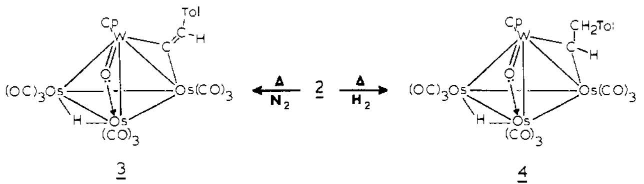

(2)

conversion of **2** to **3** or **4** does not involve loss of a ligand (i.e., CO) in order to provide a site of unsaturation for the oxidative addition of a C–H or an H–H bond. However, if the μ-oxo ligand can move reversibly from a bridging (4e$^-$ donor) to a terminal (2e$^-$ donor) position, an unsaturated intermediate is generated. This intriguing possibility is the object of further investigation.

Acknowledgment. This research was supported by National Science Foundation Grants CHE 81-00140 to J.R.S. and CHE 80-23448 to M.R.C. Instruments at the University of Illinois supported by Grants NSF CHE 79-16100 and NIH GM-27029 were utilized for NMR and mass spectra, respectively.

Registry No. 1, 85335-18-8; **2**, 88609-62-5; **3**, 88589-02-0; **4**, 88609-63-6; Os, 7440-04-2; W, 7440-33-7.

Supplementary Material Available: Listing of positional and thermal parameters for all atoms in **2** and a description of the synthesis and characterization of **3** and **4** (4 pages). Ordering information is given on any current masthead page.

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[12] The synthesis and characterization of **3** and **4** are described in the supplementary material. The structures have been determined by X-ray diffraction studies: Churchill, M. R.; Li, Y. J., unpublished results.

Mechanisms of Hole-Catalyzed Reactions: Ab Initio Theoretical Reaction Paths for Olefin Cation Radical/Olefin Cycloaddition

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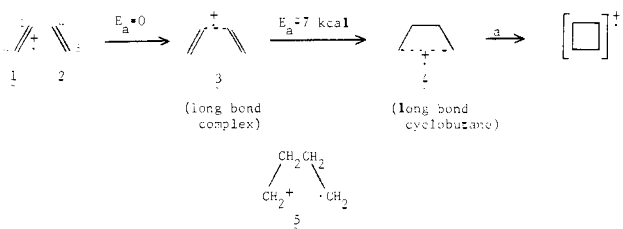
Received August 16, 1983

The existence of cation radical chain mechanisms for certain organic reactions, originally established for a few, apparently somewhat esoteric, reactions, has proved to be a pioneering observation.[1-4] Recent experimental and theoretical observations in the field of cation radical chemistry[5,6] have lead to an enhanced appreciation of the generality of this new mechanistic type and to recognition of its importance as a fundamental catalytic principle, termed hole catalysis.[7]

The phenomenon of hole catalysis is made feasible by the astonishingly low activation energies of many cation radical reactions, including most pericyclic reactions.[6] Consequently, the simple process of ionization (electron transfer to a catalyst hole), followed by a cation radical chain sequence, and terminated by electron acceptance represents a catalytic route of impressive efficiency and generality. The hole-catalyzed Diels–Alder[5] and olefin cyclodimerization[1,8] reactions are outstanding examples of hole-catalyzed reactions, which already have demonstrable utility in organic synthesis. The prototype of the latter reaction, the cycloaddition of ethene cation radical and ethene, is an attractive subject for a fully optimized, extended basis set ab initio theoretical reaction path study. Reaction path calculations of this quality have not previously been reported for any hole-catalyzed reaction, and very few such calculations have been published for any reaction path involving four or more "heavy atoms". The calculations reported here illuminate for the first time and with substantial credibility several basic aspects of cation radical cycloadditions, some of which differ sharply from those traditionally imputed to reaction paths of neutrals.

Scheme I



^{a} Only feasible when hole-delocalizing substituents are present.

