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THEORETICAL REACTION PATHS FOR CATION RADICAL CYCLOADDITIONS

THE [3+2] OR ROLE-REVERSED CATION RADICAL DIELS–ALDER

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Abstract—An extended basis set *ab initio* reaction path calculation for the prototype role-reversed cation radical Diels–Alder reveals that even this symmetry-forbidden cyclization mode proceeds without activation, at least in the gas phase. An intermediate, termed a long-bond complex, is encountered on the path, but the energy minimum is so shallow that the reaction is considered likely to be concerted when entropy effects are considered. The calculation further reveals that the factor which importantly distinguishes the role-reversed cycloaddition mode from the allowed cycloaddition mode, namely, the presence of charge predominantly on the diene moiety as contrasted to the dienophilic moiety, is maintained well along the reaction path and even in the long-bond intermediate. Competition between the role-reversed Diels–Alder and a competing [2+1] cyclobutane cycloaddition is envisioned.

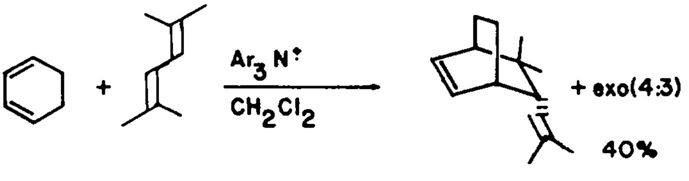
INTRODUCTION

The Diels–Alder reaction must be considered the best known and one of the most synthetically useful of the cycloaddition reactions. Its modest degree of stereo- and regioselectivity is remarkably predictable.[1] However, a recognized limitation to the generality of the Diels–Alder reaction is the poor reactivity of approximately neutral or electron-rich dienophiles.[2] The potential utility of cation radicals as highly electron deficient and therefore extremely reactive dienophiles is particularly significant in view of the complementarity of such an approach to the classic Diels–Alder reaction. That is, electron-rich compounds, normally ineffective as Diels–Alder dienophiles, are precisely those which are most readily oxidized to the corresponding cation radicals.

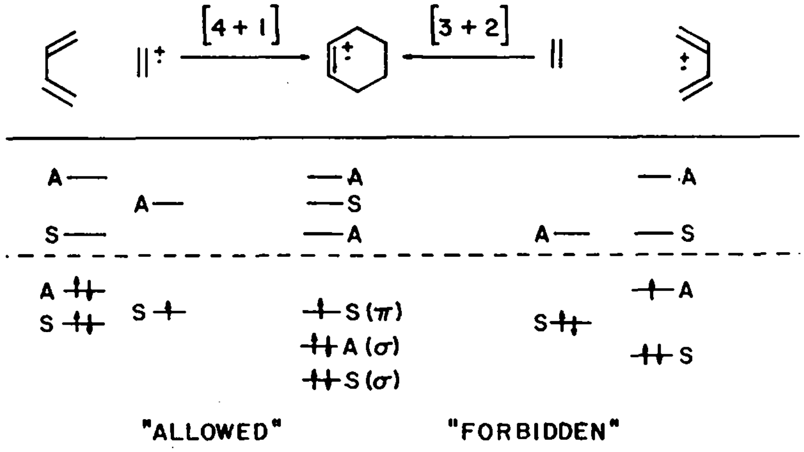
The exceptional reactivity and selectivity of cation radicals of certain electron-rich olefins and conjugated dienes as dienophilic components in Diels–Alder cycloaddition reactions is now well documented.[3-5] Indeed, it has emerged that for many dienes, electron-rich olefins and styrenes the cation radical catalyzed Diels–Alder is a viable and quite attractive synthetic method. Catalysts include aminium salts,[3] polymer supported cation radicals[6] and zeolites.[7] A photochemical procedure based on photosensitized electron transfer has also been developed.[5,8] In each case, the cation radical catalyzed Diels–Alder reaction shows phenomenal rate enhancements relative to the neutral reaction, accompanied by outstanding *endo*- and regioselectivities, which often far exceed those typical of the uncatalyzed Diels–Alder reaction.

