2B4b

LFP study on Generation of Long-lived Singlet 1,2-Diaza-4,4-dialkoxycyclopentane-3,5-diyls

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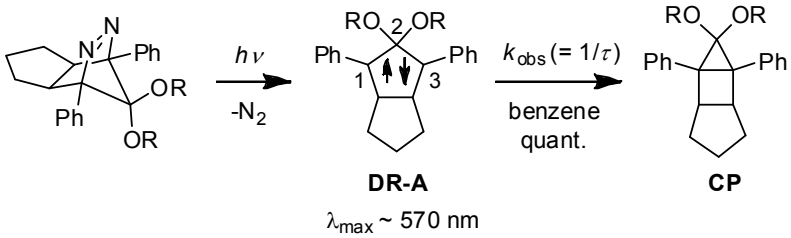
Localized singlet diradicals are key intermediates in processes involving homolytic bond-cleavage and –formation. The reactive intermediates are supposed to be extremely short-lived due to the fast radical-radical coupling reaction, thus it is difficult to obtain information about their chemical properties. So far, we have succeeded to generate and detect the relatively long-lived singlet diradicals, i.e.cyclopentane-1,3-diyls **DR-A**. We also found that the lifetime of the singlet diradicals depend on the chain-length of the alkoxy-groups, and the fate of the diradicals was of producing the corresponding ring-closing products **CP** (Scheme 1)[1]. In the present study, we report the generation and reactivity of 1,2-diaza-4,4-dialkoxycyclopentane-3,5-diyls **DR-B**[2].

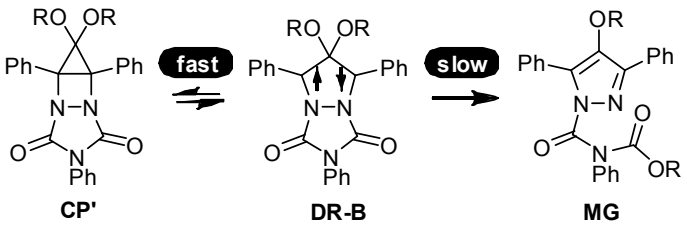
Scheme 1. Reactivity of singlet cyclopentane-1,3-diradicals



OR	τ_{293K} / ns
OMe	302
OEt	880
$OC_{10}H_{21}$	2146

In contrast to the one decay process of **DR-A**, two decay processes (i.e. fast and slow) were found for the diradical **DR-B** (Figure 1, Scheme 2). The mechanism shown in Scheme 2 was proposed, in which **DR-B** was in equilibrium with **CP'**. Surprisingly, the lifetime of **DR-B** was over 100 ms in dry toluene and major product was alkoxy migrated compound **MG**. We also report the alkoxy-group (OR) effect on the lifetime.

Scheme 2. This study



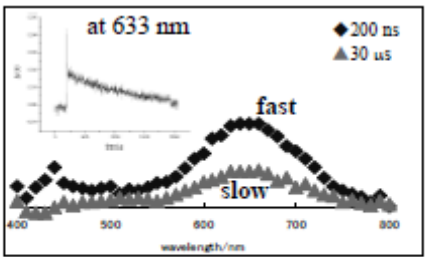


Figure 1. Transient Absorption Spectrum of **DR1** (OR = OMe). λ_{exc} = 355 nm in toluene at 293K.

References
1 (a) *J. Am. Chem. Soc.,* **2000**; *122*, 2019. (b) *J. Am. Chem. Soc.* **2002**; *124*, 6540. (c) *J. Am. Chem. Soc.,* **2004**; *126*, 574. (d) *submitted for publication*, 2 (a) *Angew. Chem. Int Ed.* **2006**; *45*, 7828. (b) *Angew. Chem. Int Ed.* **2012**, *51*, 11924