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Theoretical Investigations on the Retro-Ene Rearrangement of Propargyl Ethers

Péter Várnai[†] and György M. Keserü*[,‡]

Departments of Organic Chemistry and Chemical Information Technology, Technical University of Budapest, H-1521 Budapest, POB 91, Hungary

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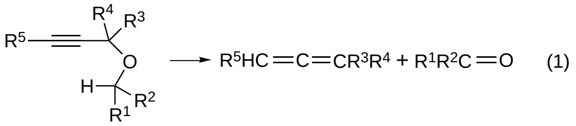
Semiempirical and ab initio calculations are presented on the retro-ene rearrangement of propargyl ethers. AM1 and correlated ab initio calculations predict the energetics of the reaction well, while density functional (B3LYP) energies underestimate the barrier height. The reaction proceeds through a planar transition structure in a concerted manner. The nucleophilic character of the migrating hydrogen suggested earlier is not borne out by our calculations. The low barrier can be explained by strong delocalization of the reacting in-plane orbitals in the transition state. Geometric, energetic, and magnetic properties of the transition state support its aromatic character.

Introduction

Olefins and acetylenes generally show high activity in pericyclic reactions, such as the Claisen or Cope rearrangements. The oxy-Cope reaction and the competitive thermal retro-ene cleavage of propargyl ethers were extensively investigated by Viola et al.[1] Vapor phase thermolysis of propargyl ethers led to allenes and carbonyl compounds (eq 1).



1; $R^1 = R^2 = R^3 = R^4 = R^5 = H$
2; $R^1 = Me$, $R^2 = R^3 = R^4 = R^5 = H$
3; $R^1 = R^2 = Me$, $R^3 = R^4 = R^5 = H$
4; $R^1 = R^2 = R^5 = H$, $R^3 = R^4 = Me$
5; $R^1 = R^2 = R^3 = R^4 = H$, $R^5 = Me$

On the basis of the thermodynamic and kinetic properties of the reaction, it was suggested[1,2] that the retro-ene reaction followed a concerted [1,5]-H shift pathway. Thermolyses of various propargyl ethers were associated with similar activation energies which were much lower than expected from the energy of the cleaving bonds.[3] This phenomenon is well-known for concerted reactions;[4] however, in this very case the six-membered transition structure requires an energetically unfavored distortion of the acetylenic bond angle ($C_1-C_2\equiv C_3$). Nevertheless, the "energy of concert" provides some energy gain of the transition state as compared to the energy of the weakest bond (i.e., C−O) to be cleaved in the reacting system.

According to the Woodward−Hoffmann rules, in thermally induced [1,5] sigmatropic shifts it is the suprafacial migration of the hydrogen which is permitted.[5] The retro-ene cleavage of propargyl ethers requires a planar six-membered transition structure. This postulated planarity was in accord with substituent effects of the acetylenic compounds.[6] The reaction proceeds with a high stereospecifity that can be exploited in the synthesis of optically active allenes.[7]

Conflicting views have been proposed concerning the charge development during the course of the retro-ene reaction. For several allyl ethers and for benzyl propargyl ether, Kwart et al.[8] suggested a symmetrical transition structure without significant charge development. Viola et al.,[2] in turn, studying the retro-ene cleavage of propargyl ethers, argued for a slight negative charge development at the carbon bearing the migrating hydrogen. The reaction was thus considered to proceed via a concerted, but nonsynchronous pathway. While Kwart et al. reported no solvent effect at all for allyl ethers,[8] for β-hydroxyacetylenes a decrease of activation energy by about 3 kcal/mol in xylene as compared to the gas phase was reported by Viola et al.[9] The mechanism of the retro-ene cleavage of acetylenes was originally explained by attributing some electrophilicity to the migrating hydrogen atom.[9] Later, the same group argued for a hydride attack on the triple bond.[2] This consideration was mainly based on the study of Houk et al.[10] on nucleophilic additions to acetylene. They showed[10] that this involves a bending of the molecule compensated for by an enhanced HOMO−LUMO interaction, which was not observed in case of an electrophilic attack. Viola et al.[1] also suggested possible charge distribution schemes in the transition states.