An example of the powerful kinetic impetus of the cation radical catalyzed Diels–Alder reaction is illustrated by the reaction of 1,3-cyclohexadiene and 2,5-dimethyl-2,4-hexadiene (Scheme 1).[3] The Diels–Alder reaction has a pronounced sensitivity to steric effcts,[2] and it is probably for this reason that the latter diene has not been reported to react in the Diels–Alder reaction under normal conditions as either a dienic or dienophilic addend. Yet, when equimolar amounts of these dienes are mixed with a catalytic amount (5–10 mol%) of tris(*p*-bromophenyl)aminium hexachloroantimonate in methylene chloride at 0°, the indicated *endo*/*exo* (4:3) Diels–Alder adduct pair is formed in 40% yield. The net result of this process is the incorporation of a relatively electron rich, hindered, trisubstituted double bond as the dienophilic component in a reaction with a relatively poor Diels–Alder diene, so as to install a quaternary carbon in the adduct under very mild conditions.

The discovery that cation radical catalysis in the Diels–Alder reaction can engender such an enormous rate enhancement poses the question of the theoretical basis for the kinetic impetus.[9,10] Few pericyclic reactions involving species with doublet spin are symmetry allowed,[11] but the cation radical catalyzed Diels–Alder reaction is such a reaction. From the orbital correlation diagrams in Scheme 2 one can see that cycloaddition of the ethene cation radical to *s-cis*-1,3-butadiene is symmetry allowed. Interestingly, the role-reversed cycloaddition of the *s-cis*-1,3-butadiene cation radical and ethene is forbidden. The predicted preference of the cation radical for the dienophilic



Scheme 1.

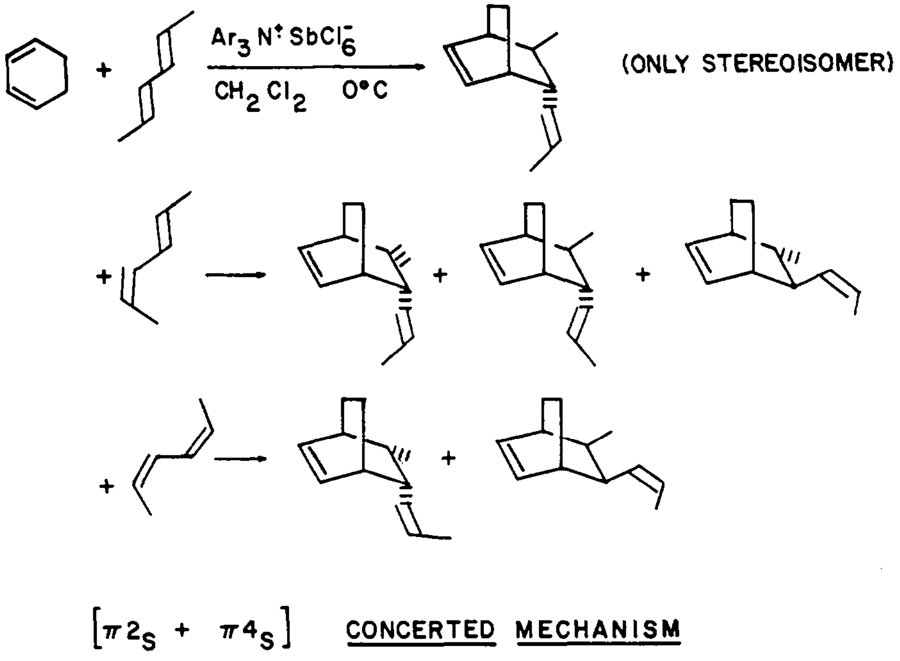


Scheme 2. Orbital correlation diagrams for the cation radical Diels–Alder.

