The Photolysis of Allenes[1]

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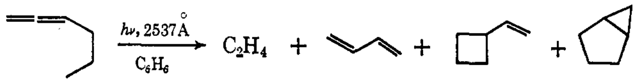
Abstract: The benzene-sensitized vapor phase photolysis (2537 Å) of several allenic hydrocarbons has resulted in the discovery of four different modes of photoreaction, one of which is unique to the allenic bond. Photolysis of 1,2-hexadiene gave 1,3-butadiene ($\phi = 0.16$) and ethylene ($\phi = 0.15$), a process analogous to a Norrish type II cleavage in ketones; vinylcyclobutane ($\phi = 0.07$), possibly by a concerted cycloaddition; and bicyclo[3.1.0]hexane ($\phi = 0.005$), by an allene-cyclopropylidene rearrangement followed by insertion into a carbon-hydrogen bond. By a similar carbene insertion 1,2-cyclononadiene gave tricyclo[4.3.0.0^{2,9}]nonane ($\phi = 0.17$). Photolyses of 1,2,6-heptatriene and 1,2,6-cyclononatriene form the Cope rearrangement products, 3-methylene-1,5-hexadiene ($\phi = 0.24$) and 2,3-divinylcyclopentene ($\phi = 0.02$), respectively. The vacuum ultraviolet photolysis of each of the allenes resulted in the products listed above as well as numerous other products in smaller amounts. The pyrolyses of 1,2,6-heptatriene, 1,2,6-cyclononatriene, and 1,2-hexadiene gave the same products as photolysis although not always with the same relative efficiencies. The identity of the excited state leading to photoproducts is not certain, but a planar singlet allene (a vibrationally excited ground electronic state) is consistent with the available data.

The photochemistry of olefins and dienes has benefited from detailed study, and important information on photochemical processes in general has resulted from these investigations. In contrast, allene photochemistry has received virtually no attention and the photochemical reactivity of allenes has remained unclear. The energies of the various excited state geometries have been calculated by Borden,[2] however, and are shown in Figure 1. The antiplanar form of the first excited singlet lies ~145 kcal above the ground state of the same geometry and can be reached by direct irradiation with wavelengths of 1800–2000 Å (a vertical transition). The rotation of one methylene through 90° gives the planar form of the first excited singlet, with a substantially decreased energy, ~90 kcal. Both the antiplanar (~100 kcal) and the planar triplet (~60 kcal) allenes lie significantly below the respective excited singlets, with the planar triplet at about the same energy as the lowest planar singlet (a vibrationally excited ground electronic state molecule).[3] The efficiencies of intersystem crossing between the antiplanar excited singlet and lowest antiplanar triplet and between the planar excited singlet and planar triplet do not appear to have been considered specifically, but because of the rather large energy separation between the states, such crossing is expected to be relatively inefficient. The low intersystem crossing probability in simple olefins results from a similar energy spread. Although the triplet states probably are not populated appreciably by direct excitation, they should be reached effectively by energy transfer from an appropriate excited triplet. We have studied the photolysis of selected allenes both by direct excitation with vacuum ultraviolet light (1600–2000 Å) and by benzene photosensitization, and the results suggest that allenes may undergo a rich variety of photoreactions.

Results

The vacuum ultraviolet[4] and the benzene sensitized photolyses (2537 Å) of four allenes were investigated in the vapor phase at pressures of 10–20 Torr. The vapor phase ultraviolet spectra did not show absorption at 2537 Å for any of the allenes. For 1,2,6-heptatriene and 1,2,6-cyclononatriene, end absorption was observed beginning at 2400 Å; the other two allenes, 1,2-hexadiene and 1,2-cyclononadiene, showed end absorption beginning at 2100 Å. Direct excitation in the vacuum ultraviolet generally resulted in the formation of numerous products and significant amounts of polymer. In contrast, the sensitized photolyses produced fewer products and could be carried to higher conversions. Essentially complete product identification was possible for the sensitized photolyses, but identification of only the major products of the vacuum ultraviolet photolyses was feasible, because of their complexity.

The benzene sensitized photolysis of 1,2-hexadiene (I) led to the formation of four products: ethylene ($\phi = 0.15$), 1,3-butadiene ($\phi = 0.16$), vinylcyclobutane ($\phi = 0.07$), and bicyclo[3.1.0]hexane ($\phi = 0.005$). All of the photoproducts are primary; a plot of product formation *vs.* time shows per cent product extrapolating to zero product at $t = 0$.