In the present study we report theoretical calculations carried out to gain information about the mechanism of the retro-ene cleavage of propargyl ethers unavailable through experiment. We addressed the following problems: (1) Does the retro-ene cleavage of propargyl ethers proceed via a concerted transition structure? (2) Do theoretical calculations adequately predict experimental activation energies? (3) Does the H-migration proceed in a synchronous or an asynchronous manner? (4) What

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[†] Department of Organic Chemistry.

[‡] Department of Chemical Information Technology.

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factors contribute to the "energy of concert" in the pericyclic retro-ene reaction of propargyl ether? To clarify the above problems, we have carried out full geometry optimization of some experimentally investigated propargyl ethers. The mechanism of the reaction was characterized by considering geometrical changes, energetics, charge distribution, and magnetic properties throughout the course of the reaction.

Methodology

In order to find a reliable method for describing the rearrangement of propargyl ethers, we tested several levels of quantum chemical calculations on propargyl methyl ether. Our aim was to reproduce the experimental gas phase energy of activation for the retro-ene reaction. The activation energy reported in this study was calculated (unless otherwise stated) as the energy difference of the sum of the total energy and the thermal energy at 300 °C between the reactant and the transition structure. We applied semiempirical calculations AM1, PM3, and MNDO with MOPAC,[11] as well as conventional ab initio and density functional techniques (DFT) with the Gaussian 94 program package.[12] Hartree−Fock (HF), second-order Møller−Plesset (MP2), and DFT calculations were performed with different basis sets. At the most accurate geometry used here (MP2(fc)/6-311+G**), the coupled cluster energy using single, double, and noniterative triple excitations (CCSD(T)) was calculated. The stationary points of the respective potential energy surfaces were characterized by analytical second derivative calculations in each case (except using the 6-311+G** basis set). The transition state was checked by intrinsic reaction coordinate (IRC) calculations.

Procedures based on single determinant approximation were validated by an MCSCF calculation, in which all the orbitals corresponding to the reacting bonds were included. Since the HF reference wave function had a CI coefficient larger than 0.95, we regard this approach as satisfactory (for sigmatropic H-shifts single determinant methods were used by others,[13] too).

In recent years DFT was utilized in calculating reaction pathways, including pericyclic reactions.[14−17] We present here our density functional calculations using the combination of Becke's three-parameter nonlocal exchange functional (B3)[18] with the gradient-corrected correlational functional of Lee, Yang, and Parr (LYP).[19] We have to stress that, contrary to thermochemical data,[20] the available DFT techniques predict a lower energy for allene than for propyne. RHF calculations reproduce the experimental relative energies well.

To get a better insight into the electronic changes in the retro-ene reaction, Bader's topological electron density analysis using the Extreme package,[21] the Natural Bond Orbital (NBO) analysis,[22] and the calculation of magnetic properties as implemented in the Gaussian 94 suite of programs[12] was carried out.

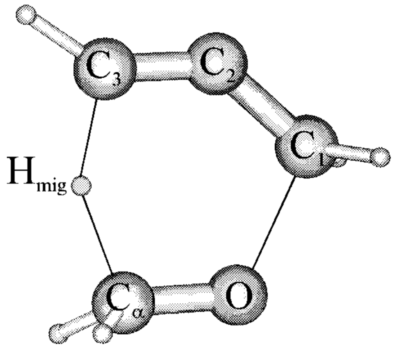

Figure 1. Transition structure **TS1** of the thermal rearrangement of propargyl methyl ether.

Results and Discussion

Reactant and Products. The conformational study of **1** for the gas phase showed[25] that the gauche form was more stable than the trans form. The gauche conformer is a minimum on the potential energy surface and was used as starting structure in further calculations. We obtained virtually identical results for the minimum energy structure of **1** with different levels of theory and different basis sets. The energy of the products is somewhat lower than that of the reactants, if the basis set superposition error (BSSE) is accounted for by the counterpoise method[23] at both HF/6-31G* and MP2/6-31G* levels of theory. The entropy change between the starting material and products is positive; thus the Gibbs free energy difference is negative.

Transition Structure. The search for the proposed[6] transition structure resulted in structure **TS1** shown in Figure 1. **TS1** is six-membered and planar, having a single imaginary frequency (-1598 cm^{-1}) which corresponds to hydrogen migration. The cleaving C_1-O bond is elongated to 1.79, 1.87, and 1.85 Å at HF, MP2, and B3LYP levels of theory, respectively, with 6-31G* basis set. The shifting H is approximately midway between the C_α and C_3 atoms. The $C_1-C_2\equiv C_3$ bond angle is distorted to 133.7, 140.8, and 138.1° at HF, MP2, and B3LYP levels of theory, respectively, with the 6-31G* basis set.