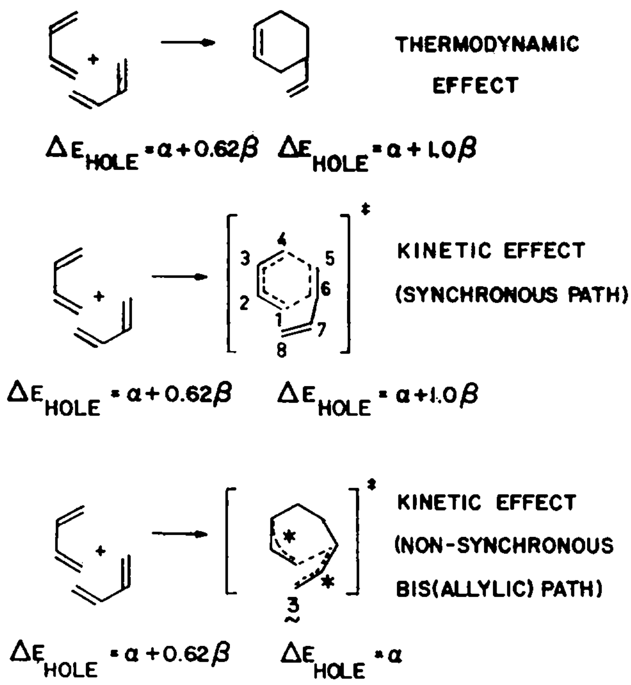
role has been observed experimentally and been termed role selectivity.[4] Indeed, this concept of role selectivity receives substantial support from mass spectrometric studies of the ionized retro-Diels–Alder reaction.[12,13] It should be emphasized that since this role selectivity is not available in the classic Diels–Alder reaction, an extra element of control is added in synthetic strategies employing the cation radical catalyzed Diels–Alder reaction.

Allowed pericyclic reactions normally proceed via concerted bond forming mechanisms. The Diels–Alder reaction is experimentally characterized by suprafacially stereospecific addition to both the diene and dienophile. The same appears to be true of the cation radical catalyzed version of the Diels–Alder reaction. A series of reactions between 1,3-cyclohexadiene and the three geometric isomers of the 2,4-hexadiene cation radical (Scheme 3) unequivocally demonstrate suprafacial stereospecificity with respect to the dienophile.[3] It has thus far been impossible to demonstrate rigorously the suprafacial stereospecificity with respect to the diene component as a result of the unreactivity of *E,Z* and *Z,Z* terminally disubstituted dienes, but suprafacial addition has been exclusively observed with every diene examined thus far. Thus, theory and experiment justify characterizing the cation radical catalyzed Diels–Alder reaction as a pericyclically allowed reaction proceeding via, at least nominally, a concerted bond forming process.

The powerful kinetic impetus of the cation radical catalyzed Diels–Alder reaction has been postulated to be derived from a unique transition state.[9] Obviously, there is little or no thermodynamic advantage for the cation radical process since the delocalization of the hole is actually diminished upon conversion of



Scheme 3.



Scheme 4. Effect of hole formation on the cation radical Diels–Alder.

the reactants to the product. This is illustrated by the dimerization of 1,3-butadiene in Scheme 4, where the reactant *s-cis*-1,3-butadiene cation radical is compared to the adduct cation radical, an olefin cation radical. Using a previously stated FMO argument,[9] the reactant diene has a HOMO (highest occupied molecular orbital) of energy $E = \alpha + 0.62\beta$ in the HMO approximation. The ethenic double bond in the adduct has a corresponding HOMO of energy $E = \alpha + 1.0\beta$. Therefore, hole formation requires 0.38β more energy in the product than in the reactants. Fully optimized MINDO/3 calculations have also been carried out on both the neutral and cation radical reaction paths for the Diels–Alder dimerization of *s-cis*-1,3-butadiene and indeed the cation radical version of the Diels–Alder reaction was found to be less exothermic. Therefore the kinetic advantage of the cation radical catalyzed Diels–Alder reaction is not related to the development in the transition state of any special product stability. In fact, this impetus is achieved in spite of any product character development. A rationalization of the kinetic impetus of the cation radical catalyzed Diels–Alder reaction based on a conventional description of the transition state of an allowed, concerted, synchronous pericyclic reaction, which would involve a cyclic (benzene-like) array of orbitals as a transition state model, is equally inadequate. Hole formation in a benzene-like cyclic system formally requires $E = \alpha + 1.0\beta$. Kinetically, the cation radical process is still 0.38β less favorable than the neutral version.

