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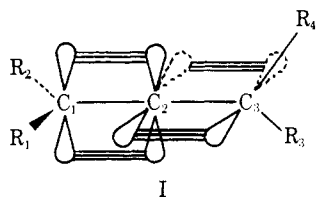
Cyclic Allenes. I. The Electronic Structure and Probable Deformation of the Allene Linkage When Included in a Ring. An INDO-MO Study

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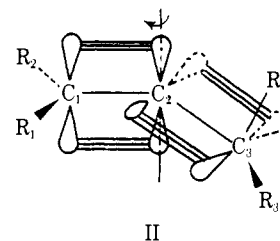
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Abstract: As a model for the medium and small cyclic allenes, INDO-MO calculations have been performed on a large number of distorted geometries of allene. Both the lowest singlet and triplet states were calculated, and the effect of geometrical distortion on total energy, charge distribution, and spin distribution were investigated. The calculations indicate that singlet 1,2-cyclooctadiene and 1,2-cycloheptadiene are probably bent at C-2 and also twisted somewhat from the orthogonal geometries. These distortions also bring about a moderate increase in charge separation, as compared with linear allenes. They further indicate that the singlet states of the smaller cyclic allenes are probably planar and bent. In these cases there is considerable charge delocalization and the allene moiety may best be considered as an allyl cation with an anion located at C-2 in the in-plane sp^2 orbital. For the triplet state the allene moiety is probably planar in all cases and is bent if the ring contains six or fewer atoms. These systems have little charge separation and may best be visualized as an allyl radical with a second unpaired electron in the in-plane p (or sp^2) orbital at C-2. Finally the calculations indicate that while 1,2-cycloheptadiene and larger cyclic allenes would have singlet ground states, 1,2-cyclohexadiene and smaller cyclic allenes may have triplet ground states.

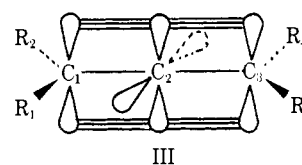
The synthesis and isolation or trapping of highly strained molecules, such as polycyclic compounds with a number of small fused rings, small and medium ring acetylenes, and *trans*-olefins, has been an area of extensive research in organic chemistry during the past thirty years. The normal allene linkage requires a fixed geometrical arrangement of seven atoms, with open chain allenes having a linear structure and two orthogonal π bonds (I).



In I, the plane defined by R_1 , R_2 , C_1 , and C_2 is perpendicular to that defined by R_3 , R_4 , C_3 , and C_2 . Molecular models suggest that the allene linkage can be included in only nine-membered or larger rings without distortion. If the ring size is decreased below this, it becomes necessary to deform the allene linkage in order to close the ring. Two deformations will facilitate ring closure. The first consists of bending the allene group at C_2 , about an axis perpendicular to one of the methylene planes. This will introduce s character into the p orbital at C_2 which is perpendicular to the bending axis and which participates in one of the π bonds. This deformation will presumably weaken that π bond (II). The second deformation would retain the linear C_1 - C_2 - C_3 linkage, but would require one of the methylene



groups to be twisted to form a more nearly planar allene. This would tend to form a linear allyl arrangement of p orbitals with one nonbonding p orbital, perpendicular to the π system at C_2 (III).



Of course, some mixture of both bending and twisting may occur and possibly is necessary in the seven- and eight-membered cyclic allenes. If both bending and twisting did occur simultaneously, it would most probably take the form of bending at C_2 , resulting in the weakening of the π bond between C_2 and C_3 (say), coupled with twisting of the C_3 methylene around this weakened C_2 - C_3 bond. This twisting of the weakened π bond while retaining the essentially normal double bond would be expected to lead to a more stable structure than would twisting of the C_1 methylene about C_1 - C_2 , which would destroy the normal π bond. In the ex-

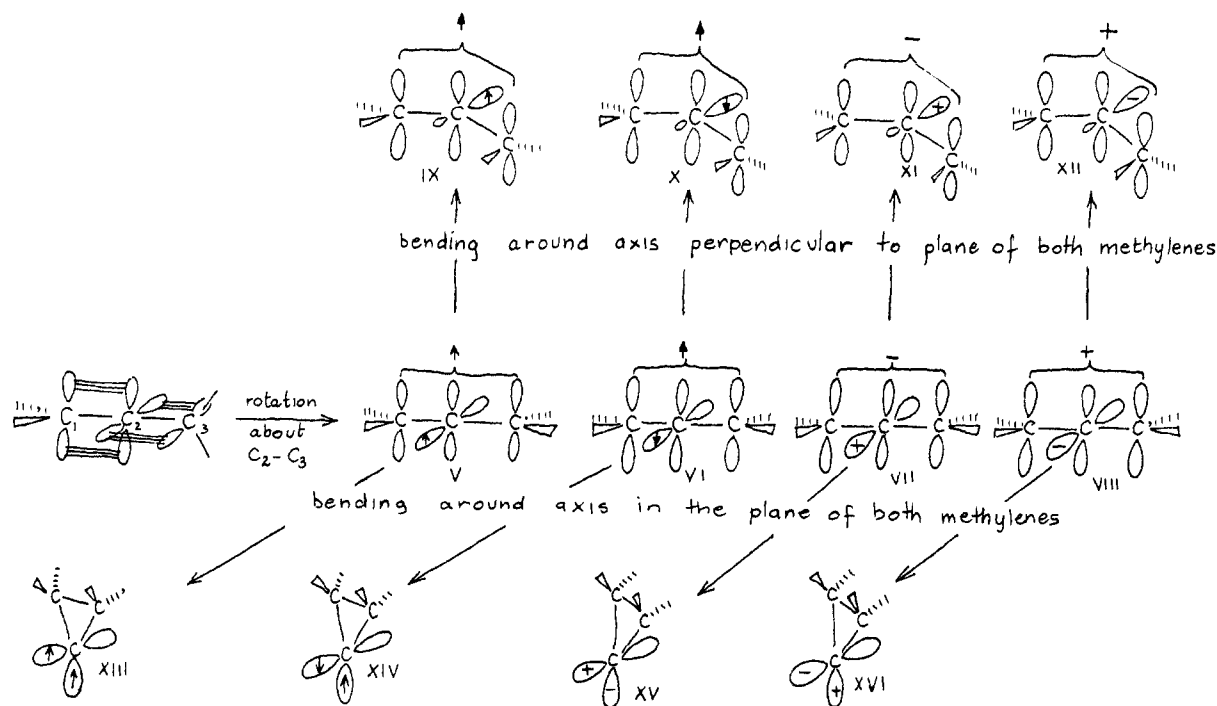
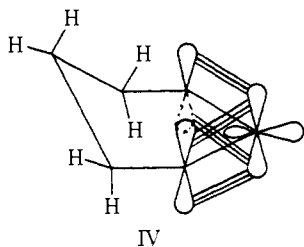


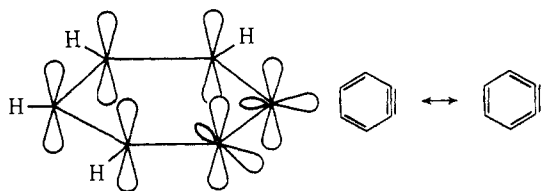
Figure 1. Some of the limiting electronic structures of allene resulting from the distortions mentioned in the text. In these structures, the small arrows represent the electron spin density ($\uparrow = \alpha$ spin and $\downarrow = \beta$ spin) and the signs represent the excess charge distributions.

treme case of this distortion for a 90° twist, the resultant orbital arrangement would be a nonlinear allyl system with a perpendicular sp^2 nonbonding orbital at C_2 . In fact it has been postulated¹ that the allene system of 1,2-cyclohexadiene is essentially planar, with C_1 , C_2 , and C_3 all sp^2 hybridized, three p orbitals forming an allyl π system and a nonbonding sp^2 orbital at C_2 (IV).



