

Spectroscopy, Photochemistry, and Tunneling Reactions of Thiophene and Benzothiophene Carbenes

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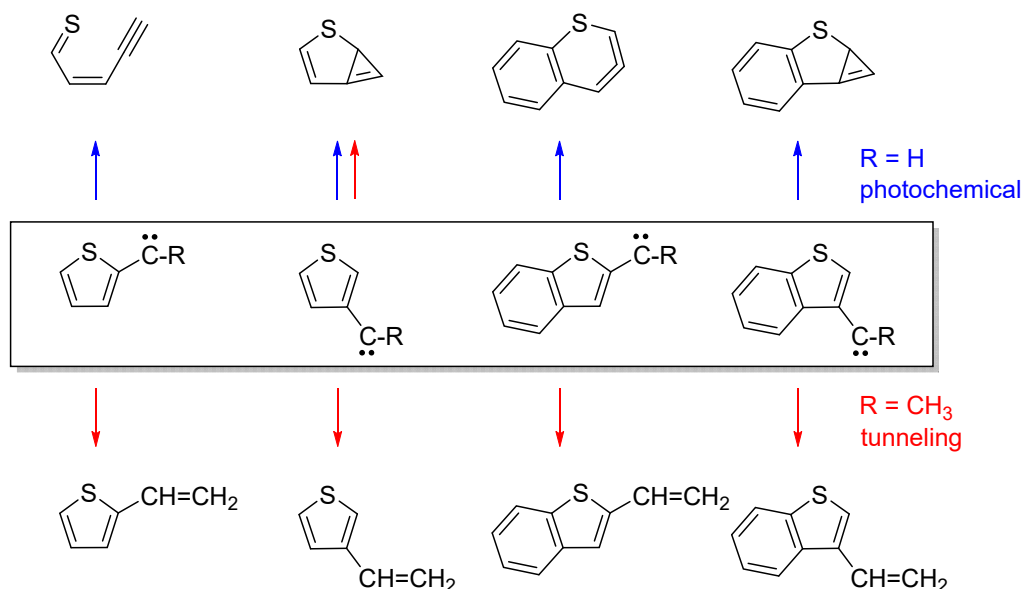
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Carbenes derived from thiophene and benzothiophene ('thienyl' carbenes) proved to be unexpectedly rich systems for studying the spectroscopy, photochemistry, and tunneling reactions of these organic reactive intermediates.

Under matrix isolation conditions (N₂, 10 K) the photoproducts of 2- or 3-thienyldiazomethane involve ring fragmentation. After considerable effort, triplet 3-thienyl carbene and its bicyclic isomer were spectroscopically characterized. EPR spectroscopy hints at a very slow spin-forbidden, heavy-atom tunneling reaction involving the cyclization of the triplet carbene to the singlet bicyclic structure. In the benzo series, neither carbene was observed: 2-benzothienyldiazomethane undergoes ring expansion, while 3-benzothienyldiazomethane undergoes cyclization.



Simple introduction of a -CH₃ (or -CD₃) substituent renders the triplet carbenes observable by EPR spectroscopy. The -CH₃ derivatives are not stable in the dark at 10 K. They undergo spin-forbidden intramolecular hydrogen migrations reactions. As expected for a tunneling process, this reactivity is completely suppressed at 10 K in the case of the -CD₃ substituent.

The significance of the work derives from the insights afforded into tunneling phenomena in organic systems.