The inability of the previous transition state models to provide an adequate rationalization for the basis of the observed kinetic effect in the cation radical catalyzed Diels–Alder reaction suggests that the structural model employed must not accurately approximate the transition states for the two processes. Although there is still some debate concerning whether the transition state for the prototype neutral Diels–Alder reaction between ethene and *s-cis*-butadiene is[14] or is not[15] approximately synchronous (i.e. involving roughly equal pericyclic perturbations at the newly forming bond sites, as was implied in the previous transition state model), there is little doubt that in reactions involving unsymmetrical addends the transition state must become quite nonsynchronous. That is, the transition state for the Diels–Alder dimerization of *s-cis*-butadiene could be modeled as though one bond were almost completely formed and there was but a relatively small pericyclic interaction at the second bond forming site. This model approaches a bis(allylic) structure. Hole formation in an allylic system is exceedingly facile since the HOMO is nonbonding. Employing the FMO framework, $E = \alpha$ in the HMO approximation; ionization in the transition state is now 0.62β more favorable than in the reactants. Therefore, not only is a highly nonsynchronous (yet concerted) model of the transition state for both the neutral and cation radical versions of the Diels–Alder reaction the most theoretically plausible, it also appears uniquely capable of providing an explanation for the tremendous kinetic impetus in the cation radical catalyzed Diels–Alder reaction.

The fully optimized MINDO/3 reaction path of the cation radical version of the dimerization of *s-cis*-1,3-butadiene was found to be in fair accord with these predictions. MINDO/3 has a tendency to overestimate the diradical nature of pericyclic reaction paths.[16, 17] Thus, not unexpectedly, MINDO/3 predicts a two-step pathway with a bis(allyl)-like acyclic intermediate. However, the 7.88 and 9.34 kcal mol^{-1} activation energies found for the two bond forming steps are in good accord with the expected large kinetic effects. The calculated effect of hole formation in the Diels–Alder reaction is thus a general lowering of the activation energy by 25–30 kcal mol^{-1} as compared with the corresponding neutral reaction.[9]

Further theoretical and experimental work has shown that hole catalysis may indeed be a general phenomenon for cycloaddition and other pericyclic reactions which can proceed via non-synchronous pathways. MINDO/3 calculations of the Huisgen-type dipolar cycloaddition of the diazomethane cation radical and ethene,[18] and the Cope sigmatropic rearrangement of 1,5-hexadiene cation radical[9] predicted these reactions to be stepwise processes with very low barriers to bond formation. In fact, the cation radical [3,3] sigmatropic rearrangement of 1,3,4-triphenyl-1,5-hexadiene has now been demonstrated in the laboratory.[19]