With smaller rings, the C_1 - C_2 - C_3 bond angle would, of necessity, be less than 120° , and the nonbonding orbital would thus possess more s character.

This type of arrangement of four orbitals occurs twice in arynes which may formally be considered to contain cumulated double bonds. The chemistry of arynes



however will not be discussed in this paper. Similarly, this four-orbital system also occurs in such potentially aromatic systems as 2,4,6-cycloheptatrienyldiene, 2,4-cyclopentadienyldiene, cyclopropenyldiene, the phenyl radical and ions, and 1,4-dehydrobenzene, but discus-

(1) (a) W. R. Moore and W. R. Moser, *J. Amer. Chem. Soc.*, **92**, 5469 (1970); (b) W. J. Ball and S. R. Landar, *J. Chem. Soc.*, 2298 (1962).

sion of these systems will be deferred until a later paper in this series.

Several other modes of deformation of allene can be visualized, some of which lead to chemically meaningful species, although they would not be expected to result in stabilization of the cyclic allenes.

(1) Instead of twisting only that methylene group, the π bond of which has been weakened by the bending at C_2 , both $R_1C_1R_2$ (with the normal π bond to C_2) and $R_3C_3R_4$ could be twisted. The total twist, ϕ , is defined as $|\phi_1| + |\phi_3|$, where ϕ_i is the dihedral angle between the plane defined by the C_i methylene and the plane C_1 - C_2 - C_3 . If $\phi_1 = \pm\phi_3$, both methylene groups are equivalent, and the geometries would be those involved respectively in the symmetrical disrotatory or conrotatory openings of cyclopropylidene to yield allene. These geometries shall not be discussed here but will be examined in detail in a subsequent paper devoted specifically to that subject. As would be expected, in almost all cases the symmetrically twisted geometries have higher energies than the corresponding asymmetrically twisted ones.

(2) Only the $R_1C_1R_2$ plane could be twisted (*i.e.*, the methylene whose plane is perpendicular to the bending axis passing through C_2). This would correspond to the twisting of the normal C_1 - C_2 π bond while leaving the weakened C_2 - C_3 π bond untouched and would be expected to produce species higher in energy than those previously mentioned. For this reason these geometries will not be considered here.

(3) Finally, the bending axis passing through C_2 need not be perpendicular to either of the methylene planes. This bending is closely related to case 1, above, in that both π bonds would be weakened.

Some of the distortions mentioned above would be expected to change quite drastically the electronic structure of the basic allene linkage from the normal ar-

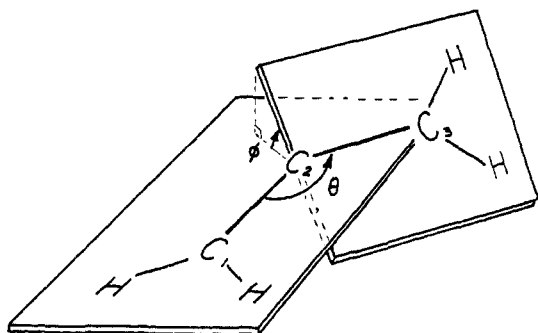


Figure 2. Definitions of the angles θ and ϕ used in describing the distorted allenes.

rangement of two orthogonal π systems. Some of the limiting descriptions for extreme distortions are given in Figure 1. Naturally, a knowledge of the extent to which each of these structures contributes to the overall description of a particularly distorted allene is essential in anticipating or rationalizing the physical and chemical properties of these strained molecules.

In order to gain a better understanding of the chemistry of allenes when included into small rings, we have performed unrestricted LCAO-SCF-MO calculations, using the INDO approximation,² on various deformed geometries of allene itself. In all these calculations, the C-C bond distances were set at 1.31 Å, the C-H bond distances at 1.08 Å, and the H-C-H bond angle at 115°, and each methylene group was kept coplanar with the central carbon of the allene linkage.³

Calculations were carried out with the C₁-C₂-C₃ chain bent at C₂ with the C₁-C₂-C₃ bond angle, θ , varying from 60 to 180° in 10° increments. At each value of θ , calculations were made in which the dihedral angle, ϕ , between the plane of the C₃ methylene group and the plane of the remainder of the molecule was increased from 0 (planar) to 90° (orthogonal). The C₁ methylene group was always kept coplanar with the three carbon atoms (see Figure 2). Both the lowest energy singlet and triplet states were calculated for each value of θ and ϕ and the effects of deformation upon total energy, singlet-triplet splitting, and charge and spin distributions were examined.

Energy Contours for Distorted Singlet Allenes. The energy contour diagram for the lowest singlet state of allene as a function of the two angles θ and ϕ is given in Figure 3. The most obvious feature of this figure is the deep energy minimum at $\theta = 180^\circ$ and $\phi = 90^\circ$, which corresponds to the normal ground state geometry of allene. The total energy calculated for this geometry was -23.2817 au. All subsequent energies will be given in kilocalories per mole and will be relative to this geometry taken as zero. Little significance should be attached to the lower portions of this diagram, *i.e.*, in the region $\theta = 60$ to 90° , since a major contribution to the total energy in this particular instance will result from nonbonded hydrogen interactions. Thus, for example, the sharp rise at $\theta = 60^\circ$ and $\phi = 0^\circ$ is undoubtedly associated with H-H repulsions, since the calculated hydrogen-hydrogen distance here is only 0.31 Å. This repulsion would be removed in, for

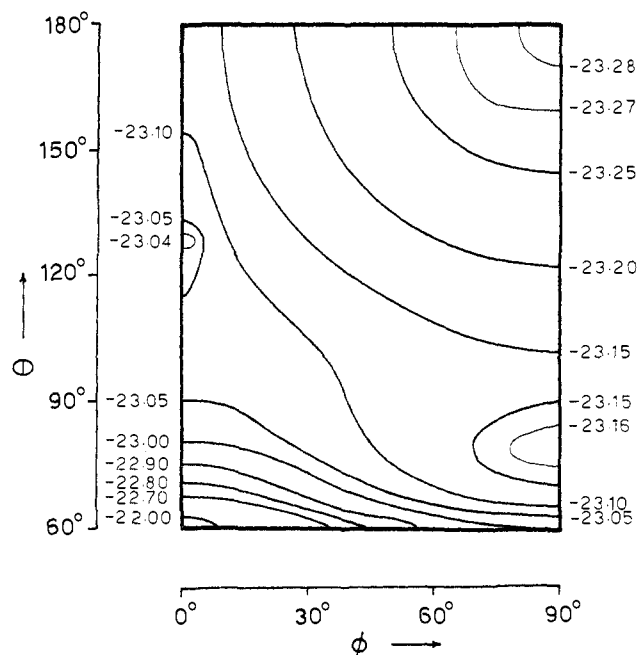
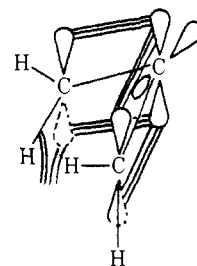
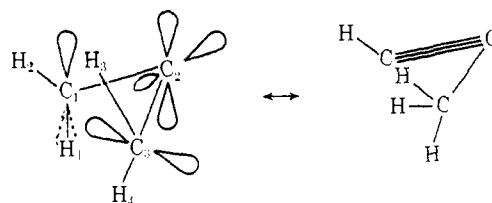


Figure 3. Energy contours (in au) of the lowest singlet state of bent and twisted allenes, as a function of the angles θ and ϕ . Note that the contours are not separated by equal intervals of energy.



example, cyclopropadiene. Presumably the local minimum at $\theta = 80^\circ$ and $\phi = 90^\circ$ is also in some way associated with the close proximity of the internal hydrogen on C₁ to the p orbital on C₃, possibly



since the C₃-H₁ interatomic distance is only 1.71 Å in this geometry. The more meaningful portions of this diagram are those corresponding to $\theta > 90^\circ$.

