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ELECTRON SPIN RESONANCE SPECTROSCOPY OF PHENYL-CYCLOALKYL CARBENES

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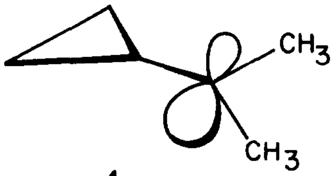
Abstract *Phenyl-cyclohexyl, phenyl-cyclopentyl, phenyl-cyclobutyl, phenyl-1-benzylcyclobutyl, and phenyl-1-benzylcyclopropylcarbene were photochemically generated in a matrix at low temperature and studied by ESR.*

Methylene is known to have a triplet ground state.[1] Theory predicts that the energy gap between the triplet and lowest lying singlet state is roughly 9 kcal/mole [2] This is in accord with several experimental values,[3] although photodetachment studies indicate a large singlet-triplet gap of approximately 20 kcal/mole.[4] Dynamic NMR studies of the dimethyl cyclopropyl carbinyl cation **1** indicate that the cyclopropyl group stabilizes the carbocation by 13.7 kcal/mole.[5] This suggests that the singlet-triplet splitting in cyclopropyl carbene **2** might be considerably smaller than in methylene The ionic singlet state of **2** might even be sufficiently stabilized to become the ground electronic state. Theory has not rigorously addressed this system at present, the singlet-triplet splitting of **2** has not been calculated explicitly. On the basis of extended Huckel calculations Hoffmann has concluded that triplet **2** is the "very probable ground state" [6] Schoeller has studied the singlet cyclopropyl carbene-cyclobutene interconversion by the MINDO/3, MINDO/2 plus CI, and STO-4/31G methods



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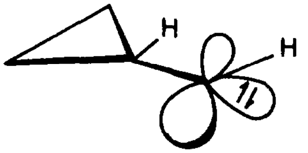
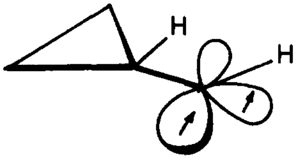
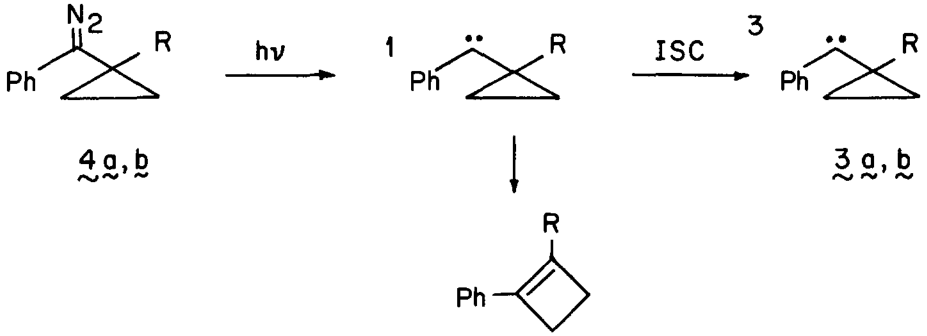


2S



2T

ESR spectroscopy is a useful method for the characterization of triplet state species [8] The matrix isolation of **2** was not attempted, however, as hydrocarbon triplet alkyl carbenes are unknown. As phenyl-alkyl triplet carbenes have been observed previously, our efforts have focused on phenyl-cyclopropyl carbene **3a**. Moss and Wetter have shown that photochemically generated phenylcyclopropyl carbene **3a** at 25°C gives 1-phenyl cyclobutene and phenylacetylene At low temperature the carbene can be captured with various olefins to give cyclopropanes These authors concluded that triplet involvment in the chemistry of **3a** is limited [9] Photolysis of phenylcyclopropyl diazomethane **4a** in 2-methyltetrahydrofuran (2 MTHF) with a 1000 watt mercury xenon arc lamp at 10-25K does not produce the ESR spectrum of **3a** The addition of a sensitizer (1-naphthaldehyde) is similarly unsuccessful Photolysis of phenyl cyclobutyl diazomethane under similar conditions gives a weak spectrum of the corresponding carbene **5a**. Intense triplet carbene spectra were observed for phenyl cyclopentyl (**12**) and phenylcyclohexyl (**11**) carbene (see Table) even at 77K A very dramatic improvement in signal intensity was observed upon replacement of the methine cyclobutyl hydrogen with a benzyl group A plausible explanation is that photochemical loss of nitrogen from the diazo precursor originally yields a singlet carbene The singlet state can suffer intramolecular rearrangement in competition with intersystem crossing (ISC) to the triplet carbene The benzyl substituent shifts the partitioning of the singlet in favor of ISC by suppressing rearrangement processes. This is a consequence of the considerable atomic motion required in the 1,2 benzyl shift or in the ring expansion reactions in the rigid matrix. The zero field splitting parameters for triplet phenyl cyclobutyl carbene 5b and phenyl cyclobutyl carbene 5a are exactly the same. The benzyl group does not significantly perturb the electron spin distribution in the triplet state Accordingly, phenyl-1-benzyl-cyclopropyl diazomethane 4b was synthesized.[10] Replacement of the methine hydrogen with benzyl permitted the observation of a previously elusive cyclopropyl substituted methylene.

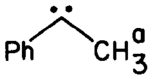
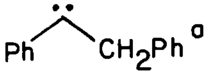
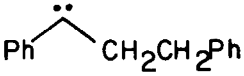
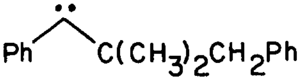
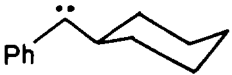
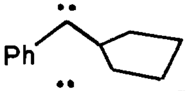
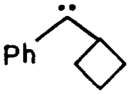
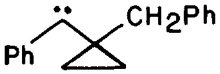


(a) R = H (b) R = CH_2Ph

The observation of a stable ESR spectrum of 3b at 23K requires that the triplet is the ground state of the carbene or within a few cal/mole of the ground state [11] If one assumes that the benzyl group of 3b does not significantly perturb the electronic structure of the phenyl cyclopropyl carbene, then 3a is also likely to have a triplet ground state, or an extremely low lying triplet state.

The zero field splitting parameter |D/hc| is relatively constant for carbenes 5-12 The value for 3b is significantly smaller than that observed for other phenyl-alkyl carbenes, indicating considerable spin delocalization into the cyclopropane ring The cyclopropyl ring is much less effective at delocalizing the carbene spin density than a second phenyl group (13) The magnitude of the effect is consistent with that found in the cyclopropyl carbinyl radical.[12] Carbon-13 labelling experiments are in progress to determine the exact spin distribution in 3b

The Zero Field Splitting Parameters of some Phenyl-Alkyl Carbenes

		|D/hc|	|E/hc|
6		0.501	0.025
7		0.496	0.027
8		0.493	0.029
9		0.502	0.027
10		0.498	0.026
11		0.492	0.025
12		0.500	0.028
5b		0.488	0.026
5a		0.488	0.026
3b		0.473	0.026
13		0.405	0 019

a) Reference 8

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