J. Org. Chem. **2001,** *66,* 5996−5999

Phenyl-Bridging in the 2-Phenylethyl Radical. A Molecular Orbital Study

Amparo Asensio[‡] and J. J. Dannenberg*

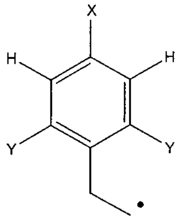
Department of Chemistry, City University of New York, Hunter College and the Graduate School,
695 Park Avenue, New York, New York 10021

jdannenberg@gc.cuny.edu

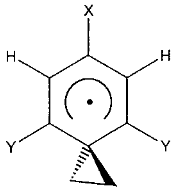
Received December 15, 2000

Density functional theory at the UB3PW91/6-31G(d.p) level on the open and bridged forms of the 2-phenylethyl radical are reported here together with activation energies and calculated rate constants for rearrangement of the bridged to the open radical. In addition, the effect of substituents on the aryl ring upon the relative energies, activation energies, and rate constants for rearrangement from the bridged to open forms are presented. Para-substituents include CH_3, CF_3. CN, CHO. OH, SH, O^-, S^-, and NO. The parent bridged radical is found to be 10.1 kcal/mol higher in enthalpy than the open form. The activation energy for conversion of the bridged to open radical is 3.96 kcal/mol. Para-substitution by CN or CHO significantly lowers the difference in energy between the species, while substitution by NO renders the bridged form more stable. Para-substitution by CN or CHO coupled with substitution with CN in the ortho-positions makes the open and bridged radical approximately equivalent in energy.

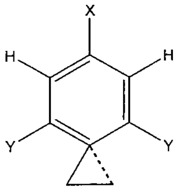
Ever since the neophyl rearrangement (2-phenyl-2-methyl-1-propyl to 2-benzyl-2-propyl radical) was observed,[1] phenyl-bridged radical species have been postulated as intermediates in phenyl 1,2-migrations of organic free radicals. Slaugh has reported that the simpler phenylethyl radical, **1a** (when substituted with ^{14}C in the 1-position), similarly rearranges to the extent of 2.3 to 5.1%.[2] A similar species was postulated to explain the photochemical rearrangement of 1-phenyl,2-bromopropane to products that could be derived from the 2-phenyl,1-propyl radical.[3] However, no direct evidence for the bridged radical, **2a**, had been found from these rearrangement experiments.



1



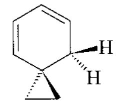
2



3

a: X=Y=H
b: X=CN, Y=H
c: X=OH, Y=H
d: X= CH_3, Y=H
e: X=CF_3, Y=H
f: X=CHO, Y=H
g: X=O^-, Y=H
h: X=SH, Y=H
i: X=S^-, Y=H
j: X=CHO, Y=CN
k: X=NO, Y=H
l: X=XN, Y=CN

Eventually, the bridged phenylethyl radical, **2a**, was unambiguously made by hydrogen abstraction from spiro[2,5]octa-4,6-diene, **4**.[4] The radical's rearrangement to **1a** was too fast to be measured by esr. Upon the basis of this observation, the rate constant for the rearrangement **2a** → **1a** (via transition-state **3a**) was estimated to be ≥ 2×10^{-2} s^{-1} at 123 K. Analysis by laser flash photolysis led to Arrhenius parameters of 9.2 ± 1.0 s^{-1} (A) and 2.8 ± 0.4 kcal/mol (E_a). The unusually low value of A obtained caused the authors to be somewhat skeptical of their results. Nevertheless, they estimated the ΔH for the equilibrium **1a** $\rightleftarrows$ **2a** to be ≥ 13 kcal/mol. Later experimental and AM1 MO investigations of similar rearrangements of 1,1-diphenylethoxyl radicals led to evidence for similar oxo-bridged radicals as intermediates.[5]



4

In this paper we explore the potential energy surface of the phenylethyl radical and several analogous species derived from substitution on the phenyl ring using molecular orbital methods. Previous calculations using STO-3G at the HF, UHF, and MP2 levels are regarded as of qualitative interest, but not quantitative.[6]

Methods

We performed the DFT calculations using the B3PW91 hybrid functional. This method combines Becke's three-parameter functional,[7] with the nonlocal correlation provided

---

[‡] Permanent address: Facultad de Farmacia, Departamento Quimica Organica, Avda Vicente Andres Estelles, 46100 − Burjassot (Valencia), Spain.