There is a saddle point at $\theta = 180^\circ$ and $\phi = 0^\circ$ with an energy of 97 kcal/mol which is the calculated energy of activation for the racemization of optically active, undistorted allenes. No experimental value for this reaction appears to be available though other theoretical estimates vary from 36.73⁴ to 92 kcal/mol.⁵

The almost circular nature of the contours around $\theta = 180^\circ$ and $\phi = 90^\circ$ indicates that the simultaneous occurrence of both twisting and bending is the most

(2) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

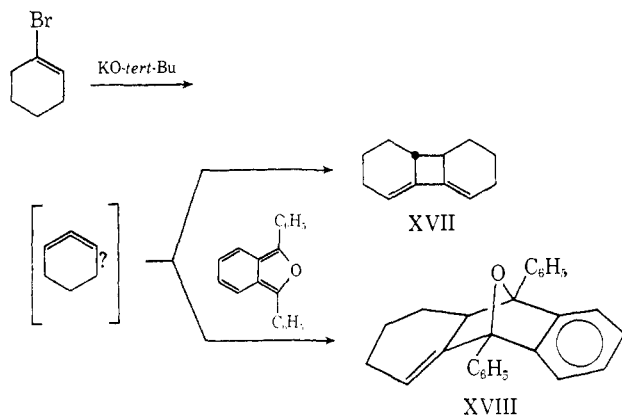
(3) "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc., Spec. Publ.*, No. 11, M146 (1958).

(4) MINDO/2 calculations: M. J. S. Dewar and M. C. Kohn, *J. Amer. Chem. Soc.*, **94**, 2699 (1972).

(5) *Ab initio* calculations: L. Radom and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4786 (1970).

efficient way of relieving ring strain. Thus, for example, a twist of 45° or a bend of 40° from the ground state geometry requires about the same amount of energy as 30° of twist combined with 30° of bend, although the latter appears to be far more efficient in relieving strain in the remainder of the ring in, for example, the seven- or eight-membered cyclic allenes.

Another point of chemical interest corresponds to the geometry anticipated for 1,2-cyclohexadiene. This compound has never been isolated although its intermediacy has been inferred during the reaction of 1-bromocyclohexene with potassium *tert*-butoxide since the cyclohexadiene dimer XVII is isolable⁶ and adducts of cyclohexadiene with, e.g., 1,3-diphenylbenzo[*c*]furan, XVIII, may be trapped.⁷ We shall return to the



chemistry of 1,2-cyclohexadiene after a discussion of the charge and spin distributions in allenes approximating this geometry.

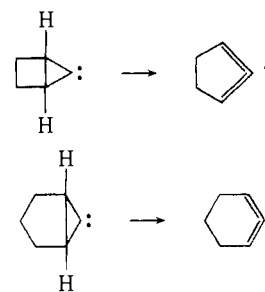
The most stable geometry of 1,2-cyclohexadiene would be expected to be in the vicinity of $\theta = 120^\circ$ and $\phi = 0^\circ$. This is quite close to a local maximum ($\theta = 127^\circ$ and $\phi = 0^\circ$) on the energy contour diagram. This point corresponds to a drastic change in the electronic structure of the allene, as shall be discussed below, and suggests the desirability for more sophisticated calculations in this region, particularly including configuration interaction. If this local maximum is real, or at least as long as the general shape of the long, gently sloping ridge along the line $\phi = 0^\circ$ is real, then an interesting fact emerges: the incorporation of the allene linkage into a five-membered ring should be no more difficult than into a six-membered ring. 1,2-Cyclopentadiene would be expected to be defined by θ ca. 110° and $\phi = 0^\circ$ and is in fact calculated to be *more stable*, albeit by 2 kcal/mol, than the configuration anticipated for 1,2-cyclohexadiene. Furthermore, if these two species were prepared by the "carbene" method⁸ from the corresponding bicyclic precursor, a greater release of strain would be anticipated in the case of the 1,2-cyclopentadiene. We have been unable to find any reference to the attempted synthesis or trapping of a five-membered cyclic allene.⁹

(6) (a) G. Wittig and P. Fritze, *Justus Liebig's Ann. Chem.*, **711**, 82 (1968); (b) the stereochemistry of XVII was determined in ref 1a.

(7) G. Wittig and P. Fritze, *Angew. Chem., Int. Ed. Engl.*, **5**, 846 (1966).

(8) W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958).

(9) The coupling of phenyllithium with 1-chlorocyclopentene to give 1-phenylcyclopentene could proceed, *a priori*, either by way of 1,2-cyclopentadiene or cyclopentene. The reaction, however, has been shown to proceed *via* the acetylene¹⁰⁻¹² as have the corresponding



Even 1,2-cyclobutadiene does not appear to be an unreasonable candidate, since the energy calculated for $\theta = 90^\circ$ and $\phi = 0^\circ$ is essentially identical with that calculated for $\theta = 120^\circ$ and $\phi = 0^\circ$, the probable geometry of 1,2-cyclohexadiene. Furthermore, the energy estimated for the 1,2-cyclobutadiene from this graph should be too high by virtue of the nonbonded hydrogen repulsions which are included in these calculations. In addition, the strain energy would be much greater in the bicyclobutane precursors. It appears, however, that 1,2-cyclobutadiene will not be capable of being prepared by the "carbene" method since carbena-bicyclo[1.1.0]butane yields products derived from tetrahydrene,¹⁵ although there appears to be no reference in the literature to specific attempts to synthesize or trap 1,2-cyclobutadiene.

Charge Distribution for Distorted Singlet Allenes.

The chemistry of the allenes can best be rationalized in terms of charge distributions in the three-carbon moiety. The contour diagram of the calculated total charge at the central atom as a function of θ and ϕ is given in Figure 4. Similar curves have been constructed for C_1 and C_3 , but their forms are extremely similar to Figure 4 with the difference that the charges are of course opposite to those at the central carbon. It is interesting that the magnitudes of the charges on C_1 and C_3 are also almost identical with the magnitudes of the charge on C_2 . Normally one would expect this not to be the case, but in this instance the charges on the methylene hydrogens are the same sign and close to 25% of the charges on C_2 , thus maintaining total neutrality of charge in the molecule. This is particularly true except in the region $\theta < 90^\circ$, at which point the calculations become unrealistic due to the nonbonded hydrogen interactions.

The charge distribution in these allenes is most readily discussed by starting with its variation for the planar structure ($\phi = 0^\circ$) as a function of the degree of bending ($\theta = 180^\circ \rightarrow 90^\circ$). A planar allene may be considered as having an allyl π system perpendicular to the plane of the molecule and a nonbonding sp^2 orbital at C_2 in the plane (see Figure 1). These orbitals contain a total of four electrons for which three configurations ap-

reactions of 1-chlorocyclohexene¹¹⁻¹⁴ and 1-chlorocycloheptene.^{10, 12, 13}

(10) L. K. Montgomery and J. D. Roberts, *J. Amer. Chem. Soc.*, **82**, 4750 (1960).