For convenience, the ethene/ethene cation radical cycloaddition path was calculated commencing with the fully optimized cyclobutane cation radical (product) which, as previously reported, has a long-bond structure of trapezoidal geometry (**4**),[9] and then progressively lengthening the long bond to afford, eventually, the two ethenic fragments (**1** and **2**). The path was calculated initially using a minimum basis set (STO-3G) to provide a basis, subsequently, for evaluating the necessity for the more expensive extended basis set calculations in future theoretical studies of cation radical reactions. The energy of each point on the reaction path was minimized with respect to all geometric variables using a convergence criterion of 1×10^{-4} au for general points and 1×10^{-5} au for energy extrema. The energy profile of the STO-3G path (Figure 1) is essentially that of a concerted reaction, except that a shallow minimum is encountered at a reaction coordinate value R_{23} = 4.400 Å corresponding to a loose π complex between a moiety that is approximately an ethene cation radical (R_{34} = 1.429 Å) and one that resembles an ethene molecule (R_{12} = 1.349 Å). The shorter pericyclic carbon-carbon distance is R_{14} = 3.121 Å, and the carbon framework is planar. Although the transition state (R_{23} = 4.350, R_{12} = R_{34} = 1.423 Å) is only 0.34 kcal mol^{-1} above the total energies of the isolated ethene plus ethene cation radical fragments, the calculated activation energy for the formation of the cyclobutane cation radical from the π complex is 4.26 kcal mol^{-1}.

The 3-21G basis set has been recommended as a split valence set that gives results comparable to those of the 4-31G basis set, but with appreciably greater economy.[10] The fully optimized 3-21G reaction path, calculated in the same way as the STO-3G path, is significantly different from the latter (Figure 1, Table I). With the extended basis set, no minimum is found for a loose π complex such as that encountered with STO-3G. The transition state is actually 12.65 kcal mol^{-1} below the energies of the isolated fragments, but an activation energy of 7.14 kcal mol^{-1} is required to form the cyclobutane cation radical (**4**) from a stable intermediate (**3**) (R_{23} = 3.062, R_{14} = 2.227, R_{12} = 1.381, R_{34} = 1.378 Å). The latter is not readily dissociated (E_a = 19.80 kcal mol^{-1}) to ethenic fragments in competition with cyclization (E_a = 7.14 kcal mol^{-1}). Unlike the STO-3G complex, the 3-21G intermediate

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[7] The term "hole" specifically refers to an "electron hole". Any entity that can accept a single electron is considered to have an electron hole. Hole catalysis refers to catalysis initiated by transfer of an electron hole from a hole catalyst to a substrate. Cation radicals, of course, represent one important class of species having an electron hole.

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Table I

species	basis set	bond lengths, Å R_{14}	R_{23}	R_{12}	R_{34}	energy, au
ethene	STO-3G				1.306	−77.0739555519
	3-21G				1.315	−77.6009887270
	6-31G*				1.315	−78.0316951773
ethene cation radical	STO-3G			1.430		−76.7975470693
	3-21G			1.405		−77.2714570308
	6-31G*			1.405		−77.7123115073
long-bond complex	3-21G	2.227	3.062	1.381	1.378	−154.904010083
	6-31G*	2.227	3.062	1.381	1.378	−155.766664364
loose complex	STO-3G	3.121	4.400	1.349	1.429	−153.877752947
transition state	STO-3G	2.350	4.350	1.423	1.423	−153.870959900
	3-21G	1.756	2.550	1.503	1.413	−154.892619984
	6-31G*	1.819	2.600	1.484	1.399	−155.754794531
cyclobutane cation radical	STO-3G	1.574	1.870	1.528	1.531	−153.969240946
	3-21G	1.602	2.004	1.514	1.509	−154.908773084