Unlike the cation radical Diels–Alder reactions discussed thus far, the [2+1] cycloaddition of a neutral alkene and an olefin cation radical is symmetry forbidden. Yet hole catalyzed cyclodimerization of olefins is known to be feasible and often very facile. Numerous examples of cation radical catalysis of cyclodimerizations of electron-rich alkenes and styrenes have been reported.[20–22] For these reactions, the cyclic array of orbitals in the pericyclic transition state can account for at least part of the observed kinetic effect, regardless of whether the reaction path is synchronous or nonsynchronous. For a synchronous path the transition state would resemble a cyclobutadiene-like array of orbitals. Hole formation would formally require only $E = \alpha$, compared to $E = \alpha + \beta$ in the reactant. In the non-synchronous path the transition state can be modeled as a tetramethylene diradical. Assuming a very small 1,4-pericyclic interaction, hole formation again requires only $E = \alpha$. Thus a large kinetic effect would be predicted for the cation radical process relative to the neutral reaction. This was confirmed calculationally by studying the [2+1] cycloaddition of ethene and the ethene cation radical using the MNDO semiempirical method.[9,23–25] The MNDO reaction path is a stepwise one involving a tetramethylene cation/radical, and the activation energy for the rate determining step is 1.3 kcal mol^{-1}, more than 60 kcal mol^{-1} less than the calculated or experimentally observed value for the corresponding neutral reaction.[26] The cation radical catalyzed Diels–Alder reaction and the [2+1] cycloaddition reaction are thus both predicted to have very low barriers to reaction. Experimental results suggest at least a modest advantage for the cation radical catalyzed Diels–Alder process relative to the [2+1] cycloaddition for diene reactants. However, some precedent now exists for selective cyclobutane adduct formation in competition with Diels–Alder addition in certain cation radical cycloadditions.[27] Interestingly, the product cyclobutane cation radical in the MNDO reaction path calculation prefers an unsymmetrical, trapezoidal, structure which has one long, one-electron bond of 1.92 Å. Indeed, there is strong theoretical support for the existence of long-bond structures for alkene σ cation radicals in general.[23] The MNDO reaction path calculation also predicts a shallow minimum for a diradical-type intermediate (tetramethylene cation radical) just before closing of the second bond to form the long-bond cyclobutane cation radical. However, the existence of a diradical-like intermediate has been virtually ruled out in at least one case by the fact that the [2+1] cycloaddition reactions of *cis*- and *trans*-anethole are stereospecific.[28] The proposed mechanism for the [2+1] cycloaddition reaction based on these results ignores the MNDO prediction of an open, tetramethylene cation/radical intermediate and foresees concerted addition of a neutral alkene and an alkene cation radical to form a long bonded cylobutane which can then electron transfer subsequent to or concomitant with collapse to the normal cyclobutane-type structure. The stereochemical integrity of the reactants is thus retained by virtue of the long-bond intermediate. In fact, this one-electron bond is moderately strong. The dissociation energy for the one-electron bond in the ethane cation radical is estimated to be at least 38 kcal mol^{-1}.[23] This is supported by a CIDNP study of *cis*- and *trans*-1,2-diphenylcyclopropane cation radicals which found these species to exist in non-equilibrating, one-electron, long-bond ground state geometries.[29]

The [2+1] reaction path was then more closely scrutinized using the *ab initio* SCF MO method (6-31G*//3-21G basis set).[25] The *ab initio* path differs in detail from the MNDO path, but once again reproduces the observed powerful kinetic effect. In fact, the reaction is now found to proceed without any activation to an intermediate which has been termed a long-bond complex (intermediate). This complex has a trapezoidal structural with pericyclic distances of 2.227 and 3.062 Å, symmetrical charge and spin distribution over both olefinic moieties, and extensive π character in these latter moieties (bond length 1.381 Å). This latter feature assures maintenance of stereochemical integrity at this first stage of the reaction. This similarity of the shorter pericyclic distance (2.2 Å) to typical alkane long-bond distances computed using this basis set (*ca* 2.0 Å) suggests the characterization of this intermediate as a "long-bond complex". Cyclization of the long-bond complex to the cyclobutane long-bond product ($E_a = 7.1$ kcal) completes the reaction. At no point on the calculated reaction path does the energy equal or exceed that of the reactants, so that the designation of the reaction as activationless appears appropriate. The mechanism which emerges involves not one but two long-bond structures, both of which maintain stereochemical integrity, but for distinctly different reasons.

All of the theoretical results obtained thus far strongly suggest that cation radical cycloadditions, whether allowed or forbidden, are characterized by extremely low activation requirements, and highly non-synchronous reaction paths. Though these reaction paths may consist of more than one formal step, the pericyclic bonds are not formed in a rigorously stepwise manner, in the most fundamental sense that the first bond is not completely made before the formation of the second bond commences. Such reactions are appropriately viewed as concerted.