(11) L. K. Montgomery, F. Scardiglia, and J. D. Roberts, *ibid.*, **87**, 1917 (1965).

(12) L. K. Montgomery, A. O. Clause, A. M. Crelier, and L. E. Applegate, *ibid.*, **89**, 3453 (1967).

(13) L. K. Montgomery and L. E. Applegate, *ibid.*, **89**, 2952 (1967).

(14) (a) L. K. Montgomery and L. E. Applegate, *ibid.*, **89**, 5305 (1967); (b) F. Scardiglia and J. D. Roberts, *Tetrahedron*, **1**, 343 (1957).

(15) (a) P. B. Shevlin and A. P. Wolf, *J. Amer. Chem. Soc.*, **92**, 406 (1970); (b) D. G. Williamson and K. D. Boyes, *ibid.*, **90**, 1957 (1968); (c) H. J. Ache and A. P. Wolf, *Fresenius' Z. Anal. Chem.*, **230**, 19 (1967); (d) R. J. Buenker and S. D. Peyerimhoff, *J. Amer. Chem. Soc.*, **91**, 4342 (1969).

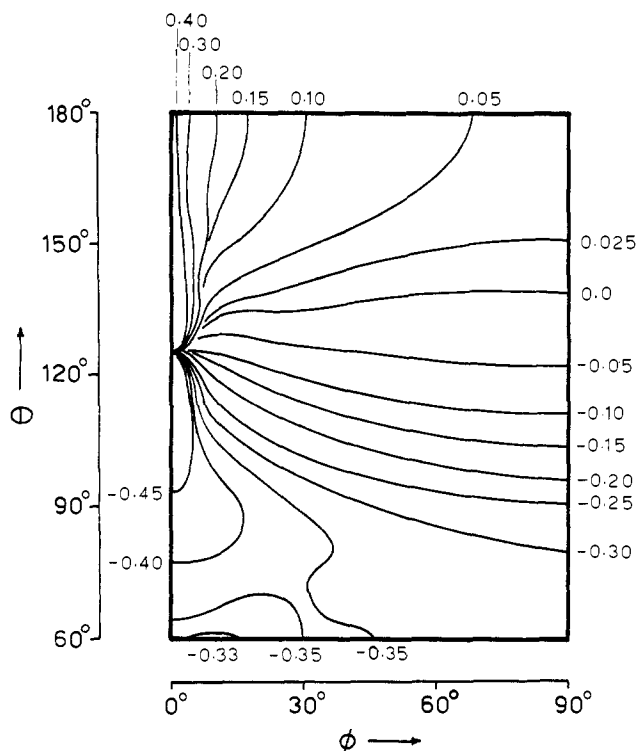


Figure 4. Contour diagram of the total excess charge density at the central atom of a distorted allene molecule as a function of the angles θ and ϕ defined in the text. Note that the separation between the contours does not correspond to equal charge increments in all cases.

pear possible (X, XI, and XII in Figure 1). *A priori* one would expect that, for a bent, planar allene, XII would be the most probable because of the s character of the in-plane orbital at C_2 . However, the four hydrogen atoms are situated in such a manner that hyperconjugation between the C-H bonds and the C_2 in-plane orbital would be a maximum. This hyperconjugation would stabilize a positive charge and destabilize a negative charge in this orbital¹⁶ and leads to the charges on the hydrogens which were noted above.

The variation in charge distribution with θ at $\phi = 0^\circ$ indicates that for $130^\circ \leq \theta \leq 180^\circ$ the planar allene is best described by XI, while for $\theta \leq 120^\circ$ the increase in s character of the nonbonding orbital outweighs the hyperconjugative destabilization mentioned above, and therefore the electronic distribution is best represented by XII. The most striking feature of this figure is the very extreme crossover point which occurs at $\theta = 127\text{--}128^\circ$. These calculations give no evidence for the existence of a structure such as X. Furthermore it should be noted that this region corresponds to the local maximum in energy described in Figure 3. Two possibilities suggest themselves: (a) the results given by the INDO approximate calculations are real and that in this region there would be anticipated a rapid change in the chemical behavior, or, more probably (b) this behavior is an artefact of the INDO approximations and necessitates more sophisticated calculations.¹⁷ This region is of particular interest since this is close to the

(16) This statement is confirmed by an examination of the eigenvalues and eigenvectors obtained in these and *ab initio* calculations.⁵

(17) This objection may be raised, albeit with less force, for all INDO calculations. *Ab initio* calculations, including configuration interaction, on allenes distorted to this geometry are in progress.

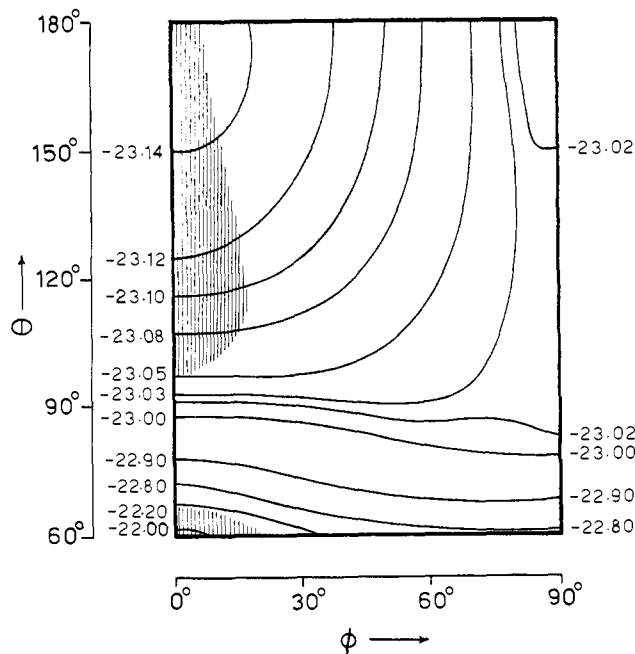


Figure 5. Energy contours (in au) of the lowest energy triplet state of bent and twisted allenes as a function of the angle of bend (θ) and of twist (ϕ). Note that the contours are not separated by equal intervals of energy.

geometry anticipated for the much studied 1,2-cyclohexadiene.

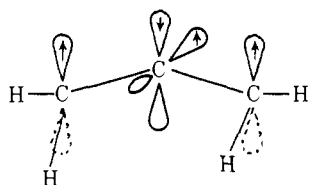
For 1,2-cyclopentadiene and 1,2-cyclobutadiene, XII probably best represents the electronic configuration of the lowest lying singlet states, whereas for 1,2-cycloheptadiene and -cyclooctadiene the geometries may well be such that no clear-cut decision can be made at this stage. 1,2-Cyclononadiene on the other hand behaves quite normally and must certainly be viewed as an essentially undistorted allene. We shall defer further analysis of the chemistry of the small cyclic allenes until after discussion of the results calculated for the triplet states of distorted allene.