(1) Kharasch, M. S.; Urry, W. H. *J. Am. Chem. Soc.* **1944**, *66*, 1438.

(2) Slaugh, L. H. *J. Am. Chem. Soc.* **1958**, *81*, 2262.

(3) Dannenberg, J. J.; Dill, K.; Waits, H. P. *Chem. Commun. (J. Chem. Soc. D)* **1971**, 1348−9. Dannenberg, J. J.; Dill, K. *Tetrahedron Lett.* **1972**, 1571−4.

(4) Effio, A.; Griller, D.; Ingold, K. U.; Scaiano, J. C.; Sheng, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 6063.

(5) Banks, J. T.; Scaiano, J. C. *J. Phys. Chem.* **1995**, *99*, 3527.

(6) Leardini, R.; Nanni, D.; Pedulli, G. G.; Tundo, A.; Zanardi, G.; Foresti, E. Palmieri, P. *J. Am. Chem. Soc.* **1989**, *111*, 7723..

(7) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

10.1021/jo0017483 CCC: $20.00

Table 1. Energetic and Geometrical Properties[a]

X	Y	ΔE	ΔH_{act}	ΔH	ΔG_{act}	k (298 K)	k (123 K)	r (TS)	r (b)
H	H	−9.84	3.96	−10.11	4.11	1.21×10^{-10}	2.62×10^{-5}	1.846	1.531
CN	H	−5.60	4.96	−6.21	5.07	2.41×10^{-9}	5.18×10^{-3}	1.884	1.546
OH	H	−10.52	4.21	−10.80	4.40	7.45×10^{-9}	8.00×10^{-4}	1.844	1.539
CH_3	H	−9.61	4.15	−9.91	4.74	4.20×10^{-9}	1.99×10^{-4}	1.849	1.542
CF_3	H	−8.38	4.01	−8.75	4.23	9.92×10^{-9}	1.60×10^{-5}	1.858	1.545
CHO	H	−4.35	5.26	−5.06	5.32	1.58×10^{-9}	1.87×10^{-3}	1.898	1.546
O^-	H	−12.20	3.57	−11.61	3.73	2.30×10^{-10}	1.24×10^{-6}	1.825	1.538
SH	H	−8.51	4.60	−9.59	5.01	2.66×10^{-9}	6.62×10^{-3}	1.861	1.540
S^-	H	−6.87	4.08	−8.64	5.30	1.62×10^{-9}	1.99×10^{-3}	1.867	1.533
CHO	CN	0.69	6.10	0.04	6.25	3.29×10^{-8}	4.17×10^{-1}	1.944	1.548
NO	H	5.72	7.71	4.22	11.86	2.58×10^{-4}	4.74×10^{-9}	1.950	1.532
CN	CN	0.28	6.08	0.35	6.25	3.27×10^{-8}	4.11×10^{-1}	1.939	1.547

[a] Energies and enthalpies are for open structures and bridged structures in kcal/mol. Rate constants (k), in s^{-1}, are calculated for the reaction from bridged to open radicals at 298 and 123 K. Bond distances (r), in Å, are for the bond being broken in the TS, or the bonds between the aryl group and the methylenes in the bridged radical (b).

by the Perdew−Wang expression.[8] Like the BLYP functional.[9] B3PW91 should practically eliminate the large spin contamination generally encountered using unrestricted Hartree−Fock (UHF) wave functions. Stable structures were fully optimized and transition states located at the UB3PW91/6-31G(p,d) level using the GAUSSIAN 98 series of programs.[10] Standard integration grids were employed. We calculated the vibrational frequencies of all stationary points to characterize them and obtain the zero point vibrational energies (ZPVE). ΔH's, ΔS's and ΔG's. These calculations used the harmonic oscillator, rigid rotor and ideal gas approximations at room temperature (298.15 K) and 1 atm of pressure.