The activation energies obtained with different quantum chemical calculations are collected in Table 1. The AM1 semiempirical method gives activation energy close to experiment, while MNDO overestimates the barrier height. This effect was also reported in the case of other thermal processes.[24] Large differences in activation energies between HF and post-HF methods show that the inclusion of correlation is essential in describing reactions quantitatively. The correlated ab initio and B3LYP activation energies are close to experimental values, the latter being consistently lower. Since the H-shift trajectory of the HF and MP2 potential energy surfaces are similar, we carried out the full geometry

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Table 1. Activation Energies for the Retro-ene Thermolysis of Propargyl Methyl Ether

method	activation energy (kcal/mol)[a]
AM1	42.4
MNDO	50.0
PM3	44.7
HF3−21G*//HF3−21G*	68.6
HF6-31G*//HF6-31G*	71.7
MP2(fc)6-31G*//HF6-31G*	45.4
MP2(fc)6-31G*//MP2(fc)6-31G*	45.2
MP2(fc)6-311+G**//MP2(fc)6-311+G** [b]	42.4
CCSD(T)6-311+G**//MP2(fc)6-311+G** [b]	45.7
B3LYP6-31G*//B3LYP6-31G*	40.1
B3LYP6-311+G**//B3LYP6-311+G** [b]	39.2
experimental[c]	40.9

[a] The values are calculated at 300 °C with ZPVEs scaled by 0.8929, except for semiempirical calculations where the values refer to 25 °C. [b] ZPVE and thermal energy corrections were used at the respective level of theory with 6-31G* basis. [c] Taken from ref 2.

Table 2. Activation Energies (kcal/mol) for the Retro-ene Thermolysis of Propargyl Ethers[a]

method	2	3	4	5
AM1	45.8	43.1	45.6	45.4
HF/6-31G*//HF/6-31G*	68.4	64.2	67.0	73.6
MP2/6-31G*//HF/6-31G*	42.3	39.0	41.7	45.2
B3LYP/6-31G*//B3LYP/6-31G*	37.1	33.7	35.5	41.9
experimental[b]	41.7	40.1	41.3	43.3

[a] The values are calculated at 300 °C with ZPVEs scaled by 0.8929, except for AM1 where the values refer to 25 °C. [b] Taken from ref 2.

Table 3. Selected Bond Lengths (Å) and the Distorted Bond Angle (deg) in the Transition Structures of Propargyl Ethers at B3LYP/6-31G* and HF/6-31G* (in parentheses) Levels of Theory

structure	$C_\alpha H_{mig}$	C_3H_{mig}	$C_\alpha O$	C_1O	C_1C_2	C_2C_3	$C_1{-}C_2{\equiv}C_3$
TS1	1.380	1.321	1.298	1.821	1.380	1.268	136.0
	(1.394)	(1.303)	(1.271)	(1.789)	(1.378)	(1.255)	(133.7)
TS2	1.390	1.306	1.304	1.780	1.388	1.271	133.6
	(1.407)	(1.282)	(1.275)	(1.743)	(1.388)	(1.260)	(130.9)
TS3	1.396	1.292	1.311	1.752	1.393	1.273	131.9
	(1.418)	(1.261)	(1.281)	(1.706)	(1.397)	(1.265)	(128.5)
TS4	1.332	1.369	1.302	1.890	1.386	1.262	139.6
	(1.355)	(1.337)	(1.272)	(1.855)	(1.382)	(1.249)	(137.0)
TS5	1.367	1.340	1.294	1.888	1.371	1.269	138.7
	(1.384)	(1.322)	(1.268)	(1.840)	(1.370)	(1.254)	(136.3)

optimization at the computationally less demanding HF/6-31G* level and improved the energy with a single-point MP2(fc)/6-31G* calculation (MP2//HF). It was discussed earlier[25] that MP2 energies at the HF-optimized structures account for most of the correlation contribution to barrier heights.