Energy Contours for Distorted Triplet Allenes. The energy contour diagram calculated for the triplet state of the distorted allenes, given in Figure 5, is largely as would be expected. The energy minimum occurs for the planar, linear geometry and, as shall be seen, is best described by structure V. The total energy for this geometry ($\theta = 180^\circ$ and $\phi = 0^\circ$) is 85 kcal/mol above the ground state singlet allene ($\theta = 180^\circ$ and $\phi = 90^\circ$) and 12 kcal/mol lower in energy than the singlet state with the same geometry. A local maximum occurs at $\theta = 180^\circ$ and $\phi = 90^\circ$, the geometry of normal ground state allene. This energy is 85 kcal/mol above the minimum calculated for the triplet ($\theta = 180^\circ$ and $\phi = 0^\circ$) and 170 kcal/mol above the minimum calculated for the singlet. Thus an optically active allene should racemize readily upon triplet excitation. No other details of this figure deserve comment except that, whereas the singlet cyclic allenes would continually have a torsional force directed toward the geometry of two orthogonal π systems, any distortion in the triplet would tend to pull the atoms into the "all-coplanar" arrangement.

One final point should be noted: within the shaded area the triplet state allene is calculated to be of lower

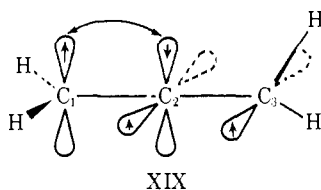
energy than the singlet state allene. Thus it would appear that any singlet allene generated with these geometries, *viz.*, 1,2-cyclohexadiene and 1,2-cyclopentadiene, may well intersystem cross to the triplet manifold.

The spin density distribution contour diagrams for these triplet allenes are quite complex and do not have the symmetry noted for the charge distribution of the singlets. However, the results can conveniently be summarized for the realistic geometries without resorting to the three relevant contour diagrams. There is a large area covering the region $\theta = 90\text{--}180^\circ$ and $\phi = 0\text{--}70^\circ$ wherein the spin density on each carbon is essentially 0.5α , and the spin density on each of the hydrogens is small and negative. This is essentially what would be expected for a planar allyl triplet. There is a



small negative (β) spin density in the p_z orbital on C_2 which is consistent with the expectation from esr studies of the allyl radical.¹⁸

This description appears to be valid even to the region $\theta = 180^\circ$ and $\phi = 85^\circ$ at which point a rapid change takes place and the description XIX becomes more ap-



propriate. In this configuration, the π bond which is weakened by bending is essentially an isolated triplet state olefin while the α and β spins in the unweakened double bond are essentially equally distributed except for a small (10–15%) excess of α spin on C_2 and a corresponding excess of β spin on C_1 . This polarization of the π cloud is consistent with the known mechanisms of spin polarization¹⁹ and is rationalized in terms of Hund's rule (for C_2) and the Pauli principle (for the $C_1\text{--}C_2$ π bond). Some difficulty must be expected in the region $\theta = 180^\circ$ and $\phi = 90^\circ$ for the triplet since two identical, orthogonal π systems are involved. For this reason we considered it of value to carry out a limited optimization of geometry for this particular species. The optimization was performed using a modification of the basic Simplex algorithm.²⁰ In these calculations, H_1 , H_2 , C_1 , and C_2 were forced to remain coplanar as were H_3 , H_4 , C_2 , and C_3 , and these two planes were constrained to be mutually perpendicular. The C–H bond lengths were fixed at 1.08 Å but both the $C_1\text{--}C_2$ and $C_2\text{--}C_3$ bond lengths and the $H_1\text{--}C_1\text{--}H_2$ and $H_3\text{--}$

(18) (a) R. W. Fessenden, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 9, 1968, No. ORGN 85; (b) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **90**, 7157 (1968).

(19) G. R. Underwood, V. L. Vogel, and J. M. Imbriolo, *Mol. Phys.*, **25**, 1093 (1973).

(20) (a) W. Spendley, G. R. Hext, and F. R. Himsworth, *Technometrics*, **4**, 441 (1962); (b) C. W. Lowe, *Trans. Inst. Chem. Eng.*, **42**, T334 (1964); (c) the Simplex method is an iterative process of optimization in many variables, the modifications of which shall be described elsewhere.

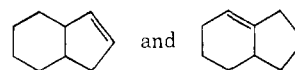
$C_3\text{--}H_4$ bond angles were allowed to vary independently. The most stable triplet allene with these constraints was found to have an energy 29.5 kcal/mol lower than the energy calculated for the triplet at $\theta = 180^\circ$ and $\phi = 90^\circ$ with a fully constrained geometry and 140 kcal/mol higher in energy than calculated for the most stable singlet. The following geometry was obtained: angle $H_1\text{--}C_1\text{--}H_2 = 108.55^\circ$; angle $H_3\text{--}C_2\text{--}H_4 = 108.66^\circ$; length $C_1\text{--}C_2 = 1.28$ Å; length $C_2\text{--}C_3 = 1.45$ Å. This result is totally consistent with the description XIX expected for such a species.

At this juncture it is of interest to examine the behavior of some of the cyclic allenes and compare this information with the results of the calculations given above.

Infrared and nmr spectroscopic studies²¹ of 1,2-cyclononadiene indicate that there is some strain in the allene moiety although in its chemical properties this is essentially a normal allene;²² apparently it has a

(21) G. C. Joshi, G. Nagendrappa, and D. Devaprabhakara, *Indian J. Chem.*, **7**, 296 (1969).

(22) 1,2-Cyclononadiene has been prepared by elimination of HX from halocyclononenes^{1b,23} and by the "carbene" method.²⁴ It undergoes electrophilic additions with a wide variety of compounds,^{25b,25} cycloadditions (including dimerization),^{24g,26} reductions,^{23b,27} oxidations,^{23b,25e,28} and isomerizations.^{23b,29} In all of these reactions the products are essentially those which would be expected by analogy with the chemistry of acyclic allenes. However, there are several reactions of 1,2-cyclononadiene in which the presence of the ring seems to be important. Transannular as well as simple 1,2 addition occurs in its bromination.^{25f-i} Pyrolysis yields acyclic



products.³⁰ The intermediacy of a (presumably singlet) planar diradical



has been suggested³⁰ in this reaction. Inspection of the contour diagrams in this paper indicates that a planar, singlet diradical (see Figure 3) would be unstable with respect to the normal allene. The planar, triplet diradical (see Figure 5) could, however, be an intermediate. Finally, on photolysis 1,2-cyclononadiene forms products derived from 9-carbenabicyclo[6.1.0]nonane to a much greater extent than would be predicted from the photochemistry of acyclic allenes.^{31a-c} It has been suggested^{31c} that the origin of this effect may lie in stabilization, by ring induced bending at C-2, of the structure XI which is the only singlet form allowed, by symmetry, to cyclize.^{31c} Our calculations (see Figure 4), however, indicate that this charge distribution occurs only if the C–C–C bond angle is less than 130° , which is a considerable amount of bending to be induced by the presence of the ring. In addition, the calculations described in this paper indicate (see Figure 3) that the planar singlet is unstable with respect to the orthogonal singlet at all values of the C–C–C angle. Therefore, some other explanation of the photochemical behavior of 1,2-cyclononadiene should be sought. (It should be noted that the triplet state is probably not involved, as the orthogonal triplet, the only form for which the closure is symmetry allowed,^{31c,d} is unstable (see Figure 5) with respect to the planar triplet.)

(23) (a) W. J. Ball and S. R. Landar, *Proc. Chem. Soc., London*, 143 (1961); (b) W. R. Moore and R. C. Bertelson, *J. Org. Chem.*, **27**, 4182 (1962); (c) A. T. Blomquist, R. E. Burge, Jr., and A. C. Suscys, *J. Amer. Chem. Soc.*, **74**, 3636 (1952); (d) A. T. Blomquist and J. C. Bohrer, *ibid.*, **74**, 3643 (1952).

