

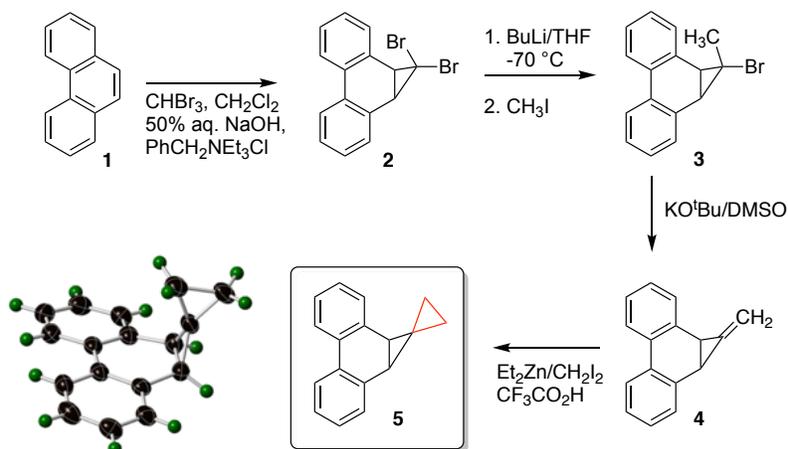
Narrative Report

PRF# 58437-UR4

Project Title “New Photochemical Approaches to Cyclopropylidenes from Phenanthrene-Based Spiropentanes”

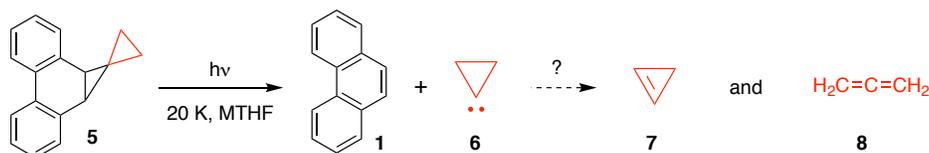
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Research progress: A phenanthrene-based spiropentane precursor (**5**) to the parent cyclopropylidene was successfully synthesized by the route shown in Scheme 1. The first step of the synthetic sequence was the phase-transfer catalyzed addition of dibromocarbene to phenanthrene (**1**), using our improved procedure,¹ to obtain the 1,1-dibromo cyclopropane adduct **2**. Compound **2** was then subjected to bromine-lithium exchange at low temperature with butyllithium and then treated with iodomethane to produce the methyl derivative **3**. Dehydrobromination of **3** with potassium tert-butoxide led to the methylenecyclopropane **4**. Finally, the desired precursor **5** was synthesized from **4** by the action of diethylzinc and diiodomethane in trifluoroacetic acid.² Precursor **5** was fully characterized by ¹H and ¹³C NMR, and IR spectra along with GC-MS data. The X-ray crystal structure of **5** was determined and is also shown in Scheme 5.



Scheme 1: Synthetic route to a phenanthrene-based spiropentane precursor (**5**) to cyclopropylidene. The X-ray structure is also shown (with thermal ellipsoids drawn at a 50% probability level).

A sample of **5** was then sent to the laboratory of the P.I.'s collaborator, Professor Manabu Abe at Hiroshima University, Japan, for measurements of low-temperature photolysis in a solid matrix. A 0.1 M solution of **5** in 2-methyltetrahydrofuran (MTHF) was transferred into quartz EPR-tube and degassed under high vacuum of $\sim 2 \times 10^{-2}$ Pa. After three freeze-pump-thaw cycles, the tube was vacuum sealed and the MTHF matrix was irradiated using 266 nm laser at 20 K (Scheme 2). An X-band EPR spectrum was recorded at 1000 – 5000 G during 20 minutes of photolysis at 20 K, and is shown in Figure 1. The EPR spectrum appears to show signals for the triplet biphenyl moiety of the precursor as well as for the phenanthrene byproduct. Both of these signals subside when the light source is turned off. Further analysis of data is currently underway. It is anticipated that cyclopropylidene (**6**) will undergo 1,2-hydrogen shift and/or ring opening to give cyclopropene **7** and allene **8**.³ A detailed computational study of cyclopropylidene (**6**) is also in progress.



