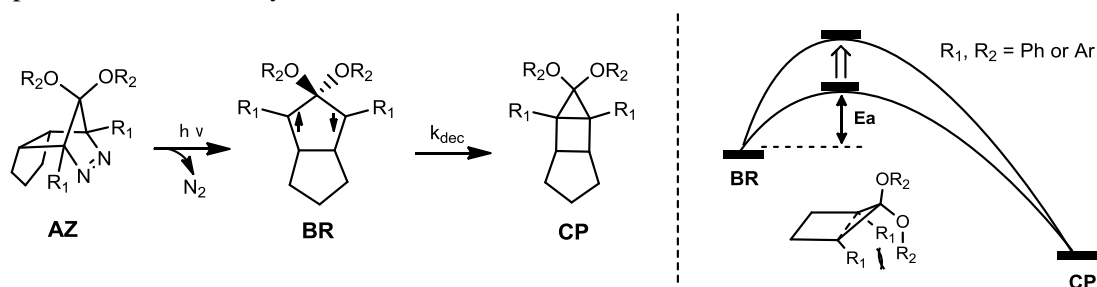


# Kinetic Stabilization of Singlet 2,2-Dialkoxycyclopentane-1,3-diyls

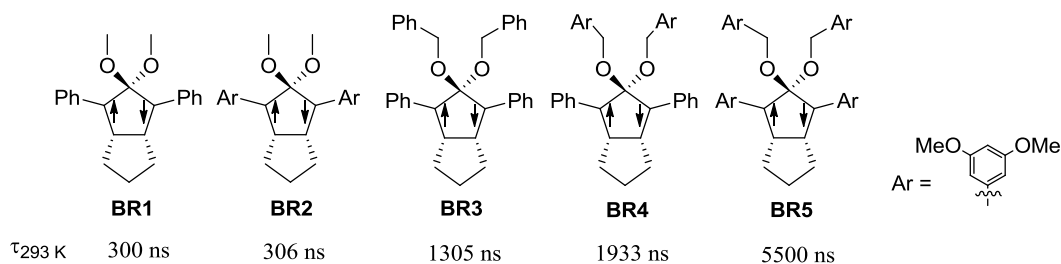
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Biradicals are defined as molecules in which two electrons occupy two degenerate, or nearly degenerate, molecular orbitals. Localized singlet biradicals are key intermediates in processes involving homolytic bond-cleavage and bond-formation reactions in cyclic compounds. However, the reactive intermediate is generally quite short-lived, because a radical-radical coupling process is usually occurs without an energy barrier. Thus, it is difficult to detect and characterize the singlet biradicals. In the last decade, we have succeeded in generating detectable singlet biradicals **BR**, i.e. 2,2-dialkoxycyclopentane-1,3-diyl using the denitrogenation of the corresponding azoalkanes **AZ** (Fig. 1).<sup>[1-8]</sup> The electron-withdrawing groups at C(2) position are necessary to pull down energetically the singlet state below the triplet state of the 1,3-diyls.



**Fig. 1** Generation and kinetic stabilization of singlet biradicals

In the present study, the substituent effect at C(1)-(3) positions on the lifetime of the singlet 1,3-biradical was examined. The lifetime of the singlet biradicals were found to be dramatically increased when the sterically hindered substituents, such as 3,5-dimethoxyphenyl group (Ar), were introduced at the C(2) position and also at the C(1) and C(3) position of the 1,3-diyls. The kinetic stabilization was found to be effective to elongate the lifetime of the singlet biradicals.



**Fig. 2** Substituent effect on the lifetimes of singlet biradicals

## References

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