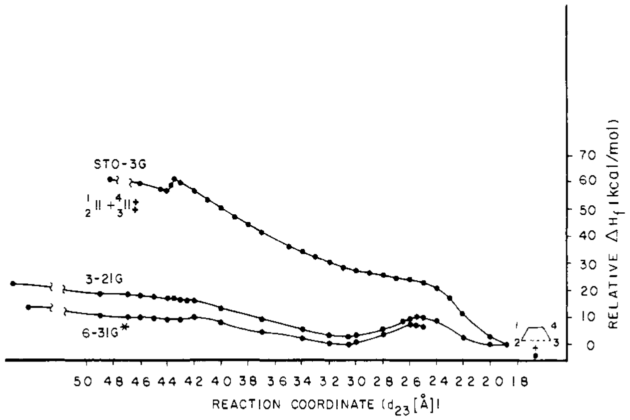

Figure 1.

has ethenic moieties that are approximately equivalent and, very significantly, that retain very extensive π character (see R_{12} and R_{34} lengths), and all four carbons remain essentially sp^2 hybridized. The shorter intermolecular distance R_{14} (2.227 Å) is interestingly close to that of the stable long (one electron) bond in the ethane cation radical (2.022 Å in 3-21G),[11] suggesting a possible widespread tendency of cation radicals to form one-electron bonds. For emphasis of this point, the 3-21G complex will be referred to as a *long-bond complex*. Point calculations in the 6-31G* basis set, using the optimized 3-21G geometries, closely reproduce the shape of the 3-21G profile (Figure 1) and provide strong support for the validity of the 3-21G results. Interestingly, the 6-31G* profile does suggest an extremely shallow minimum (*ca.* 0.4 kcal mol^{-1}) for a loose π complex.

All of the calculations confirm a phenomenally low activation energy for hole-catalyzed olefin cyclodimerization, which contrasts vividly with the 62.5 kcal mol^{-1} activation energy required for the corresponding neutral reaction.[12] The extended basis set calculations implicate a long-bond complex as an intermediate (Scheme I). The extensive ethenic π character of both moieties in this intermediate, however, precludes cis–trans isomerization and permits stereospecific suprafacial addition, as observed experimentally in the dimerization of *trans*- and *cis*-anethole.[8] This stereochemical behavior contrasts with that expected for a tetramethylene cation radical (**5**), the structure of the intermediate predicted by MNDO,[6] which should be subject to at least some *cis*–trans isomerization prior to cyclization to the long-bond cyclobutane cation radical. As shown previously, the energy of the one-electron bond in the latter is easily sufficient to maintain stereochemical integrity.[9]

Acknowledgment. We thank the Robert A. Welch Foundation (F-149) and the University of Texas Computation Center for substantial support.

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Asymmetric Synthesis of Quaternary Carbon Centers

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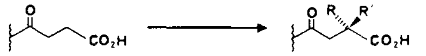
Received October 31, 1983
Revised Manuscript Received January 3, 1984

A recent review by Martin[2] outlining synthetic methods to furnish quaternary carbon centers also points to the lack of efficient routes for generating this moiety in an enantioselective manner. If one sets aside the useful routes now available for chiral tertiary alcohols[3] and amino acids,[4] the statement in the Martin review is a correct assessment of the situation. Except for the studies by Koga wherein high enantioselectivity is observed for α,α'-disubstituted cycloalkanones[5] and α-substituted cyclic carboxaldehydes[6] no efficient methodology exists to date.

We now report that α-disubstituted carboxylic acids of the type **2** can be enantioselectively prepared from γ-keto acids **1** via a



1 **2**

novel and stereoselective sequence. Furthermore the method also provides a route to enantiomerically pure 3,3-disubstituted dihydronaphthalenes, **11**. The asymmetric synthesis of **2** is based on the bicyclic lactam **3**, which was prepared from *l*-valinol and 3-benzoylpropionic acid by azeotropic removal of water (toluene, *p*-TsOH, 8 h).[7] A single diastereomer of **3** was obtained in 85%

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