Results and Discussion

We performed calculations on the potential energy surfaces for the rearrangement **1a** ⇄ **2a**. In addition we calculated the analogous surfaces for the rearrangements of the substituted radicals, **1(b−l)** ⇄ **2(b−l)** to investigate the effects of substituents upon the surface. In particular, we sought to determine which (if any) substitutions might lead to a stable bridged radical. The relevant energies, enthalpies, and free energies (298 K) are summarized in Table 1. For all calculations, $<S^2>$ was close to the expected value of 0.75 and always <0.80. For purpose of discussion, the enthalpies will be used in the following discussion.

The parent 2-phenylethyl radical is predicted to be lower in enthalpy in its open form, **1a**, by 10.1 kcal/mol. This value is close to, but slightly less than, the value of $E_a \geq 13$ kcal/mol, suggested by the laser flash photolysis study. However, there is a statistical factor of 2 that should be taken into account, as there are twice as many possible open as bridged structures. Using the free energy of activation (11.83 kcal/mol) and the factor of 2, we calculate a predicted equilibrium constant of 1.9×10^8, slightly less than, but close to, the predicted $\geq 10^9$. The TS leading from the bridged to the open form is 14.1 kcal/mol relative to the open radical. The enthalpy of activation for the opening of the bridged species, **2a**, is calculated to be 4.0 kcal/mol. This value can be compared with the Arrhenius E_a of 2.8 kcal/mol reported (with some skepticism since the same Arrhenius analysis produced an unlikely log A/s^{-1} value of 9.2).[3] However, once again a statistical factor of 2 must be taken into account. Just as there are two equivalent open radicals, **1a**, there are two independent paths, via two equivalent TS's, **3a**, to forming them. The predicted unimolecular rate constant for the reaction, **1b** → **1a**, can be estimated from transition-state theory from the equation $k = (k_B T/h)e^{-\Delta G/RT}$, where k_B is the Boltzmann constant, T is the temperature in K, h is Planck's constant, and R is the gas constant. Using the free energy of activation (4.1 kcal/mol) and the factor of 2, we calculate a rate constant of 2.6×10^5 s^{-1} at 123 K, consistent with the reported value of $\geq 2 \times 10^2$ s^{-1}.

In the optimized geometry of the open radical, **1a**, the dihedral angle between the terminal C−C bond and the plane of the aromatic ring is 49°. There appears to be a stabilizing interaction between the p-orbital of the terminal CH_2 and the proximate aryl C−H bond (C···H is 2.6 Å). This interaction can be compared to C−H···π interactions observed in other systems.[11] The C−C bond lengths between the ring and the methylenes in the bridged radical, **1b**, are 1.539 Å. In the optimized TS between **1a** and **1b**, the incipient bond is 1.846 Å.

A comparison of the energetic parameters for the substituted radicals is presented in Table 1. One of the major reasons for examining the effect of substituents upon the potential surface is to ascertain which, if any, substitution patterns might lower the relative energy of the bridged radical. If we can successfully predict that a particularly substituted phenylethyl radical will prefer the bridged structure, experimentation may lead to esr confirmation of the intermediate. The rate constants in Table 1 are all calculated as delineated above for the unsubstituted radical. Rate constants at room temperature (298 K) and the temperature appropriate to the reported attempt to observe the spectrum discussed above (123 K). Substitution at the para-position by CH_3, CF_3, OH, O^-, SH, or S^- has only a small effect upon the energy difference between the open and bridged structures. Substitution by CN an CHO both lower the relative

---

(8) Perdew, J. P.; Wang, Y. *Phys. Rev.* **1992**, *B 45*, 13244.