(24) (a) L. Skattebøl, *Tetrahedron Lett.*, 167 (1961); (b) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **27**, 4179 (1962); (c) P. D. Gardner and M. Narayana, *ibid.*, **26**, 3518 (1961); (d) L. Skattebøl, *Acta Chem. Scand.*, **17**, 1683 (1961); (e) C. L. Osborn, T. C. Shields, B. A. Shoulters, C. G. Cardenas, and P. D. Gardner, *Chem. Ind. (London)*, 766 (1965); (f) H. Nozaki, T. Aratani, and R. Noyari, *Tetrahedron*, **23**, 3645 (1967); (g) A. C. Cope, W. R. Moore, R. D. Bach, and H. J. S. Winkler, *J. Amer. Chem. Soc.*, **92**, 1243 (1970).

geometry very close to $\theta = 180^\circ$ and $\phi = 90^\circ$ ³² and a relatively normal electronic distribution. 1,2-Cyclooctadiene has not been isolated although its detection in solution by ir spectroscopy has been reported.³⁴ Attempts to concentrate the compound resulted in dimerization.^{1b, 23a} Chemical evidence for its fleeting existence includes catalytic hydrogenation to cyclooctane³⁴ and trapping with HCl³⁴ and bromine.³⁵ None of these data requires unusual charge distributions.

In view of this apparent instability of the cyclooctadiene, it is surprising that 1,2-cycloheptadiene is reported³⁶ as being capable of being distilled (120°) and is claimed to have been characterized by molecular weight determination (93.1; cf. 94) and by oxidation with ozone to the expected³⁷ adipic acid and with potassium permanganate to the expected³⁷ pimelic acid. This material was reportedly prepared by the dehalogenation of 1-chloro-2-bromocyclohept-1-ene with sodium, for which an intermediate cycloheptyne was proposed. The aromatic trimer of cycloheptyne was isolated. There is nothing in our calculations to suggest unusual stability for this molecule, and in view of the fact that no other attempt to isolate the compound^{1b, 23a, 38} has been successful this report appears to be in error. However, to our knowledge, there is no record in the literature of any attempt to repeat this reaction or to identify the product.

The chemistry of 1,2-cyclohexadiene has been thoroughly studied largely due to the effort of Moore

(25) (a) R. K. Sharma, B. A. Shoulders, and P. D. Gardner, *J. Org. Chem.*, **32**, 241 (1967); (b) R. D. Bach, *Tetrahedron Lett.*, 5841 (1968); (c) R. D. Bach, *J. Amer. Chem. Soc.*, **91**, 1771 (1969); (d) R. D. Bach and H. F. Henneke, *ibid.*, **92**, 5589 (1970); (e) R. D. Bach, U. Mazur, R. N. Brummel, and L.-H. Lin, *ibid.*, **93**, 7120 (1971); (f) D. K. Wedegaertner and M. J. Millam, *J. Org. Chem.*, **33**, 3943 (1968); (g) M. S. Baird, C. B. Reese, and A. Shaw, *Tetrahedron*, **27**, 231 (1971); (h) C. B. Reese and C. A. Shaw, *J. Amer. Chem. Soc.*, **92**, 2566 (1970); (i) L. R. Byrd and M. C. Caserio, *ibid.*, **93**, 5758 (1971); (j) T. L. Jacobs and R. Macomber, *J. Org. Chem.*, **33**, 2988 (1968).

(26) (a) W. R. Moore, H. W. Anderson, S. D. Clark, and T. M. Ozretich, *J. Amer. Chem. Soc.*, **93**, 4932 (1971); (b) G. Wittig, H. L. Dorsch, and J. Meske-Schueller, *Justus Liebigs Ann. Chem.*, **711**, 55 (1968); (c) L. Skattebøl and S. Solomon, *J. Amer. Chem. Soc.*, **87**, 4506 (1965); (d) S.-H. Dai and W. R. Dolbier, Jr., *ibid.*, **94**, 3946 (1972); (e) W. Weyler, Jr., L. R. Byrd, M. C. Caserio, and H. W. Moore, *ibid.*, **94**, 1027 (1972); (f) M. Bertrand, J.-L. Gras, and J. Goré, *Tetrahedron Lett.*, 1189 (1972); (g) W. R. Moore, R. D. Bach, and T. M. Ozretich, *J. Amer. Chem. Soc.*, **91**, 5918 (1969).

(27) (a) M. M. Bhagwat and D. Devaprabhakar, *Tetrahedron Lett.*, 1391 (1972); (b) D. Devaprabhakar and P. D. Gardner, *J. Amer. Chem. Soc.*, **85**, 1458 (1963).

(28) P. Kolsaker and B. Teige, *Acta Chem. Scand.*, **24**, 2101 (1970).

(29) W. R. Moore and H. R. Ward, *J. Amer. Chem. Soc.*, **85**, 86 (1963).

(30) J. K. Crandall and R. J. Watkins, *Tetrahedron Lett.*, 1251 (1970).

(31) (a) H. R. Ward and E. Karafiath, *J. Amer. Chem. Soc.*, **90**, 2193 (1968); (b) H. R. Ward and E. Karafiath, *ibid.*, **91**, 522 (1969); (c) H. R. Ward and E. Karafiath, *ibid.*, **91**, 7475 (1969); (d) W. T. Borden, *Tetrahedron Lett.*, 447 (1967).

(32) Another indication that 1,2-cyclooctadiene has this normal geometry, or one very similar to it, is the fact that it, like acyclic 1,3-disubstituted allenes, occurs as a pair of resolvable enantiomers.^{24g, 26a, g, 33}

(33) (a) G. Krow, *Top. Stereochem.*, **3**, 31 (1970); (b) P. Crabbé, E. Velande, H. W. Anderson, S. D. Clark, W. R. Moore, A. F. Drake, and S. F. Mason, *Chem. Commun.*, 1261 (1971); (c) W. R. Moore and R. D. Bach, *J. Amer. Chem. Soc.*, **94**, 3148 (1972).

(34) E. T. Marquis and P. D. Gardner, *Tetrahedron Lett.*, 2793 (1966).

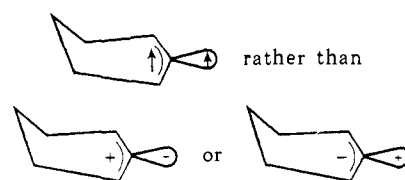
(35) C. B. Reese and A. Shaw, *ibid.*, 4641 (1971).

(36) A. E. Favorskiĭ, *J. Gen. Chem. USSR*, **6**, 720 (1936).

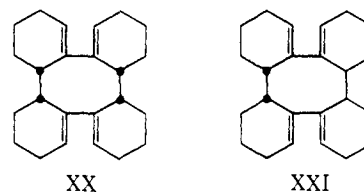
(37) D. R. Taylor, *Chem. Rev.*, **67**, 317 (1967).

(38) (a) G. Wittig and J. Meske-Schueller, *Justus Liebigs Ann. Chem.*, **711**, 76 (1968); (b) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); (c) W. R. Moore and H. R. Ward, *Chem. Ind. (London)*, 594 (1961); (d) W. R. Moore and H. R. Ward, *J. Amer. Chem. Soc.*, **83**, 2019 (1961); (e) E. T. Marquis and P. D. Gardner, *Chem. Commun.*, 726 (1966).

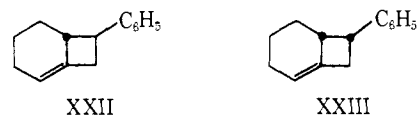
and coworkers.^{1a, 39} We address ourselves here to the question of the probable electronic structure of this species. From our calculations, it would appear that the most stable electronic configuration is the triplet.