The vacuum ultraviolet photolysis (1600–2100 Å) of I yielded twelve products, four of these were identified as ethylene, 1,3-butadiene, vinylcyclobutane, and 2-hexene. The presence of bicyclo[3.1.0]hexane could not be established because of the formation of several minor products with similar retention times. When 1,2-hexadiene was pyrolyzed in the gas phase at 350°, the formation of four major products was observed, identical with the ones which were identified in the vacuum ultraviolet photolysis, but in different ratios.

The formation of only one product, tricyclo[4.3.0.0^{2,9}]nonane (III), was observed when 1,2-cyclononadiene (II) was irradiated at 2537 Å. The quantum yield for the formation of III is 0.17, and III is a primary product

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[1] Preliminary accounts of this work have appeared: H. R. Ward and E. Karafiath, *J. Amer. Chem. Soc.*, **90**, 2193 (1968); **91**, 522 (1969).

[2] W. T. Borden, *J. Chem. Phys.*, **45**, 2512 (1966).

[3] R. Hoffmann, *Tetrahedron*, **22**, 521 (1966).

[4] The vacuum ultraviolet lamp and wavelength distribution is described in J. S. Wishnok, Ph.D. Thesis, Brown University, 1968.

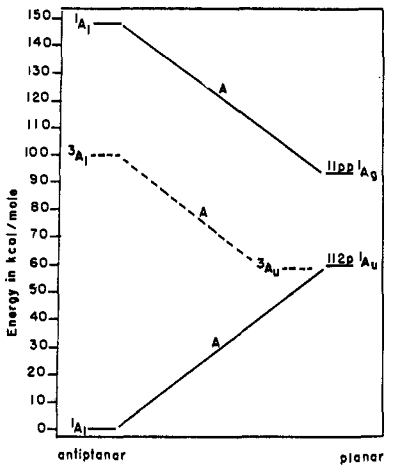
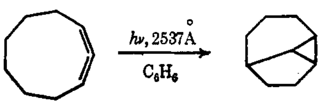


Figure 1. Correlation of the lowest singlet and triplet states of allene: ——, singlet; - - - triplet.[2]

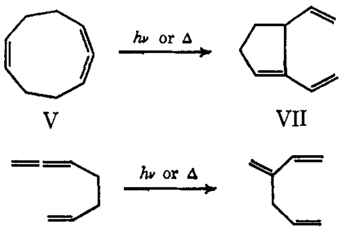
as indicated by a linear plot, with zero intercept, of the formation of III *vs.* time.



II III

When II was irradiated in the vacuum ultraviolet, four isomeric products were formed. One of these was identified as III by retention times and mass spectra. By comparison of retention times of the other photoproducts with those of several C_9 isomers the absence (<0.001%) of the following was established: 1,3-cyclononadiene, 1,4-cyclononadiene, 1,5-cyclononadiene, and all of the photoproducts of 1,3-cyclononadiene.[5] Compound III also forms in the benzene sensitized solution phase photolysis of II. Three other products in slightly lesser amounts than III were also detected in the photolysate, but none of these could be obtained in sufficient purity for characterization. The benzophenone sensitized solution phase photolysis of II was also investigated.[6] The major product was benzpinacol along with several minor products, but compound III was not evident among them.

With benzene photosensitization at 2537 Å, 1,2,6-heptatriene (IV) and 1,2,6-cyclononatriene (V) isomerized to trienes VI and VII. Product identification was



V VII

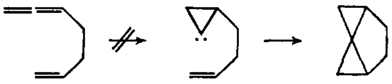
IV VI

based on the identity of glpc retention times and mass spectra with those of authentic samples, obtained from the pyrolyses of IV and V.[7] Catalytic hydrogenation (10% palladium on carbon, ethanol) of the photolysate and pyrolysate of V yielded products which had identical retention times and mass spectra (*m/e* 126). Irradiation of IV to higher conversions yielded two other isomers;[8] these compounds were also evident when VI was photolyzed under the same conditions. The photoisomerization is not reversible; the photolysis of VI does not produce IV.

Compound VII can itself be photoisomerized, but it does not revert to V on irradiation. The isomerization product of VII was identical with the one formed when V was photolyzed to higher conversions. This secondary product was formed only in very low conversions, and isolation and characterization was not feasible. The quantum yields for the formation of VI and VII were 0.24 and 0.02, respectively. A plot of per cent product formation *vs.* time gave a straight line for each case, with an intercept at zero, indicating that VI and VII form directly from excited IV and V.