RESULTS

The MINDO/3 reaction path calculation for the 1,3-butadiene cation radical/*s*-*cis*-1,3-butadiene Diels–Alder cycloaddition provides theoretical support for the proposed kinetic impetus of the cation radical Diels–Alder reaction through its prediction of an extraordinarily low activation energy for this prototype reaction.[3] However, the details of the MINDO/3 reaction path, which emerges as a two-step reaction involving an acyclic cation/radical intermediate analogous to familiar diradical intermediates, appear to require further scrutiny in view of the observed stereospecificity of the reaction and the tendency of MINDO/3 to generate stepwise reaction paths even for such cycloadditions as the prototype neutral Diels–Alder (butadiene/ethene), which is widely considered to be concerted. To further clarify the details of the reaction path and to obtain a still better estimate of the kinetic impetus of the cation radical Diels–Alder, an *ab initio* SCF MO reaction path calculation was considered desirable. Minimum basis set *ab initio* calculations have a pronounced tendency, opposite to that of MINDO/3, to favor concerted reaction paths,[30] and since the credibility of such calculations is in any case not significantly greater than that of MINDO/3, it was considered essential to target an extended basis set calculation. The 3-21G basis set, which gives results roughly comparable to those from the more elaborate 4-31G set but with greater economy, especially in the rapidity of convergence to optimal geometries, was adopted.[31] The choice of a reaction system for the calculation presents a somewhat more difficult problem. The ideal reaction system for the cation radical Diels–Alder is, unfortunately, not the butadiene/ethene system but the butadiene/butadiene reaction system. This circumstance has its basis in the role specificity of the reaction, i.e. the proposed preference of the cation radical for the dienophilic role.[3] In the butadiene/ethene calculational system the most ionizable component is the diene, as a consequence of which the actual reaction system is the butadiene cation radical/ethene system, i.e. the role-reversed cation radical Diels–Alder. Unfortunately, the ideal diene/diene cation radical reaction system was not a practical option because of the large number of "heavy" atoms (eight carbons). Indeed, the present authors are not aware of a fully optimized, extended basis set reaction path calculation on a doublet reaction ensemble containing even six such heavy atoms (such as in the role-reversed cation radical Diels–Alder) which had been reported at the time of writing. Nevertheless, such a reaction path appeared feasible, and was considered likely to yield new information and insight on cation radical cycloadditions generally and the Diels–Alder specifically. The Gaussian 76 program was implemented using the University of Texas Dual Cyber 170/150 System. The 3-21G basis set recommended by Binkley *et al.*[32] was input as an external basis set using the UHF procedure. All calculations were subjected to 4–5 optimization cycles.[25] Subsequent to the 3-21G optimizations, static 4-31G (4-31G//3-21G) and 6-31G(6-31G//3-21G) calculations were carried out for geometries corresponding to energy maxima or minima on the reaction path. The path was initiated by performing optimized 3-21G (3-21G//3-21G) calculations on the individual reactants [*s-cis*-1,3-butadiene cation radical (**1**)] and ethene (**2**) and on the product [cyclohexene cation radical (**6**)]. The reaction ensemble was then set up by locating a π complex between the diene cation radical and ethene using MNDO. The analogous π complex (**3**) was also found to represent a minimum on the 3-21G//3-21G potential energy surface. The cycloaddition reaction was then simulated by incrementally decreasing the C_4—C_5 distance. This procedure leads to another shallow minimum referred to here as LBINT (long-bond complex or intermediate = **4**). Completion of the reaction required a new reaction coordinate (closing the C_1—C_6 distance), and this proceeded through an energy maximum (TS2 = **5**) which is still well below the original reactants in energy. The 6-31//3-21G reaction path diagram is illustrated in Fig. 1, and the geometries and energies of the various energy otpima are illustrated in structures **1**–**6**.