The experimental behavior of this species is interesting and worthy of some comment at this point. Its preparation has been attempted by the treatment of 1-bromocyclohexene as mentioned above^{6,7} and also by the "carbene" method, *viz.*, treatment of 6,6-dibromobicyclo[3.1.0]hexane with methyllithium.^{1, 39} The most significant reactions of the product of these reactions appear to us to be the formation of dimers, trimers, etc. When this product was generated at -80° by the "carbene" method the tetramers, XX and XXI, were formed along with small amounts of trimers.¹

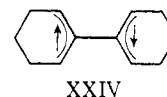


However, reaction in refluxing ether¹ produced mainly the dimer XVII. In neither case could any carbene products be isolated. Although neither the allene nor the carbene could be trapped with cyclohexene, isobutylene, or furan,¹ in the presence of styrene³⁹ two isomeric adducts, XXII and XXIII, are formed without



the production of any poly(styrene).

To rationalize these data, Moore and Moser³⁹ have proposed that initially 1,2-cyclohexadiene is generated with the geometry IV as the singlet diradical. It was suggested that this singlet could be trapped by styrene without causing its polymerization. Because of the dependence of the product composition on temperature they suggested that, in the absence of styrene, an "excited dimer," formulated as a singlet diradical, XXIV, is formed. At low temperatures this could



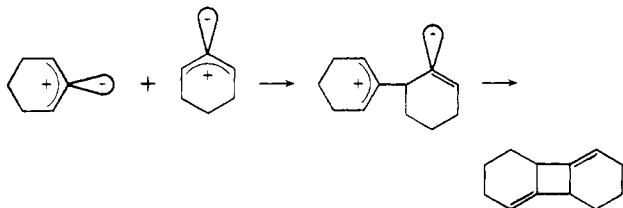
accumulate in sufficiently high concentrations to dimerize to the allene tetramer or to react with another molecule of allene to yield the trimer. However, at higher temperatures they suggested that the "excited dimer" crossed to the ground state triplet. This triplet could then cyclize in an allowed⁴⁰ conrotatory

(39) W. R. Moore and W. R. Moser, *J. Org. Chem.*, **35**, 908 (1970).

(40) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

manner to give the observed dimer.⁴¹ The singlet, however, would be predicted to undergo disrotatory closure to give the *cis* isomer,⁴¹ a product which is not observed.

Based on the assumption that the dimers, trimers, etc., are not isomerized under the reaction conditions⁵⁰ to the thermodynamically most stable isomer, it appears that the zwitterionic forms can be ruled out since their coupling would be expected to lead to isomers which are not observed, *e.g.*



This then raises the question: are these calculations correct in predicting the stability of the triplet diradical form? Moore and Moser³⁹ ruled out this possibility on the basis that this would lead to a triplet diradical adduct with styrene which, it was assumed, would induce polymerization of the styrene. The corresponding singlet diradical, it was proposed, might well have a sufficiently short lifetime so as not to cause any polymer formation. It should be noted, however, that the triplet 1,4 diradical may have a sufficiently short lifetime so that no polymer would be observed. Thus, for example, Viehe⁵¹ has proposed the intermediacy of the, presumably triplet, diradicals, XXV and XXVI, in the oligomerization of *tert*-butylfluoroacetylene. This postulate was based upon trapping experiments involving styrene and acrylonitrile in which no polymer was formed. Given this result then,

(41) Although symmetry considerations based on zeroth order extended Hückel calculations would predict that the planar, singlet 2,2'-bisallyl diradical should close in a disrotatory manner,⁴²⁻⁴⁴ more sophisticated calculations⁴⁴ throw doubt upon this conclusion. Furthermore, the lowest singlet state of this species is believed to have the two π systems effectively orthogonal,^{45, 46} for which calculations support both conrotatory^{43, 44} and disrotatory⁴⁴ closure. Experimentally, the mode of closure does not appear to be completely resolved, some experiments indicating conrotatory closure,^{43, 46, 47} some disrotatory closure,^{26g, 42, 48} and some suggesting a competition between both modes.⁴⁹

(42) O. J. Muscio, Jr., and T. L. Jacobs, *Tetrahedron Lett.*, 2867 (1969).

(43) T. L. Jacobs, J. R. McClenon, and O. J. Muscio, Jr., *J. Amer. Chem. Soc.*, **91**, 6038 (1969).

(44) B. A. Odell, R. Hoffmann, and A. Imamura, *J. Chem. Soc. B*, 1675 (1970).

(45) (a) J. J. Gajewski and C. N. Shih, *J. Amer. Chem. Soc.*, **89**, 4532 (1967); (b) W. von E. Doering and W. R. Dobier, Jr., *ibid.*, **89**, 4534 (1967).

(46) J. J. Gajewski and C. N. Shih, *ibid.*, **91**, 5900 (1969).

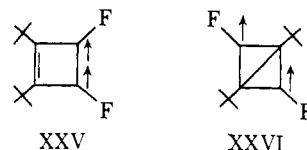
(47) (a) T. L. Jacobs and W. L. Petty, *J. Org. Chem.*, **28**, 1361 (1963); (b) A. Roedig and N. Detzer, *Justus Liebigs Ann. Chem.*, **710**, 1 (1967); (c) A. Roedig and N. Detzer, *Angew. Chem.*, **80**, 482 (1968); (d) R. Maurin, G. Leandri, and M. Bertrand, *Bull. Soc. Chim. Fr.*, 530 (1971); (e) E. V. Dehmlow, *Tetrahedron Lett.*, 4283 (1969); (f) S. R. Byrn, E. Maverick, O. J. Muscio, Jr., K. N. Trueblood, and T. L. Jacobs, *J. Amer. Chem. Soc.*, **93**, 6680 (1971).

(48) (a) P. D. Landor and S. R. Landor, *J. Chem. Soc.*, 2707 (1963); (b) M. Bertrand, H. Reggio, and G. Leandri, *C. R. Acad. Sci., Ser. C*, **259**, 827 (1964); (c) E. V. Dehmlow, *Chem. Ber.*, **100**, 3260 (1967).

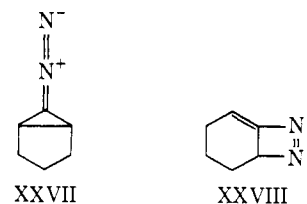
(49) (a) H. A. Staab and H.-A. Kurmeier, *ibid.*, **101**, 2697 (1968); (b) J. J. Gajewski and W. A. Black, *Tetrahedron Lett.*, 899 (1970); (c) E. V. Dehmlow and G. C. Ezimora, *ibid.*, 1265 (1972).

(50) (a) The dimer, XVII, is stable under the reaction conditions; (b) W. R. Moore, P. D. Mogoiesko, and D. D. Traficante, *J. Amer. Chem. Soc.*, **94**, 4753 (1972).

(51) (a) H. G. Viehe, R. Merényi, J. F. M. Oth, and P. Valange, *Angew. Chem.*, **76**, 884 (1964); (b) H. G. Viehe, R. Merényi, J. F. M. Oth, J. R. Sanders, and P. Valange, *ibid.*, **76**, 922 (1964); (c) R. Merényi, J. F. M. Oth, J. R. Sanders, and P. Valange, *Angew. Chem., Int. Ed. Engl.*, **3**, 755 (1964); (d) H. G. Viehe, *ibid.*, **4**, 776 (1965).

