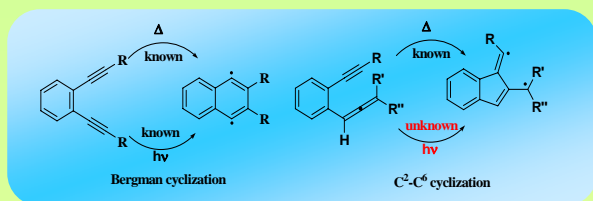




Mechanistic Study of the Photochemical C²-C⁶ Biradical Cyclization of Enyne-Allenes

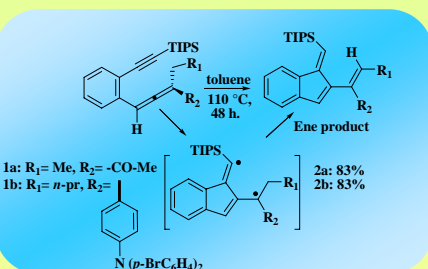
Introduction:

Photochemical analogs of thermal biradical cyclizations have been a major concern of research in recent years due to their high applicability to photodynamic therapy (PDT).¹ Although the Bergman cyclization of enediynes can be accomplished via the photochemical route, very little research has gone into probing the photochemical cyclization of enyne-allenes.²



Recently, we have established the first examples of photochemical Myers-Saito and C²-C⁶ cyclizations using cyclohexenyne-allenes with an internal triplet sensitizer at the allene terminus.² The present study will now try to extend the photochemical investigations towards the cyclization of **benzannulated enyne-allenes** (e.g. **1a** & **1b**), in particular since theoretical studies by Engels *et al.* calculated high excitation energy T₁(S₀) for these enyne-allenes.³ The mechanism of the photochemical reaction (triplet vs. singlet; biradical vs. carbene) will be interrogated.

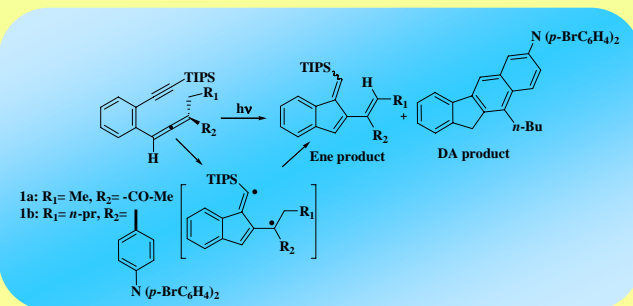
Thermal cyclization:



► Upon heating, enyne-allenes **1a** and **1b** cyclized smoothly along the C²-C⁶ biradical pathway.⁴

Photochemical cyclization:

► Upon photolysis (at 300 nm) enyne-allene **1a** provided a mixture of *E*- (22%) and *Z*- (30%) isomeric Ene products, while **1b** furnished a mixture of Ene (32%) and DA (18%) product.



Solvent, conditions	Ene product	DA product
1a toluene, 1,4-CHD, 300 nm, 36 h	52% (<i>E/Z</i> isomer)	-
1b toluene, 1,4-CHD, 300 nm, 6 h	32%	18%

1,4-CHD: 1,4-cyclohexadiene

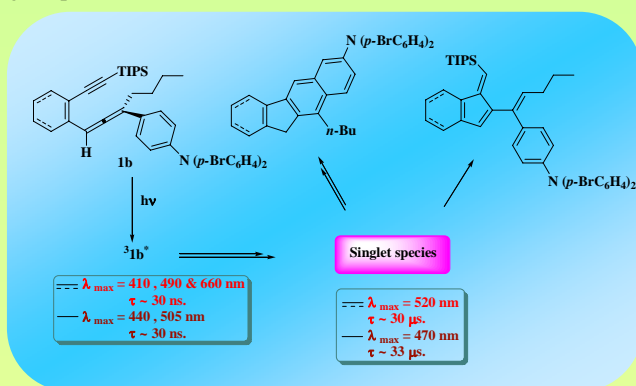
Acknowledgments:

We are greatly indebted to the DFG for financial support and to the Fonds der Chemischen Industrie for assistance.

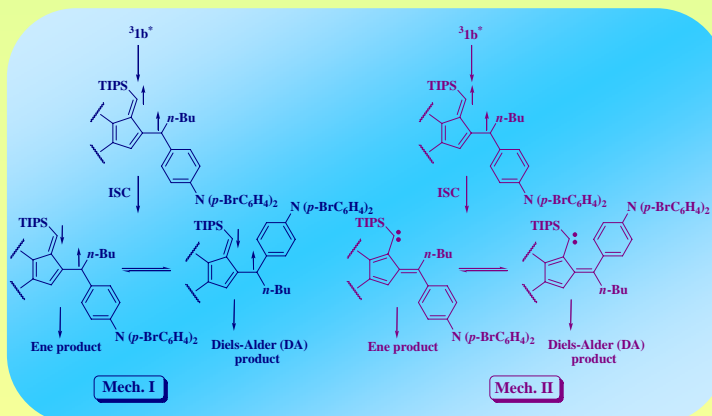
References: 1) Boyle, R. W.; Dolphin, D. *Photochem. Photobiol.* **1996**, *64*, 469. 2) Schmittel, M.; Mahajan, A. A.; Bucher, G. *J. Am. Chem. Soc.* **2005**, *127*, 5324. 3) Spöler, C.; Engels, B. *Chem. Eur. J.* **2003**, *9*, 4670. 4) a) Schmittel, M.; Strittmatter, M.; Kiau, S. *Tetrahedron Lett.* **1995**, *36*, 4975. b) Schmittel, M.; Kiau, S.; Strittmatter, M. *Angew. Chem., Int. Ed.* **1996**, *35*, 1843. 5) Forster, E. W.; Grellmann, K. H. *Chem. Phys. Lett.* **1972**, *14*, 536.

Laser Flash Photolysis (LFP):

A LFP study of **1b** (aromatic and cyclohexyl system) showed two transients. The first one was quenched by ³O₂ (λ_{max} at 505 is typical for a triplet state of triphenylamine derivative⁵). Hence, we assigned this transient to a triplet ³**1b**^{*} species. The second transient was not quenched by ³O₂ and *n*Bu₃SnH; thus it was consequently assigned to a singlet species.



Is the singlet species in the photochemical reaction a singlet biradical (Mech.I) or a singlet carbene (Mech.II)?



► As trapping experiments in ethanol did not lead to incorporation of the OEt group, a carbene mechanism can be excluded.

How can a singlet biradical produce Ene and DA products in the photochemical reaction, but only Ene product in the thermal case?

Temperature dependence of the photochemical cyclization of **1b** strongly suggests that two rotamers dictate the product formation at low temperature but that they are interconvertible at higher temperature.

Solvent	Irradiation time	Temp. in °C	Ene product	Diels-Alder product
toluene	6 h	20	32 %	18 %
toluene	3 h	40	27 %	8 %
toluene	1 1/2 h	60	27 %	trace

Conclusions: The LFP study suggests that the C²-C⁶ cyclization proceeds along the triplet manifold. The primarily formed triplet C²-C⁶ biradical undergoes ISC to the singlet biradical that allows for the formation of the Ene and DA products. These two reaction channels show a marked temperature dependence.