In the vacuum ultraviolet photolysis of IV, the formation of VI also was evident along with numerous other products. Mass spectral analysis indicated that compound IV fragments to a large degree when photolyzed in the vacuum ultraviolet, even at short irradiation time and low intensity. The primary and the secondary products of the sensitized photolysis also are present in the vacuum ultraviolet photolysate of V, along with some minor products.

A possible photoproduct of IV, tricyclo[4.1.0.0^{4,6}]-heptane (VIII), could arise from the closing of the allene to a cyclopropylidene and subsequent addition to the terminal double bond. By comparison of the retention



IV VIII

times of the photoproducts to an authentic sample of VIII,[9] it was established that VIII is not a photoproduct of IV ($\phi < 0.002$).

The measurements of the quantum yields for product formation in all of the benzene sensitized photolyses were based on a *cis*-2-butene actinometer. The benzene sensitized isomerization of *cis*-2-butene to *trans*-2-butene (at 2537 Å, under conditions of pressure and temperature similar to those used in the allene photolysis) has received careful scrutiny, and the quantum yield for isomerization is accurately known.[10-13] Thus, if *cis*-2-butene and an allene are photolyzed in separate experiments, keeping the same benzene pressure and the same lamp and cell configurations, it is possible to determine the amount of light absorbed by benzene in the benzene-butene system and, indirectly, by the benzene-allene system. Since the benzene-*cis*-butene system has received criticism[14] as a technique for the measure-

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(5) K. M. Shumate and G. J. Fonken, *J. Amer. Chem. Soc.*, **88**, 1073 (1966).

(6) D. R. Arnold and A. H. Glick, *Chem. Commun.*, 813 (1966).

(7) L. Skattebøl and S. Solomon, *J. Amer. Chem. Soc.*, **87**, 4506 (1965).

(8) Direct photolysis of VI in solution gives a single product, 1-(prop-2-enyl)cyclobut-1-ene; sensitized solution phase photolysis yields only 2-methylenebicyclo[2.1.1]hexane: J. L. Charlton, P. deMayo, and L. Skattebøl, *Tetrahedron Lett.*, 4679 (1965).

(9) L. Skattebøl, *Chem. Ind.* (London), 2146 (1962).

(10) R. B. Cundall and P. A. Griffiths, *Trans. Faraday Soc.*, **61**, 1968 (1965).

(11) M. Tanaka, M. Kato, and C. Sato, *Bull. Chem. Soc. Jap.*, **39**, 1423 (1966).

(12) E. K. C. Lee, H. O. Denschlag, and G. A. Haninger, Jr., *J. Chem. Phys.*, **48**, 4547 (1968).

(13) A. Morikawa and R. G. Cvetanovic, *Can. J. Chem.*, **46**, 1813 (1968).

ment of the extent of intersystem crossing in benzene, it must be emphasized that the present use of the system requires none of the assumptions that are open to question in the triplet yield measurements, but is simply a convenient way to measure the amount of 2537-Å radiation absorbed by the benzene.

Discussion

At the present time there is no information available on the quenching of excited benzene by allenes, and the closest analogies appear to be the studies of energy transfer to olefins,[10–13] dienes,[12,13] and ketene.[15] The combination of a much longer lifetime for $^{3}B_{1u}$ benzene ($\sim 5 \times 10^{-5}$ sec) than for $^{1}B_{2u}$ (6×10^{-7} sec), a larger cross section for energy transfer (50 to 0.2 Å^2 for 1,3-butadiene),[12,14] and an efficient intersystem crossing ($\phi_t = 0.72$)[15] strongly support the generally accepted idea that transfer from the $^{3}B_{1u}$ state is usually predominant. The transfer of energy between $^{3}B_{1u}$ benzene and a planar olefin would be an endothermic process[16] and would be expected to occur with low probability. To account for olefin isomerization, an energy transfer to an olefin with molecular geometry similar to that of the lower vibrational levels of the olefin excited state usually is assumed (nonvertical transition). Hammond[17] recently has suggested that energy transfers, which would be endothermic if they occurred vertically, instead may proceed from a loose complex between donor and acceptor to give both molecules in vibrationally excited ground electronic states. In such a case the olefin serves as a catalyst for the radiationless decay of the $^{1}B_{2u}$ or $^{3}B_{1u}$ benzene, and in the process could receive vibrational excitation.