(9) Cioslowski, J.; Liu, G.; Moncrieff, D. *J. Org. Chem.* **1996**, *61*, 4111. Cioslowski, J.; Liu, G.; Matinov, M.; Piskorz, P.; Moncrieff, D. *J. Am. Chem. Soc.* **1996**, *118*, 5261.

(10) Gaussian 98 version A7, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.

(11) For a recent review, see Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253.

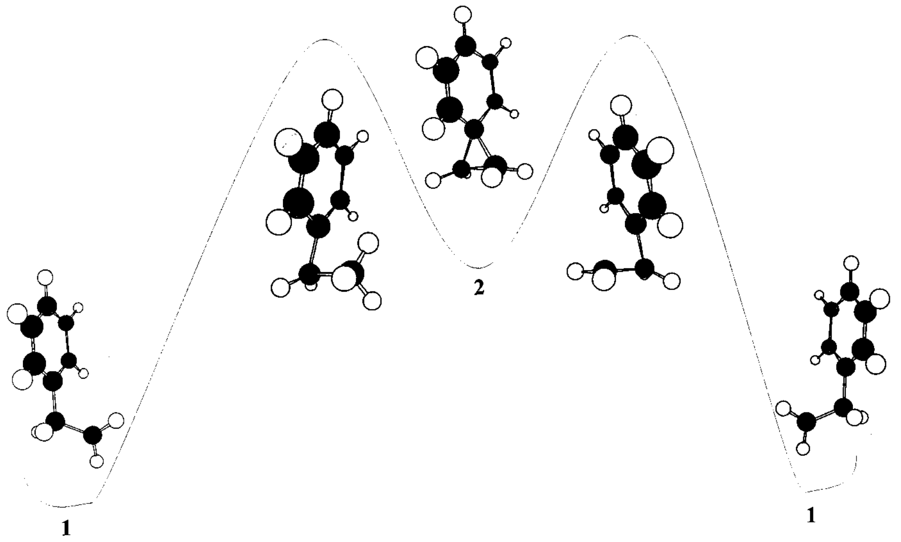


Figure 1. Reaction path for rearrangement.

energy of the bridged structure significantly compared to those substituents enumerated above, However, radicals substituted with CN or CHO in the para-position remain more stable in their open form. Para- substitution with NO renders the bridged more stable than the open radical by 4.2 kcal/mol Trisubstitutions, with CN's in the two ortho-positions and either a CN or a CHO in the para-position, make the two radical forms roughly equivalent in energy.

Except for these last three substituted radicals, the predicted rate constants for the rearrangement from bridged to open radical are all too great to be seen under the experimental conditions used in ref 3. The rate constants for the trisubstituted radicals barely meet the kinetic criterion for observation of an esr spectrum under these conditions ($k < 1 \times 10^2$ s^{-1} at 123 K). However, the p-NO radical, **2k**, should be easily observable as it is more stable than the open radical, **1k**, so it should be the predominant radical.

The NO moiety has long been associated with free radical stabilization in nitroxide radicals. For example, di-*tert*-butyl nitroxide is a classical example of a stable free radical.[12] The behavior of the nitroso group as a simple substituent is less well documented, presumably due to its relative instability. Nevertheless, one can easily understand the strong electron-withdrawing[13] and radical-stabilizing character of NO by considering three simple free radicals: allyl, cyanomethyl, and nitrosomethyl. Allyl is symmetrically delocalized, with equal spin on each terminal carbon. Cyanomethyl can be thought of as an allyl where one terminal carbon has been replaced by a nitrogen. Since the nitrogen atomic orbitals (AO's) are lower than those of carbon, the bonding π-orbital is polarized toward the N. The SOMO is thus polarized toward the C, placing more spin density at the terminal C than at the N. The nitrosomethyl radical can be thought of as an allyl where two C's are replaced by an N and an O. The N and O AO's are sufficiently lower than those of C so that the π^* N−O orbital is lower than the carbon p-orbital. Thus, the SOMO becomes similar to the N−O π^*-orbital. Most of the spin resides on the N and O. The radical is greatly stabilized.