Symmetry constraints were not imposed in any of the calculations since they would have improperly constrained the reaction path, which emerges as a highly unsymmetrical one. The reactant geometries are relatively unexceptional. As expected, the *s-cis*-diene cation radical is essentially planar, but the cyclohexene cation radical is significantly twisted about the one electron π bond (*ca* 13°). The calculation probably underestimates the actual extent of twist, since extended basis set *ab initio* calculations at the single configuration SCF level generally fail to predict twisting in the ethene cation, which experimentally is observed to be highly twisted (25°).[24] Evidently the tendency toward twisting is even greater in **6** than in cation radicals of simple alkenes, since the SCF MO calculation now at least qualitatively reproduces this phenomenon. The structure of the first intermediate encountered on the reaction path, π complex **3**, foreshadows the remainder of the reaction path in that it already partakes of the unsymmetrical character of the path. The energy of the complex is 2.9 kcal mol^{-1} less than that of the reactants ($E = -2.9$ kcal) and the structure is that of a minimally perturbed diene cation radical interacting weakly with an ethene molecule in an unsymmetrical pericyclic fashion (the pericyclic distances R_{45} and R_{16} are 3.36 and 3.98 Å, respectively). The energy rises slightly as the C_4—C_5 distance is decreased, and the path passes through a maximum (TSI, $E = -2.2$ kcal) at $R_{45} = 2.60$ Å ($R_{16} = 3.77$ Å). It then proceeds to a second energy minimum (LBINT) slightly more stable than the preceding π complex ($R_{45} = 1.62$ Å, $R_{16} = 3.21$ Å, $E = -4.0$ kcal). The conversion from

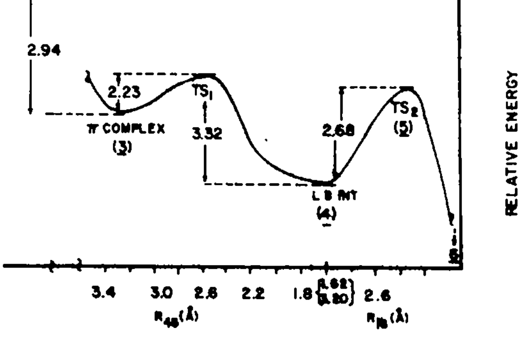
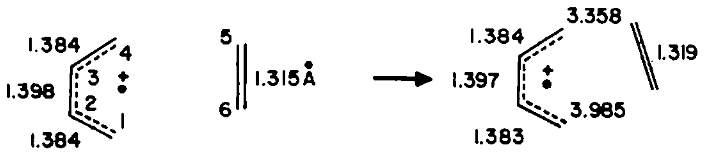
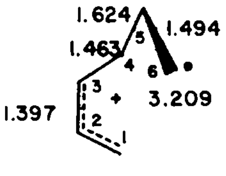


Fig. 1.



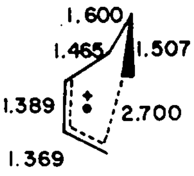
1 2 3 (pi complex)

E = −154.590248 −78.004387 −232.599327



4 (LB INT)

−232.6010

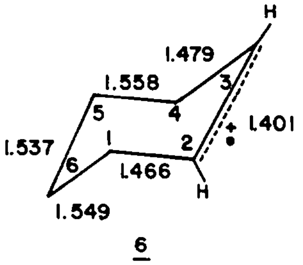


5 (TS2)

−232.5967

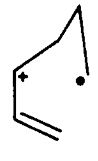
π complex to LBINT is formally reminiscent of the first step of the MINDO/3 path which predicts an acyclic cation/radical intermediate and a basically non-pericyclic path. However, the steady decrease of R_{16} in this part of the *ab initio* path to a value (3.21 Å) substantially less than in the MINDO/3 calculation (3.47 Å) might possibly be construed as reflecting feeble but significant pericyclic character in this part of the *ab initio* path, i.e. a weak attractive interaction between C_1—C_6 signalling a rudimentary beginning to the C_1—C_6 bond process. Furthermore, the C_4—C_5 bonding process largely accomplished in this step is evidently not quite complete, as revealed by the unusually long C_4—C_5 bond (1.62 Å). The corresponding bond length in the MINDO/3 calculation is 1.548 Å. The lengthened bond in LBINT is analogous to the long bonds found in many cation radicals (though the lengthening is normally somewhat higher)[23] and suggests that the cation/radical sites in the *ab initio* calculations are not as effectively isolated from each other as in the MINDO/3 case but rather interact significantly via the long bond. The reaction paths therefore resemble more closely the *ab initio* path calculated for the [2+1] cycloaddition.