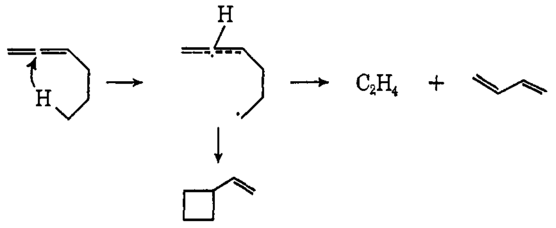
Wilzbach and Kaplan[18] have established that benzene adds to olefins on irradiation in condensed phase. Such adducts form much less efficiently, if at all, in the vapor phase, even though interaction between excited benzene and olefin must have occurred in order to give *cis–trans* isomerization of the olefin. An economical explanation for the different results in condensed and vapor phase is that an adduct between benzene or benzvalene and an olefin will decompose if it is not stabilized by collisions. Such an adduct might partition to give either geometric isomer of the olefin, perhaps through an intermediate olefin triplet. Alternatively, the olefin resulting from the decay of the adduct may possess enough vibrational energy to allow isomerization. Similar adducts have been proposed in the interaction between excited ketones and olefins,[19] a process which also gives *cis–trans* olefin isomerization. These adducts are believed to give olefin triplets on decomposition.

The lowest lying triplet allene that retains its ground state geometry (antiplanar) lies ~15 kcal above the $^{3}B_{1u}$ state of benzene. Vertical energy transfer from the $^{1}B_{2u}$ to the antiplanar allene is endothermic by ~40 kcal. Nonvertical energy transfer to the planar allene is exothermic for both spin states. Thus, of the several possibilities for the allene photosensitization, only vertical transfer from benzene to form the antiplanar triplet or the antiplanar excited singlet allene can be dismissed (assuming, of course, that the calculated energies of the allene excited states are accurate). Nonvertical transfer, presumably involving a complex or an adduct, can lead to a planar triplet, a planar excited singlet, a planar vibrationally excited ground state, or to products or intermediates directly from decomposition of the adduct. However, it is certain that a benzene adduct is not essential for product formation, since the same products are formed by direct irradiation with vacuum ultraviolet light in the absence of benzene.

The quantum yields, as reported, do not depend on the identity of the benzene excited state which transfers energy to the allene, and no correction has been made for energy absorbed by the benzene which is not "useful," *i.e.*, not available for transfer. Fluorescence measurements have not yet been done on the benzene–allene system, but it is reasonable to assume that at least some energy is lost by benzene fluorescence, perhaps as much as 18%.[15] If it could be established that only the $^{3}B_{1u}$ state of benzene participates in energy transfer, and, as is probable, that each $^{3}B_{1u}$ transfers energy to an allene, the quantum yields as reported should be multiplied by 1.4, to give the number of product molecules formed from each excited allene molecule.

Because of the diversity of the photochemical reactions of allenes, the consideration of several different mechanistic pathways is necessary. Either a concerted or a stepwise process can lead to the formation of the major photoproducts of 1,2-hexadiene. In Scheme I the dissociation of the intermediate biradical species can lead to ethylene and butadiene *via* C–C bond cleavage. Bond formation between carbons 3 and 6 yields vinylcyclobutane. This same biradical has been proposed in the Hg 6 ($^{3}P_{1}$) sensitized reaction of cyclohexene,[20] where the formation of vinylcyclobutane, ethylene, and 1,3-butadiene was also observed, along with other products, but in ratios rather different from those in the allene photolysis. However, bond formation between carbons 1 and 6 should be possible, and probably favored, leading to the formation of cyclohexene. A similar biradical has been proposed by Padwa[21] as an intermediate in the photolysis of 1-phenyl-5-hexen-1-one. As expected, ring closure to the cyclohexene (IX) dominated the vinylcyclobutane (X) by a ratio of 4:1. Since cyclohexene was not detected in the photolysate of I (<0.001%) an alternate process (Scheme II) must be considered. This concerted mechanism would result in the formation of vinylcyclobutane alone, because the

Scheme I



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(14) W. A. Noyes, Jr., and C. Burton, *Ber. Bunsenges. Phys. Chem.*, **72**, 146 (1968).

(15) W. A. Noyes, Jr., and S. Ho, *J. Amer. Chem. Soc.*, **89**, 5091 (1967).

(16) T. Terao, S. Hirokami, S. Sato, and R. J. Cvetanovic, *Can. J. Chem.*, **44**, 2173 (1966).