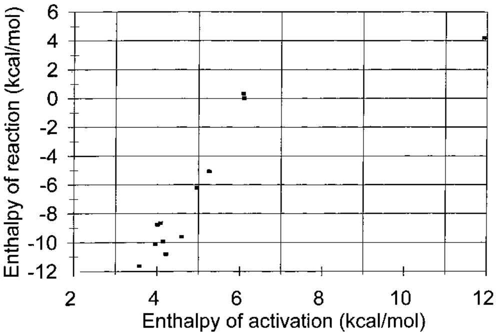


Figure 2. Variation of the enthalpy of activation with the enthalpy of reaction for **2** → **1**.

One should note that while all of the mono (para)-substituted open radicals prefer a geometry with the terminal CH_2 interacting with an ortho C−H of the aryl ring, when CN groups occupy the two ortho-positions, steric hindrance prevents this. Both **1j** and **1l** prefer conformations with this C−C bond roughly perpendicular to the aryl ring. Thus, the change in relative stability for the bridged vs open structures upon adding the ortho CN groups (i.e., comparing **2b** and **2f** with **2l** and **2j**) must be due to an increase in energy of the **1** structure, as well as a decrease in that of the **2** structure.

A comparison of the activation enthalpies for rearrangement of bridged to open radical correlates well with the corresponding enthalpies of reaction (Figure 2) and with the C−C distance in the TS for the bond being broken (Figure 3). This behavior would be expected from the Hammond postulate.[14] As the bridged radical, **2**, becomes higher in energy, it becomes closer in structure to the TS, **3**. Correspondingly, the activation energy for the rearrangement **2** → **1** increases as the enthalpy of the reaction increases.

---

(12) Coppinger, G. M. *J. Am. Chem. Soc.* **1957**, *79*, 501. Bartlett, P. D.; Funahashi, T. *J. Am. Chem. Soc.* **1962**, *84*, 2596.

(13) The Hammett para-σ^- constant as measured from acidity of phenols has been reported to be 1.629 (vs 0.891 for p-CN from the same series of experiments) by Fickling, M. M.; Fischer, A.; Mann, B. R.; Packer, J.; Vaughan, J. *J. Am. Chem. Soc.* **1959**, *81*, 4226−30.

(14) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

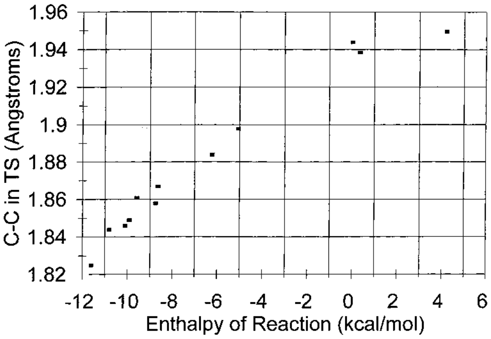


Figure 3. Variation of C−C distance in TS for bond being broken with enthalpy of activation.

Conclusion

The calculations presented here strongly suggest that the bridged 2-phenylethyl radical exists with a lifetime that would be difficult to measure by esr techniques, as previously reported. However, appropriately substituted bridged radicals, **2**, can be made that would be as stable (**2j**, **2l**) or more so (**2k**) as the corresponding open radical, **1**. Syntheses of one or more of the radicals should lead to experimental esr observation of the bridged species.

Acknowledgment. This work has been supported by a grant from PSC-CUNY, the CUNY Graduate School computational facility, and the Conselleria de Cultura, Educacio i Ciencia de la Generalitat Valenciana (Spain).

Supporting Information Available: The results of all calculations including structures in GAUSSIAN 98 archive format. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0017483