The methods selected above were then applied to propargyl ethers (**2**-**5**) substituted at different positions (Table 2). All the methods reproduced the experimentally observed trends; however, MP2//HF calculations gave the smallest deviation (the largest difference between experiment and calculation was for **1**). The B3LYP functional is indeed very applicable to reproduction of the observed trend in activation energies; it gives, however, in accordance with earlier findings,[15] barriers lower than the experiment by 4−6 kcal/mol. Structural parameters of the transition structures (**TS1**−**TS5**) are collected in Table 3.

Geometries obtained by B3LYP/6-31G* (compared to HF/6-31G*) indicate a balanced cleaving and forming of CH bonds, the bond length of $C_\alpha{-}H_{mig}$ and $C_3{-}H_{mig}$ being almost equal in the transition structure. Also, in this case the $C_1{-}C_2{\equiv}C_3$ bond angle deviates less from linearity than HF level calculations predicted. On introducing methyl groups to C_α (**TS2** and **TS3**) the distortion of the bond angle becomes more pronounced, although the activation energy decreases. Also, hydrogen migrates more easily: the ratio of breaking and forming C−H bond lengths (R) is 1.04, 1.06, and 1.08 for **TS1**, **TS2**, and **TS3**, respectively. In **TS4** the methyl groups at C_1 have a somewhat different effect on the transition structure: the $C_1{-}O$ bond elongates significantly. This may be due to the disappearance of the stabilizing hyperconjugation effect present in other cases (e.g., in **TS1**). In **TS4** the migrating hydrogen is closer to C_α than to C_1 ($R = 0.97$) and the $C_1{-}C_2{\equiv}C_3$ angle is the least bent. When the methyl group is at C_3 (**TS5**), the $C_1{-}O$ is rather long and no easy H shift ($R = 1.02$) or strong distortion was observed. From these energetic and structural data, one can conclude that the more the $C_1{-}C_2{\equiv}C_3$ angle is bent and also the more the migration of H progressed, the easier the reaction proceeds. Good correlation between our calculated geometric and energetic properties and those suggested earlier based on experiments indicate that the reaction proceeds via the concerted transition structure characterized above.

Synchronicity. Properties of the transition structure help us to understand the mechanism of a reaction. It is very difficult to assign the mechanism to the synchronous or asynchronous type in pericyclic reactions.[10,27] In special cases, where symmetry is present, classification is somewhat easier. In our case, the asymmetry of the transition structure as well as the polarity introduced by the oxygen might imply an asynchronous pathway.

On the basis of Hammet plots, Viola et al.[2] considered a slightly increased polarity in the transition state. In fact, the activation energy decreased[2] when thermolysis was carried out in xylene. The same group first presumed[9] a positive net charge on the migrating hydrogen, but later, on the basis of the study[10] of a hydride ion attack on acetylene, suggested a hydride ion attack at the acetylenic bond.[1] Kwart et al., who observed no solvent effects, argued[8] for a symmetrical transition structure with no increase in polarity in the transition state.

We calculated properties at several points along the reaction pathway as defined by IRC. Wiberg bond indices, calculated for **TS1**, showed a balanced cleaving and forming of bonds throughout the reaction coordinate: $C_\alpha{-}H_{mig}$ 0.50, $C_3{-}H_{mig}$ 0.43, and $C_1{-}O$ 0.46. According to our quantum chemical calculations (at both HF and MP2 levels), polarity only slightly increased as reflected by dipole moment changes of +0.2 on the way to the transition state. However, close to the transition state a dipole moment drop of −0.35 was observed that may be due to the local symmetry of the migrating hydrogen between the two carbon atoms. Solvent effect calculations using the Onsager method with xylene ($\epsilon = 2.4$) resulted in a +0.2 kcal/mol activation energy change that is indicative of the modest polarity of the transition state. Charge distribution derived by natural population analysis[22] (NPA) did not indicate negative or positive character of the migrating hydrogen. Charge development at the migrating hydrogen along the reaction coordinate is not larger than the charge at a hydrogen in a common C−H bond cleavage (−0.06 e). The carbon,