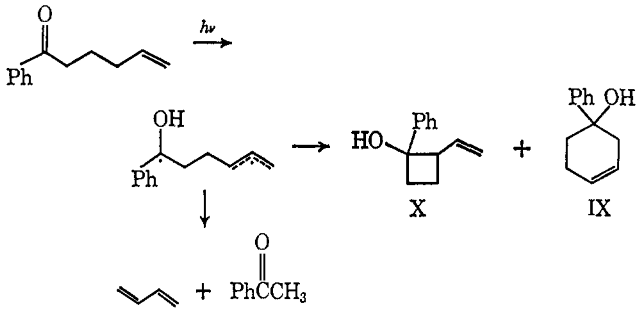
(17) S. Murov and G. S. Hammond, *J. Phys. Chem.*, **72**, 3797 (1968).

(18) K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 2066 (1966); K. E. Wilzbach, A. L. Harkness, and L. Kaplan, *ibid.*, **90**, 1116 (1968).

(19) S. M. Jaspar, M. Pomerantz, and E. W. Abrahamson, *Chem. Phys. Lett.*, **2**, 137 (1968).

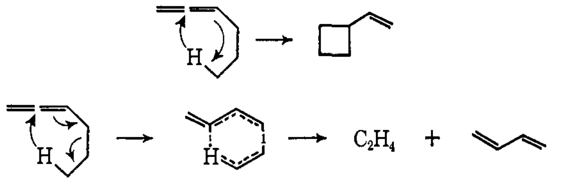
(20) G. R. deMaré, O. P. Strausz, and H. E. Gunning, *Can. J. Chem.*, **43**, 1329 (1965).

(21) A. Padwa and D. Eastman, *J. Amer. Chem. Soc.*, **91**, 462 (1969).

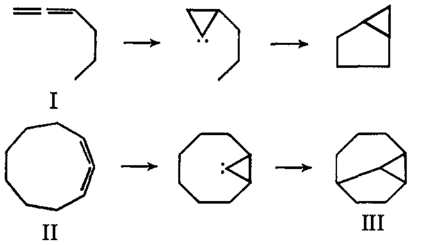


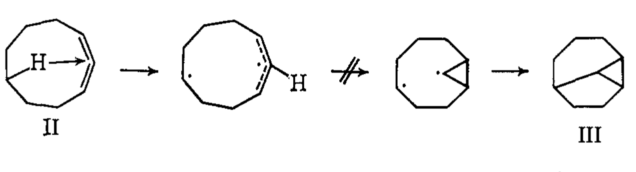
geometry of the molecule prevents reaching a suitable conformation for a concerted bond formation between the two terminal carbons. For the fragmentation of 1,2-hexadiene to ethylene and butadiene, a concerted process is also possible, analogous to the Norrish "type II" mechanism for the photodissociation of ketones.[22] The quantum yields for formation of ethylene and 1,3-butadiene are equal within experimental error, as required by such a fragmentation.

Scheme II



The most reasonable pathway for the conversion of I to bicyclo[3.1.0]hexane, and for the conversion of II to tricyclo[4.3.0.$0^{2,9}$]nonane (III), is the closing of the allene to a cyclopropylidene followed by insertion into a C–H bond. The only apparent alternative to the cyclopropylidene intermediate is a transannular hydrogen atom abstraction by the center carbon of the allene to give a biradical, followed by an allyl–cyclopropyl radical isomerization and radical coupling. The allyl radical–cyclopropyl radical conversion is unattractive on thermodynamic grounds; such an isomerization is endothermic by 30 kcal/mole and the reverse exothermic process has an energy of activation of 22 kcal/mole.[23] If the first biradical that is formed were to couple directly, the formation of a bicyclo[5.2.0] or a bicyclo-[4.3.0] ring system would be expected.





The allene–cyclopropylidene conversion has been treated theoretically.[24] The closing of an antiplanar triplet allene to a cyclopropylidene is exothermic and is symmetry allowed, while the planar triplet closure is symmetry forbidden. Borden[25] has suggested that a complex formed between sensitizer and allene might lead to either the triplet cyclopropylidene or the planar triplet allene.

Of all the allene singlets, Borden[25] finds one to be of the proper symmetry for concerted closure to cyclopropylidene. This state (11pp in Borden's nomenclature) places two electrons in the allyl orbitals of the planar allene and restricts the remaining two electrons to the orthogonal p orbital of carbon two. This state is calculated to lie above the 112p (three electrons in the allyl, one in the p) for linear allene, and should be only slightly populated in sterically unrestricted allenes. Significantly, the 11pp state becomes more stable than 112p as the allene group is bent,[25] as it must be in the 1,-2-cyclononadiene system. The fact that cyclopropylidene formation is major only for the cyclononadiene seems to be more than a coincidence. The 11pp state should be easily reached by direct irradiation, for it directly correlates with the first excited antiplanar singlet. Population of 11pp by benzene sensitization is less obvious. If intersystem crossing occurs in the energy-transfer complex, as suggested by Hammond, 11pp might result directly from the complex decomposition. Alternatively, the planar triplet allene might intersystem cross directly to 11pp, if, because of the bending of the allenic group, the two states are similar in energy. The inefficient formation of bicyclo[3.1.0]hexane from I may result from a low population of the 11pp state, as well as the molecular geometry which does not hold a C–H bond always in the proper position for carbene capture as does II.