Closure of LBINT to the cyclohexene cation radical requires only 2.7 kcal mol^{-1} of activation, the transition state occurring at approximately R_{16} = 2.70 Å. One additional aspect of the LBINT structure is noteworthy. Because the two cation/radical sites are nonequivalent, one being allylic (C_1—C_2—C_3) and the other being of the simple alkyl type (C_6), the charge and spin distributions are actually highly unsymmetrical. Indeed the structure strongly resembles that of an allylic cation loosely coupled (mainly via the long bond) to an alkyl radical. Indeed, this coupling appears to be reflected in the structure and charge distribution in that the C_1—C_2 bond is shorter than the C_2—C_3 bond and there is considerably more positive charge on C_3 than C_1 (see 7). Significantly, the positive charge, which had originated on the diene moiety, remains predominantly upon this moiety throughout the major part of the reaction path, including the long-bond complex LBINT. This observation tends to confirm the sharp distinction between the role-reversed and allowed cation radical Diels–Alder modes revealed by orbital correlation diagrams. It should now be of considerable interest to ascertain if, in the allowed process, the positive charge which originates on the dienophilic moiety remains preponderantly there (especially at C_6) during the relevant part of the reaction path. It is further significant that, in the long-bond complex, the C_3—C_6 distance (3.048 Å, relevant to cyclobutane formation in a [2+1] cycloaddition) is quite comparable to and even a little smaller than the C_1—C_6 distance (3.209 Å, relevant to the [3+2] cycloaddition). Since the positive charge at C_3 actually exceeds that at C_1 in this complex, the possibility that [2+1] cycloaddition could effectively compete with [3+2] cycloaddition appears to be quite plausible.



6

−232.6437



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The present reaction path now represents the second cation radical cycloaddition path which has been computed by an extended basis set *ab initio* SCF MO procedure. As in the previous instance, the reaction is foreseen as activationless and an intermediate which might be characterized as a long-bond complex is suggested. The question now arises of the implications of the presently computed reaction path with respect to the stereospecificity of the role-reversed cation radical Diels–Alder and the detectability of an intermediate such as LBINT. It is, first of all, noteworthy that the activation energy for closure of LBINT, though very small, is of the order of typical torsional barriers, so that *a priori* one could consider stereorandomization by rotation about the C_5—C_6 bond at least as a potential competitor to cyclization. However, as noted for the long-bond intermediate in the [2 + 1] cycloaddition, the existence of the long bond lends additional π character to the C_5—C_6 bond, thereby increasing the torsional barrier. Since the elongation of the C_4—C_5 bond is much less here than in the [2 + 1] cycloaddition (where the long bond length is 2.23 Å), the torsional barrier should be far less affected. However, it is interesting to note that LBINT represents an extremely flat minimum with respect to stretching the C_4—C_5 bond, the energy increasing by less than 0.3 kcal when this bond is stretched to 1.90 Å. Consequently, it is felt that (as a result of configuration interaction or vibronic interactions) the actual long-bond intermediate structural minimum could easily lie at a more typical long bond length and thus correspond to a relatively high C_5—C_6 torsional barrier. The possible existence of a weak C_1—C_6 bonding interaction in LBINT, which would also act to hinder torsion, has also been mentioned. It should also be noted that the present calculation involves a single configuration SCF MO approach, and that configuration interaction could well be substantial for these open shell species.[33] It is hoped that estimates of the correlation energies will be available in the near future. Finally, and most importantly, it is by no means clear that intermediates such as those found on the 3-21G potential surface will persist on the free energy surface. A tendency has been identified in barrierless cycloadditions having large negative entropies of activation to wash out intermediates corresponding to shallow potential energy minima, thereby yielding a concerted reaction.[34] Nevertheless, it is important to note that cation/radical intermediates analogous to the one (LBINT) found in the present calculation have apparently been detected by mass spectrometric[35] and CIDNP[36] techniques. These experimental observations may provide precedent for the type of intermediate found in the present calculation, though they do not appear to have provided information on the long-bond character or the possible weak pericyclic character of the intermediate. It is also important to note that if the diene component has an *s-trans* conformation, a cation/radical intermediate is still possible, even in the normal cation radical Diels–Alder mode. Such intermediates may be longer lived than those obtained from *s-cis* dienes.

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