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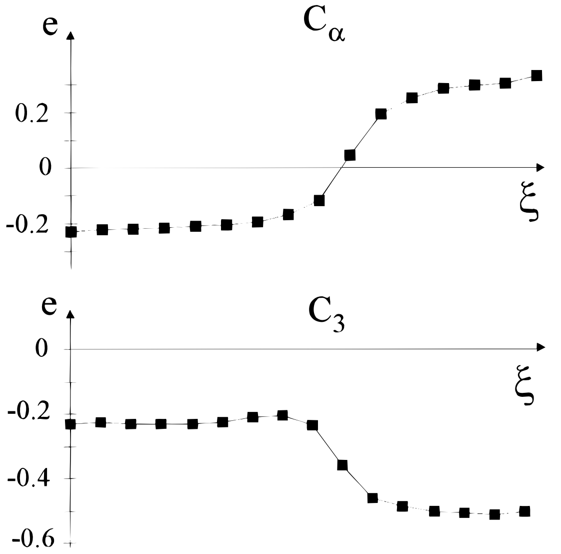

Figure 2. NPA-derived partial charges (*e*) on C_α and C_3 atoms along the reaction coordinate (ξ).

donating the hydrogen (C_α), is becoming more positive (+0.28 e) in the transition state. This is in accordance with the increased electronegativity of the oxygen in formaldehyde but contrary to expectations based on Hammet plots[2] (Figure 2). As the reaction proceeds, the carbon accepting the migrating hydrogen (C_3), is becoming more negative (−0.13 e), gradually approaching the charge distribution of allene (Figure 2). As far as the charges on other participating atoms are concerned, no pronounced changes were detected. The electron flow along the reaction coordinate is in accord with the difference in electron distribution of reactant and products. Since the main argument for hydride attack is based on the frontier orbital changes in the transition state, we have checked the LUMO and HOMO energies along the reaction coordinate. The LUMO, i.e., the in-plane π-orbital is shown in the transition state in Figure 3. It is stabilized (−2.25 eV) by the bending of the acetylenic bond angle as could be anticipated by analogy with acetylene.[10] Nucleophilic attack on the triple bond thus would be favored over an electrophilic one. However, in contrast to hydride addition to simple acetylenes,[10] the energy of HOMO in propargyl ethers is rising (+1.65 eV) toward the transition state (in-plane π*-orbital, Figure 3). Thus, changes in frontier orbitals may favor both nucleophilic and electrophilic attack on the triple bond.

Synchronicity of the retro-ene reaction might be somewhat surprising, because the dissociation energy of $C_1{-}O$ bond is significantly lower than that of the $C_\alpha{-}H_{mig}$ bond (76.9 and 102.5 kcal/mol, respectively).[3] However, in view of the transition structure geometry and energetics it can be concluded that the reaction proceeds without the total dissociation of either the $C_1{-}O$ or the $C_\alpha{-}H_{mig}$ bond in the transition state, i.e., at a lower energy level than bond dissociation energies. Therefore, we think that in concerted reactions arguments for asynchronicity based on bond energies may not be conclusive.

Aromaticity. At this point our calculations did not corroborate earlier speculations about the mechanism of the retro-ene reaction of propargyl ethers.[1] Distortion of the linear acetylenic bond angle to attain the values in transition structure **TS1** requires 14.3 and 14.7 kcal/mol in propyne at HF/6-31G* and B3LYP/6-31G* levels of theory, respectively. The estimated energy of concert is ca. 35 kcal/mol considering the $C_1{-}O$ bond dissociation energy.[3] How can a transition structure including a distorted acetylenic−allenic bond still be so stable? An answer to this question may be delocalization present in the transition state. The strong stabilizing effect of the perpendicular π-interaction present in pericyclic transition states is well-known.[28,29] According to geometric, energetic, and magnetic properties, the Cope rearrangement of 1,5-hexadiene proceeds through a concerted and synchronous mechanism via an aromatic transition state.[30] This general feature of pericyclic reactions was investigated in hydrogen shifts, too.[30,31] Viola et al. noticed the resemblance of the planar transition structure to an aromatic system.[2,9]