When allenic compounds contain an additional double bond in the γ–δ position, they exhibit a photochemical behavior very different from that of their saturated analogs. No evidence was found for the formation of any products that could arise from cyclopropylidene insertion in the photolysis of IV and V; instead trienes VI and VII were formed. Three different mechanistic pathways can be proposed for the isomerization of 1,2,6-heptatriene: (a) a stepwise, diradical process, (b) a 1,3-sigmatropic shift, or (c) a 3,3-sigmatropic shift, the latter corresponding to the valence isomerization of 1,5-dienes known as the Cope rearrangement. The stepwise isomerization should lead to products of cross-coupling of the radicals so produced, and the absence of such products can be taken as evidence against a. The Cope rearrangement (c) and one mode of b give VI; the other mode of b is regenerate. The available data do not allow us to choose between the possibilities b and c for the photochemical isomerization of IV.

In the case of 1,2,6-cyclononatriene only a 3,3 shift leads directly to the observed product, VII. A 1,3 shift gives XI or XII and can give rise to VII only by an additional 1,3 shift. If either XI or XII forms during the photolysis, then it must rearrange or polymerize very efficiently, since no evidence was found for the presence of any precursor to VII in the photolysis of V, even at low conversions (0.1%). Further XI or XII would have to be a much better energy acceptor than 1,-2,6-cyclononatriene, since the allene is always present in

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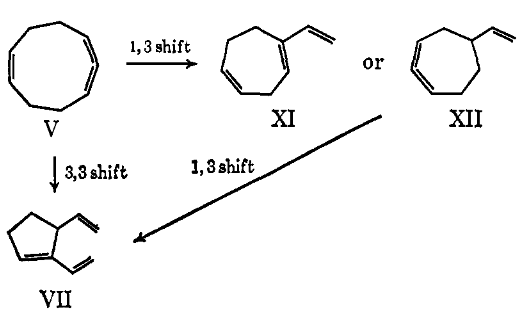
(22) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 382.

(23) O. P. Strausz, P. J. Kozak, G. N. C. Woodall, A. G. Sherwood, and H. E. Gunning, *Can. J. Chem.*, **46**, 1317 (1968).

(24) W. T. Borden, *Tetrahedron Lett.*, 447 (1967).

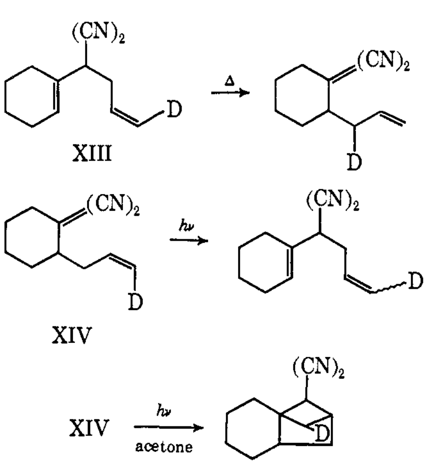
(25) W. T. Borden, personal communication.



great excess over any other species during the photolysis. While there is no information available on the relative quenching efficiencies of allenes, compared to other unsaturated compounds, the inordinately large difference which would be required here is not expected. Therefore we conclude that the photorearrangement of V → VII proceeds either *via* the Cope mechanism or (less likely) by an analogous stepwise process.

The thermal valence isomerization of 1,5-dienes has been studied extensively,[26] and the results lead to the conclusions that the reaction is concerted and intramolecular. The formation of cyclic transition state (a chairlike or boatlike conformation) is supported by the considerably negative entropies of activation. In the case of 3,4-dimethyl-1,5-hexadiene the chairlike conformation is more stable by 5.7 kcal/mole.[27] The consideration of orbital symmetry relationships confirms the preference of the chairlike transition state in the thermal Cope rearrangement.[28] However, in systems where geometrical considerations necessitate the adoption of the boatlike transition state, the Cope rearrangement proceeds with no special difficulty.[28] Examination of molecular models reveals that 1,2,6-heptatriene can adopt the boat- or chairlike conformations with equal facility, but 1,2,6-cyclononatriene is severely strained in the chairlike arrangement.[7] It is interesting that the ease of reaching the thermally preferred arrangement does not fully control the reaction rates in this system. The results of vapor phase pyrolyses at short contact time indicate that V → VII is more facile, at least at temperatures above 300° (V → VII/IV → VI > 1). The photochemical isomerizations show the reverse proclivity of the thermal ones; V → VII/IV → VI = 0.1.