Scheme 2: Low temperature photolysis of precursor **5** in 2-methyltetrahydrofuran (MTHF).

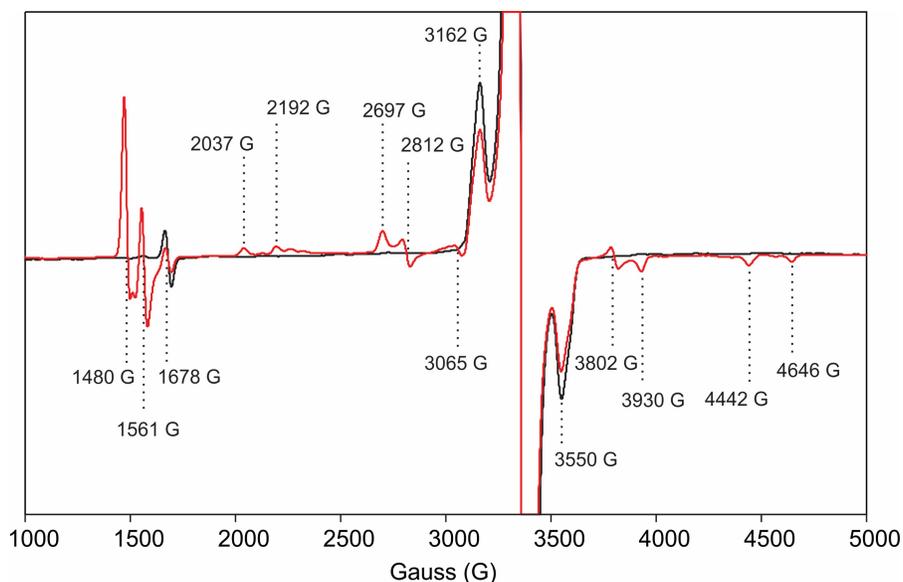


Figure 1. EPR spectra obtained during 20 minutes of photolysis of **5** using 266 nm laser irradiation (red) and after 1 m in dark conditions (black) at 20 K in glassy MTHF matrix.

Impact of research on P.I.: Thanks to this grant the P.I. has now been able to tap into the versatility of phenanthrene-based carbene precursors. These precursors are much safer to handle and easier to synthesize especially in a laboratory that is driven by undergraduate students. It has now become possible to investigate the smallest cyclic carbene and learn about its fundamental properties through these alternative precursors.

Impact of research on students: Students in the P.I.'s laboratory have been able to participate in original research work with funding from this grant. They have received invaluable research training in many areas including synthesis, purification, analysis with instrumentation, mechanistic studies, and computational chemistry. They have also benefited from the international collaboration with colleagues in Japan.

- (1) Nguyen, J. M.; Thamattoor, D. M. "A simple synthesis of 1,1-dibromo-1a,9b-dihydrocyclopropa[1]phenanthrene." *Synthesis* **2007**, 2093-2094.
- (2) de Meijere, A.; Khlebnikov, A. F.; Kozhushkov, S. I.; Miyazawa, K.; Frank, D.; Schreiner, P. R.; Rinderspacher, B. C.; Yufit, D. S.; Howard, J. A. K. "A convergent route to enantiomerically pure higher [n-2]triangulanedimethanol derivatives and [n]triangulanes ($n \geq 7$)." *Angew. Chem., Int. Ed.* **2004**, *43*, 6553-6557.
- (3) Yoshimine, M.; Pacansky, J.; Honjou, N. "Ab initio studies of the C₃H₄ surface. 3. Thermal isomerization." *J. Am. Chem. Soc.* **1989**, *111*, 4198-4209.