three bicyclics: *cis*-bicyclo[4.3.0]non-2-ene (**9**, 2%), bicyclo[4.3.0]non-1(2)-ene (**32**, 5%), and bicyclo[4.3.0]non-1(9)-ene (**33**, 4%). Ab initio calculations reported here show that cyclopropylidene should have a singlet ground state. Estimates of the energy of triplet cyclopropylidene (3.3-3.4 eV above allene) and planar triplet allene (2.2 eV) show that either species can result from nonvertical energy transfer from triplet benzene (3.66 eV). Competitive diradical and cyclopropylidene triplet mechanisms are proposed.

1,2-Cyclononadiene (**1**), with its allenic chromophore bent ca. 10° from linearity, is the smallest unsubstituted cyclic allene which is kinetically stable at ambient temperature.¹ The photochemistry of this archetypal cyclic allene was first described in a classic paper by Ward and Karafiath.² Benzene-sensitized irradiation yielded tricyclo[4.3.0.0^{2,9}]nonane (**3**, $\Phi = 0.17$ in the vapor phase), while

direct irradiation afforded four C₉ isomers, one of which was believed to be **3**. The remaining products were not identified. In what appeared to be a general reaction of both linear and cyclic allenes, a cyclopropylidene intermediate (**2**) was proposed. Subsequently, Gilbert reported formation of cycloadducts **4** and **5** from irradiation of **1** in benzene solution.^{3a}

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