The only studies that we have discovered which bear on the photo-Cope rearrangement are those of Cookson.[29] Using deuterated dinitriles XIII and XIV, he has demonstrated that while thermal rearrangement of XIII proceeds by a 3,3 shift, the direct photolysis of XIV is best explained by a 1,3 shift. The acetone sensitized photolysis of XIV gives only a bicyclohexane derivative. To the extent that these results relate to the photolysis of the 1,2,6-trienes, they suggest that V (and possibly IV as well) are reacting in the thermal mode, as a vibrationally excited ground electronic state molecule.



Several of the reactions that we have found in allene photolyses are of the general types of valence isomerization that of late have been examined fashionably in light of molecular orbital symmetry considerations. However, the allenes (with the exception of the allene-cyclopropylidene rearrangement) have the requisite symmetry for simple treatment only if the allene double bond which formally is unchanged during the rearrangement is ignored. Since the allene group has very different reactivity from an isolated double bond, such neglect clearly is not in accord with chemical fact. Thus we have restrained from applying symmetry arguments, because the necessary assumptions for their application seem unrealistic.

Summary

Even though the allene photolyses reported here show wide variance in their reaction types, it is possible to detect (or construct) a certain consistency in these reactions, which at least serves as a basis for discussion. Four of the photoreactions, I → $C_2H_4 + C_4H_8$, I → vinylcyclobutane, IV → VI, and V → VII, can be envisioned as proceeding by bond formation at the center carbon of the allene, followed or accompanied by rebonding or rehybridization in the remainder of the molecule. This is not the position at which reaction occurs between free radicals and ground-state allenes, where reaction at the terminal carbon often is preferred.[30] It has been suggested that the reactivity of the center carbon in the antiplanar allene is lower than might be expected, since reaction there generates the allyl radical only after a 90° bond rotation.[30] Of course, this is not the case for planar allene (whatever its spin multiplicity) where bonding at the center carbon gives the allyl radical directly.

Using a planar model, it is useful to reconsider the conversions discussed above. The fragmentation of I to ethylene and 1,3-butadiene and the rearrangement to vinylcyclobutane require a hydrogen atom transfer to the center allene carbon from a carbon γ to the allene group. If the transfer occurs before, and not concurrent with, rebonding in the remainder of the molecule, it must occur in the singlet state, because closing to give vinylcyclobutane and no cyclohexene demands formation of the four-membered ring before any significant change occurs in molecular geometry. A triplet biradical would not be expected to close so rapidly. The fact that the photoreactions of I, IV, and V can be reproduced by pyrolysis further argues for an intermediate

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[26] Reviews on valence isomerizations: W. von E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 115 (1963); S. J. Rhoads, "Molecular Rearrangements," Vol. I, P. deMayo, Ed., Interscience Publishers, New York, N. Y., 1963, p 649.

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ground electronic state planar allene in the photolyses.[31]

A planar ground state allene could be found by intersystem crossing from the planar triplet, from decay of a planar excited singlet, or directly from the decomposition of an allene–photosensitizer adduct. Such a planar state may represent a second minimum in the ground-state rotational potential curve,[32] which would reduce the rate of rotation to antiplanar allene and allow opportunities for other reaction modes. When the allene group is bent, as in 1,2-cyclononadiene, the 11pp state may become the lowest energy planar singlet, and closure to a cyclopropylidene may be allowed.

Borden[25] has proposed routes involving triplet cyclopropylidene intermediates to all of the photoproducts that we have observed. Our results do not exclude this possibility, but we regard it as uneconomical, at least in cases where thermal and photochemical reactions give identical products.

Experimental Section

Gas Chromatography. Analytical determinations were carried out on an Aerograph Model 1200 flame ionization instrument. Aluminum columns with the following liquid phases were used: A 20 ft × $^1/_8$ in. 10% Carbowax 20M on 80–100 mesh Chromosorb P; B, 20 ft × $^1/_8$ in. 15% TCEP on 80–100 mesh Chromosorb P; C, 15 ft × $^1/_8$ in. 10% QF-1 on 80–100 mesh Chromosorb P; D, 20 ft × $^1/_8$ in. 10% Squalane on 90–100 mesh Chromosorb W; E, 20 ft × $^1/_8$ in. 10% UCON 50-H on 90–100 mesh Chromosorb W; F, 25 ft × $^1/_8$ in. 20% SE-30 on 90–100 mesh Chromosorb W; G, 20 ft × $^1/_8$ in. 15% SF-96 on 90–100 mesh Chromosorb W; and H, 15 ft × $^1/_8$ in. silica gel.