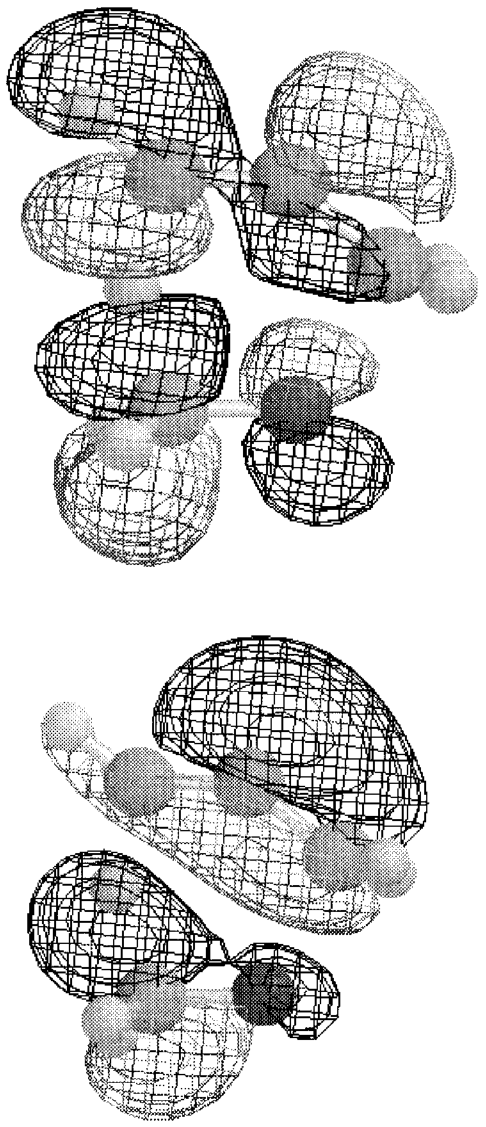

Figure 3. LUMO (above) and HOMO (below) orbitals of **TS1** at the HF/6-31G* level of theory.

In the case of propargyl ethers, electrons could delocalize in the extensively overlapped, reacting, in-plane

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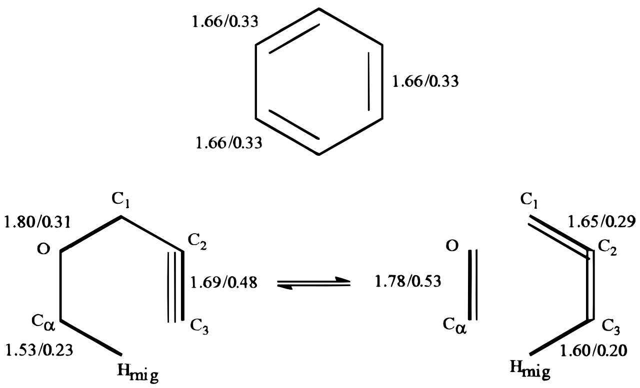

Figure 4. Electron delocalization in benzene and **TS1** characterized by NBO occupancy numbers for bonding/antibonding orbitals.

orbitals. The cyclic system involves six electrons, i.e., it is aromatic according to Hückel's rule. In the following we examine the aromatic character[32] of the transition state.

The transition structure is a perfect ring according to Bader's topological electron density analysis;[21] the required six-bond critical points and one-ring critical point are present. Electron density values at the bond critical points are characteristic for a system in which all six bonds are changing in a concerted manner and indicate a forming C_α−O double bond (0.35) and a cleaving C_1−O bond (0.11). The corresponding ellipticity values are 0.02 and 0.04, respectively. The latter value is high for a cleaving single bond; the π-character indicated by ellipticity is due to the hyperconjugation mentioned above. Indeed, in the case of **TS4**, the ellipticity is only 0.008 for the cleaving C_1−O bond.

A detailed NBO analysis[22] of electron density found, similar to benzene, three conjugated bonds in the ring (Figure 4). In the resonance structures, bonding MOs corresponding to the reacting bonds have low, while the antibonding MOs have relatively high, occupancy. This is characterized by the bonding/antibonding occupancy numbers of the respective natural bond orbitals. These structures show signs of high delocalization; the interaction between the filled and the vacant orbitals is significant. However, while these orbitals are perpendicular to the plane of the ring in the case of benzene, those for **TS1** are in the plane of the ring.