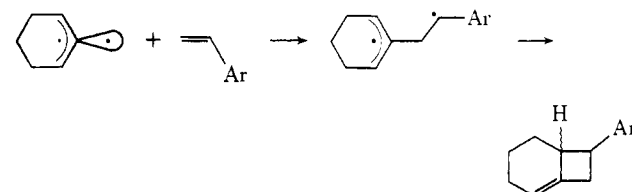


the experimental data for 1,2-cyclohexadiene do appear to be compatible with intersystem crossing to the triplet manifold. Dimerization of two of these triplet allenes, forming a singlet diradical, leads to products while trapping with styrene might lead to a diradical with a sufficiently short lifetime such as to avoid polymerization. It is also possible that the styrene captures the singlet allene before it intersystem crosses to the triplet. At this stage it would appear desirable to attempt the formation of both the singlet and triplet states of 1,2-cyclohexadiene. Appropriate starting points for such an experiment would appear to be the direct and sensitized photolyses of 6-diazobicyclo[3.1.0]hexane, XXVII, and 7,8-diazabicyclo[4.2.0]octa-1,7-diene, XXVIII, carried out both in the presence

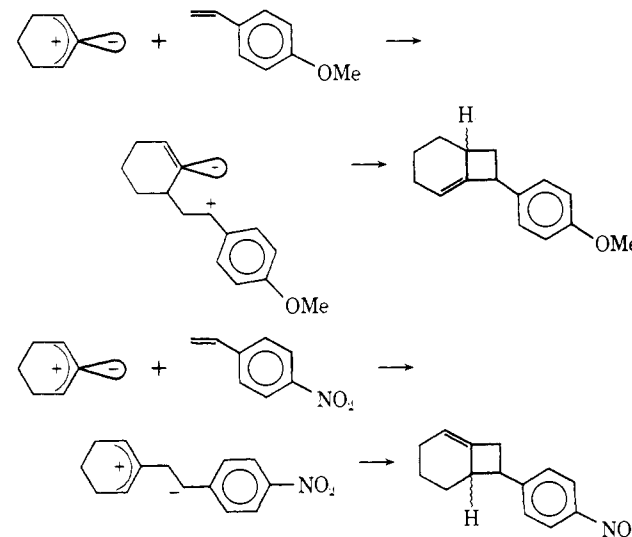


and the absence of styrene.⁵²

(52) If the adducts with styrene are shown to be formed from the singlet allene it may also be possible to experimentally distinguish, by trapping 1,2-cyclohexadiene with styrenes having electron withdrawing and electron releasing substituents in the para position, which of the possible electronic distributions (singlet diradical, X, or zwitterionic, XI or XII) is utilized. If the singlet diradical is involved both substituted styrenes should give products analogous to those, XXII and XXIII, formed by styrene itself.



However, if zwitterionic forms are involved a different type of product would be expected for *one* of the styrenes (assuming that the attack occurs at the carbon which, in the allene, would satisfy the electronic demands of the para substituent in the styrene).



If the charges in the allene were reversed the *p*-nitrostyrene would form products analogous to those of *p*-methoxystyrene, and *vice versa*.

As mentioned above, there appears to have been no serious attempt to generate 1,2-cyclopentadiene. From our calculations this suggests itself as a fruitful field of study since not only should such species be readily available from the bicyclopentane precursors, but the decrease in the internal bond angle may well be sufficient to cause the drastic change in the electronic structure of the allene moiety suggested by these calculations. If such were the case, the chemical behavior

of this species would be expected to be very much different from that of 1,2-cyclohexadiene.

Acknowledgments. We gratefully acknowledge financial support from the Petroleum Research Fund, administered by the American Chemical Society. One of us (P. W. D.) is on educational leave of absence from Union Carbide Corporation, Chemicals and Plastics Division, Research and Development Laboratories, Tarrytown, New York.

Substituent Effects in the Radical Trichloromethylation of 9-X-Anthracenes. An Observed Linear Free Energy Relationship¹

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Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331. Received October 17, 1973

Abstract: The reaction rates of the trichloromethyl radical addition to a series of 9-substituted anthracenes relative to *trans*-stilbene have been determined at 70.0°. It is demonstrated here that there is a definite substituent dependence for this addition reaction, and that when the logarithms of the relative rates are plotted *vs.* Brown's σ_p^+ substituent parameters for the 9-X-anthracenes, good correlation is obtained ($r = 0.970$) with $\rho^+ = -0.83$. Significant deviations from this line are observed for two types of compounds. The deviation for compounds such as 9-nitroanthracene is explained in terms of steric inhibition of resonance. Compounds with readily abstractable hydrogen atoms such as 9-methylanthracene tend to undergo appreciable side-chain reaction.

We have reported on the relative reactivities of a series of arylmethanes toward hydrogen atom abstraction by the trichloromethyl radical.^{3,4} The kinetics were shown to exhibit a spread of about three powers of ten for the 13 compounds studied. Not only were the reactivities dependent on the aryl moiety but also were quite dependent on the position of the methyl group; the three methylanthracenes had, for example, a rate spread of about 20. Experimentally it was known, however, that the course of reaction of this series of compounds was not clean. The scope of possible reactions involving addition to the aromatic ring *are outlined* in Scheme I. The magnitude of the radical addition problem was clearly illustrated when a series of arylmethanes was subjected to hydrogen abstraction by bromine atom.⁵ Gilliom and coworkers found that compounds which were anthracene or pyrene derivatives did not afford side-chain bromination but rather a rapid ring substitution reaction. The above considerations served to spur our interest in the reaction of the trichloromethyl radical with aromatic systems.

In an early investigation on the process of radical addition to aromatics, Kooyman and Farenhorst

(1) Presented at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1973.

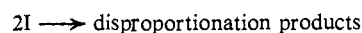
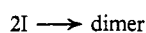
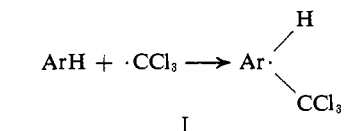
(2) (a) National Defense Education Act Title IV Fellow, 1971-present; (b) National Science Foundation Trainee, 1966-1970.

(3) J. D. Unruh and G. J. Gleicher, *J. Amer. Chem. Soc.*, **91**, 6211 (1969).

(4) J. D. Unruh and G. J. Gleicher, *J. Amer. Chem. Soc.*, **93**, 2008 (1971).

(5) R. B. Roark, J. M. Roberts, D. W. Croom, and R. D. Gilliom, *J. Org. Chem.*, **37**, 2042 (1972).

Scheme I. Trichloromethyl Radical Addition to Aromatic Hydrocarbons and Reaction Pathways Available to the Intermediate Radical



studied the addition of trichloromethyl radicals to *n*-hexadecene and styrene.⁶ They found that these reactions were retarded by added aromatic hydrocarbon and from the extent of retardation were able to measure the relative rates of reactivities of the various aromatics toward the trichloromethyl radical. It was found that an approximate linear relationship held between the logarithms of the relative rate constants and the maximum free valencies (F_{max} , as calculated by a Hückel molecular orbital approach) for the respective aromatic compounds. In a related study, Levy and Szwarc developed a method for determining the reactivities of methyl radicals toward a series of aromatic hydrocarbons.⁷ The similarity of the results implies that

(6) E. C. Kooyman and E. Farenhorst, *Trans. Faraday Soc.*, **49**, 58 (1953).

(7) M. Levy and M. Szwarc, *J. Amer. Chem. Soc.*, **77**, 1949 (1955).