

Supporting Information
for
Stereochemistry of the C-S Bond Cleavage in
***Cis*-2-methylcyclopentyl Phenyl Sulfoxide Radical Cation**

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Instrumentation. ^1H -NMR spectra were recorded on a 300 MHz spectrometer in CD_3CN . GC-MS analyses were performed on a gas chromatograph equipped with a 30m x 0.25 mm silica capillary column coated with 5% diphenyl- and 95% dimethylpolysiloxane from 50 to 250 °C coupled with a mass selective detector at 70 eV. GC analyses were carried out on a gas chromatograph equipped with a 30m x 0.25 mm silica capillary column coated with 5% diphenyl- and 95% dimethylpolysiloxane from 50 to 250 °C.

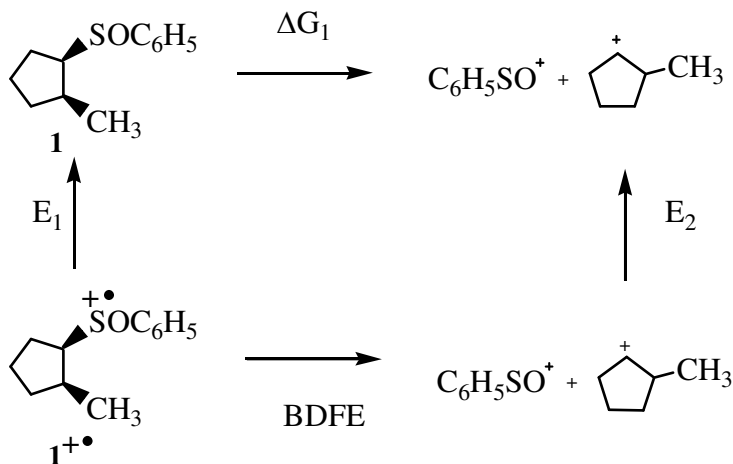
Materials. Acetonitrile (HPLC grade) was distilled over CaH. TiO_2 (anatase, dried at 110 °C) and Ag_2SO_4 were commercially available. *Cis*-2-methylcyclopentyl phenyl sulfoxide (**1**) was prepared by oxidation of the corresponding sulfide with sodium periodate in aqueous ethanol^{S1} and characterized according to ^1H NMR ^{13}C NMR and mass spectral data reported in the literature.^{S2} *Cis*-2-methylcyclopentyl phenyl sulfide was prepared by reaction of *trans*-2-methyl-cyclopentanol with *N*-benzenesulfonyl-succinimide.^{S3} 3-Cyano-*N*-methylquinolinium perchlorate was prepared and characterized as previously described.^{S4}

1-Methylcyclopentanol, *trans*-2-methylcyclopentanol, 2-methylcyclopentanols (mixture of isomers *cis/trans*) and diphenyl disulfide are commercially available. 1-Methylcyclopentyl acetamide was prepared from 1-methylcyclopentanol by the Ritter reaction.^{S5} Mp: 97-98°C (Lit. 98-99°C).^{S6} GC-MS m/z (rel. intensity) 126 (7), 112 (19), 99 (22), 84 (30), 70 (100), 60 (93), 56 (37). 2-Methylcyclopentyl acetamides (mixture of isomers *cis/trans*) were prepared by acetylation of *cis/trans*-2-methylcyclopentylamines synthesized according to the literature.^{S7} GC-MS m/z rel. intensity) M^+ 141 (7), 126 (4), 112 (6), 98 (29), 82 (17), 70 (28), 60 (100), 56 (94), 55 (10).

Phenyl benzenethiosulfonate and phenyl benzenethiosulfinate were prepared according to literature procedures.^{S8}

C-S bond dissociation free energy for *cis*-2-methylcyclopentyl phenyl sulfoxide radical cation

The C-S bond dissociation free energy (BDFE) value for *cis*-2-methylphenyl phenyl sulfoxide radical cation ($\mathbf{1}^{+\bullet}$) was calculated by using the following thermochemical cycle (Scheme S1):



Scheme S1

$$\text{BDFE} = \Delta G_1 + F(E_2 - E_1)$$

E_1 values is the peak reduction potential of $\mathbf{1}^{+\bullet}$ - $\mathbf{5}^{+\bullet}$ E_1 taken as 2.0 V vs SCE (peak reduction potential of methyl phenyl sulfoxide radical cation.^{S9} E_2 is the oxidation potential of the secondary cyclopentyl radical which can be estimated equal to that of the isopropyl radical (0.47 V vs SCE).^{S10}

ΔG_1 , the C-S bond dissociation free energy of the neutral $\mathbf{1}$, was determined from the C-S bond dissociation energy (BDE) applying an entropic correction ($T\Delta S^\circ$) of 10 kcal mol⁻¹ (this value has been considered similar to the entropy change associated with the homolytic C-S bond cleavage of thioanisole^{S11}). For the C-S BDE of $\mathbf{1}$ we have added 2.2 kcal to the calculated C-S BDE of *t*-butyl phenylsulfoxide obtained by DFT calculations (36.2 kcal mol⁻¹)^{S9} on the basis of the different stability of isopropyl and *t*-butyl radical.^{S12}

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