A very recent approach to describe the aromatic character of pericyclic transition states is the quantification of magnetic properties of the transition structure.[33,34] Aromaticity is indicated by downfield chemical shifts of the exocyclic protons and high magnetic susceptibility exaltation value due to ring current. It was reported earlier that there is no direct relationship between the energy of concert and the magnetic susceptibility exaltation, although this latter reflects the cyclic electron delocalization that stabilizes the transition state.[30] Benzene has larger magnetic susceptibility (−72.7 cgs, ppm) than hexa-1,3,5-triene (−34.4 cgs, ppm) and also larger magnetic anisotropy (−49.1 and −14.8 cgs, ppm for benzene and hexa-1,3,5-triene, respectively). The magnetic properties obtained for the transition state of the retro-ene cleavage of propargyl methyl ether are collected in Table 4. The chemical shifts were calculated using the GIAO scheme,[35] and the magnetic susceptibility values were obtained by the IGAIM method[36] at the HF/6-31G* optimized structure.

Table 4. Calculated and Measured (in parentheses) ^{1}H Chemical Shift Values (ppm), Total Magnetic Susceptibility (χ_{tot}), and Anisotropy (χ_{anis}) Values (cgs, ppm) at the HF/6-31G* Optimized Geometry

	$\delta(C_\alpha H_{mig})$	$\delta(H_{mig})$	$\delta(C_1H)$	$\delta(C_3H)$	χ_{tot}	χ_{anis}[a]
1	3.44 3.46 2.63	3.18[b]	3.32 4.06 } 3.69[b]	2.36	−37.40	+7.30
	(3.42)		(4.09)	(2.45)		
TS1	3.79	−0.19	6.56	3.56	−49.02	-47.63
Δ	0.61	−3.37	2.87	1.20	−11.62	-54.93

[a] $\chi_{anis} = \chi(33, \text{out of plane}) - 0.5[\chi(11) + \chi(22), \text{in plane}]$. [b] Averaged values.

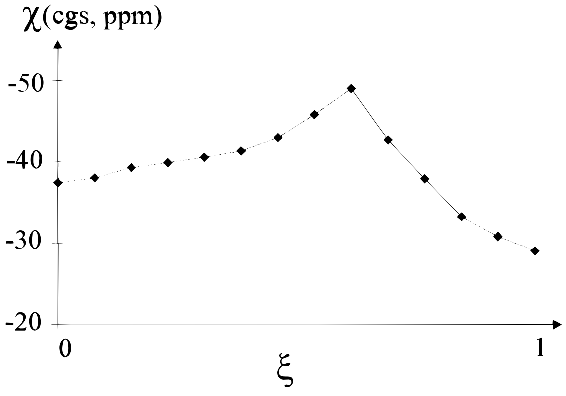

Figure 5. Changes in total magnetic susceptibilty (χ in cgs, ppm) along the reaction coordinate (ξ).

Protons outside the ring in the transition structure are shifted downfield relative to the corresponding signal of the minimum (Table 4). The C_1−H proton signal goes through a maximum along the reaction coordinate, and its maximum value (6.56 ppm) is close to that of benzene (7.59 ppm). The migrating proton lying in the shielded region shows a high upfield shift, and the value of −0.19 ppm is a minimum along the reaction coordinate. This phenomenon is characteristic for a shifting hydrogen.[33] Further, the total magnetic susceptibility (χ_{tot}) has a maximum along the reaction coordinate at the transition state (Figure 5). The value of −49.0 cgs, ppm is very close to that of benzene (−49.1 cgs, ppm at the same level). However, only the out of plane component of the susceptibility increase; the in-plane components are unaffected by structural changes. This is reflected by the anisotropy value of −47.6 cgs, ppm (anisotropy of the magnetic susceptibility in benzene is −72.7 cgs, ppm at the same level of theory). Cyclic delocalization and ring current effect are thus shown in magnetic properties associated with the transition structure.

Conclusion

The retro-ene rearrangement of propargyl ethers to allenes proceeds through a concerted and planar transition structure. The charge distribution in the transition state claimed earlier[1] and the hydride character of the

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[32] For excellent reviews on σ delocalization, see: Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209. Dewar, M. J. S. *Mol. Struct. Energ.* **1988**, *6*, 1. Cremer, D. *Tetrahedron* **1988**, *44(24)*, 7427.

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migrating hydrogen are not apparent according to our calculations. Instead, in our opinion, the significant energy of concert is explained by the delocalization in the six reacting in-plane orbitals. The aromatic character of the transition state was characterized by its geometric, energetic, and magnetic properties.

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Supporting Information Available: Full characterization of transition strucure **TS1** at HF/6-31G* and B3LYP/6-31G* levels of theory (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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