Preparative gas chromatography was carried out on an Aerograph Model A-90 thermal conductivity gas chromatograph. The following columns were most useful: I, 20 ft × $^3/_8$ in. 15% Carbowax 20M on 80–100 mesh Chromosorb W; J, 20 ft × 0.25 in. 20% Squalane on 100/120 mesh Anakrom; and K, 25 ft × 0.25 in. 20% UCON-50 H on 100/120 mesh Anakrom. An Aerograph Model 200 flame ionization instrument, equipped with an effluent splitter, was used for photoproduct isolation. Compound III was isolated on column I at 90°; vinylcyclobutane was isolated on column K at 30°.

Preparation of Allenes. The allenes were synthesized by the method of Moore and Ward[33] using commercial potassium *t*-butoxide (MSA) and methyllithium (Foote Mineral Co.). The allenes were distilled through a spinning band column, and were further purified (to 99.99%) on the following columns: 1,2-cyclononadiene on column I at 90°, 1,2,6-heptatriene on column J at 50°, 1,2,6-cyclononatriene on column I at 80°, 1,2-hexadiene on column K at 30°.

Photolyses. The benzene-sensitized photolyses were carried out in a Vycor (7910) tube measuring 2.5 × 50 cm. In a typical photolysis, 15 μl of allene and 2 μl of benzene were placed in a small trap which was attached to the Vycor tube by standard taper joints. The allene–benzene mixture was cooled with liquid nitrogen, and the tube was evacuated. After one or two cycles of degassing, the Vycor tube was isolated from the vacuum system, and the trap was allowed to warm to ambient temperature. A bank of ten 25-W germicidal lamps (GE 25T8) was used as a light source. A high-speed fan was employed for cooling. Temperatures during the photolyses ranged from 25 to 30°. Solution phase photolyses were carried out with a Hanovia 450-W medium-pressure mercury-arc lamp. Extensively purified *n*-pentane was used as a solvent.

Table I. Retention Times of Major Photoproducts Relative to Benzene

Compound	Column	Temp, °C	Retention time
Vinylcyclobutane	D	30	0.79
	F	30	0.81
	E	30	0.36
Bicyclo[3.1.0]hexane	D	30	1.4
	F	30	1.2
	G	30	1.3
2,3-Divinylcyclopentene	A	70	2.7
	D	80	6.0
	B	80	1.6
3-Methylene-1,5-hexadiene	E	50	0.87
	F	50	0.53
	D	50	1.4
Tricyclo[4.3.0.0^{2,9}]nonane	A	80	4.3
	B	100	4.6
	C	50	3.3

Product Identification. Ethylene and 1,3-butadiene were identified by their gc retention times and mass spectra; vinylcyclobutane was isolated and its structure was assigned by the identity of its nmr and ir spectra with published spectra.[34] Bicyclo[3.1.0]hexane was identified on the basis of the identity of retention times and mass spectra with those of an independently synthesized sample.[35]

The structure of III was assigned on the basis of identity of spectra and chromatographic behavior with those of an independently synthesized sample.[36] The nmr spectrum consisted of four unresolved multiplets at δ 2.6, 1.8, 1.4, and 0.8. The ir spectrum showed an absorption band at 3045 cm^{-1}; the mass spectrum exhibited a parent peak at *m/e* 122 and a fragmentation pattern similar to that of *cis*-hydrindane, but displaced to higher mass by two mass units. The photoproduct and the synthetic product had identical retention times on three columns. Catalytic hydrogenation of III (platinum oxide, acetic acid, trace of perchloric acid) yielded two products (*m/e* 124), one of which was identified as *cis*-hydrindane on the basis of retention times and mass spectra.

Nmr spectra were taken on a Varian A-60 spectrometer[37] in carbon tetrachloride, using tetramethylsilane as an internal standard. Mass spectra were taken on a Hitachi–Perkin–Elmer RMU-6D spectrometer[37] by using a gas chromatograph–mass spectrometer combination in which part of the effluent from the gas chromatograph passed directly into the inlet of the mass spectrometer.

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