

Effects of Chain Length on Behavior of Biradicals Generated from Norrish Type I Reaction of 2,2-Diphenylcycloalkanones. Isolation and Photochemistry of Intermediate Methylene cyclohexadienyl Ketones

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Abstract: The reaction course of biradicals, $O=C^{\uparrow}-(CH_2)_{n-2}-C^{\uparrow}Ph_2$, generated from Norrish type I reaction of 2,2-diphenylcycloalkanones with various ring sizes, is switched from intramolecular disproportionation ($n=6, 7$) to acyl-phenyl recombination ($n \geq 9$) in methanol.

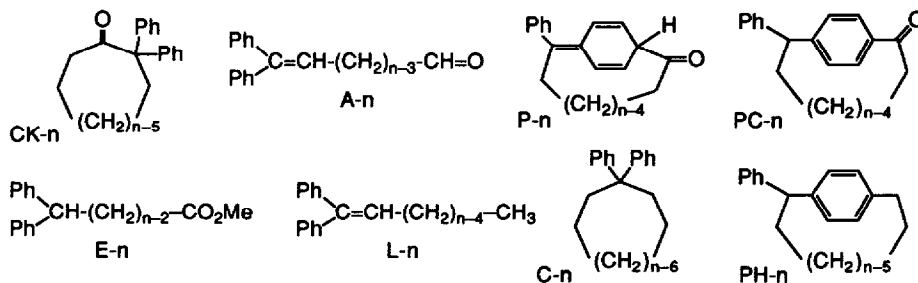
Norrish type I (photochemical α -cleavage) reactions of cyclic ketones usually proceed from ketone triplets to generate triplet biradicals, which afford, after intersystem crossing, disproportionation and/or cyclization products,^{1,2} and much attention has been focused on the nature of intersystem crossing and chain dynamics of biradicals.³ Among the triplet biradicals, $O=C^{\uparrow}-(CH_2)_{n-2}-C^{\uparrow}Ph_2$, generated from α -cleavage of n -membered 2,2-diphenylcycloalkanones (CK- n), those from 2,2-diphenylcyclohexanone give exclusively an unsaturated aldehyde (A-6), as reported previously.² Herein we wish to report switching of the reaction courses of this series of triplet biradicals depending upon the chain length n and the role of intermediate methylenecyclohexadienyl ketones in the reaction course.

Irradiation of 2,2-diphenylcycloheptanone (CK-7) with 313-nm light in methanol gave exclusively an unsaturated aldehyde (A-7) in 76% yield, but neither cyclophane-type products nor methyl ester (E- n) was detected;⁴ the photochemical behavior is very similar to that of CK-6. However, 2,2-diphenylcyclododecanone (CK-12) and 2,2-diphenylcyclotridecanone (CK-13) afforded paracyclophanyl ketones (PC- n , $n=12$ and 13; 50 and 27% yield, respectively) together with decarbonylated cyclophanes (PH- n , $n=12$ and 13; 27 and 37%, respectively); there are no significant amounts of aldehydes (A- n).

As previously reported for CK-6,² the α -cleavage of CK- n takes place in the triplet state to generate triplet biradicals (3BR - n), which lead to products by way of intersystem crossing to the corresponding singlet biradicals (1BR - n). Intramolecular hydrogen transfer (disproportionation) in 1BR -7 gives A-7, and cyclization between the acyl and phenyl groups followed by proton shift in the resulting methylenecyclohexadienyl ketone, P- n , gives PC- n , where n is 12 or 13. Thus, the reaction course is very much different between CK- n with a smaller ring size and those with a larger ring size. The reaction processes are proposed in Scheme 1.

The photochemistry of CK-9 and CK-11 is rather complicated but informative. Prolonged irradiation of CK-9 with 313-nm light in methanol afforded an open-chain (L-9; 23%) and a cyclic decarbonylation product (C-

9; 33%) together with aldehyde A-9 (31%); however, work-up of the sample solution at early stages gave a methylenecyclohexadienyl ketone (P-9) and A-9. The quantum yield for CK-9 disappearance was 0.39 at low conversion. Time development of products monitored by HPLC during the photolysis of CK-9 indicated that, as the starting ketone is consumed, P-9 is rapidly formed in the early stage but decreases with time, and that other products, A-9, C-9, and L-9, increase slowly (Fig. 1). Moreover, photolysis with 313-nm light in methanol of the isolated P-9⁵ gave A-9, C-9, and L-9 in a similar ratio (Fig. 2).⁶ These results indicate that ¹BR-9 derived from CK-9 through ³BR-9 competitively undergoes acyl-diphenylmethyl recombination (cyclization) returning to the starting ketone and acyl-phenyl recombination (pre-cyclophane formation) giving P-9, which is, however, so photolabile as to give rise to the secondary products under the reaction conditions (Scheme 1; $n=9$).



Similar studies on CK-11 indicate that P-11 is the primary product, and thermally converted to PC-11 or photolyzed into PH-11, A-11, and L-11.^{7,8} Prolonged irradiation of CK-11 afforded PC-11 (74%) and PH-11 (14%) together with small amounts of A-11 and L-11. The quantum yield for CK-11 disappearance was 0.36 at low conversion. The present results show that the reaction course of CK- n is switched at $n=9$ from intramolecular hydrogen transfer to acyl-phenyl recombination, and that the decarbonylation products and A- n ($n \geq 9$) are formed as secondary products from photolysis of the primary product, P- n .⁹

Behavior of the triplet biradicals was directly observed by means of laser flash photolysis of CK- n .^{10,11} As shown in Fig. 3, pulsed laser excitation of CK-9 at 308 nm in methanol exhibited an absorption band with a lifetime of 123 ns around 335 nm due to the corresponding triplet biradical. All the ketones CK- n employed in this work exhibited similar transient absorptions with lifetimes of ca. 100 ns under similar conditions, and the

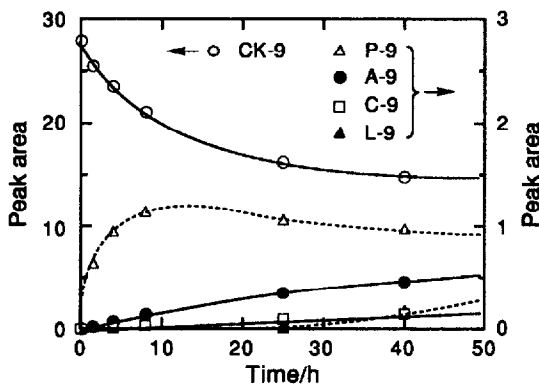


Fig. 1. Time Development of CK-9 Disappearance and Product Formation. The ordinate is relative peak area of HPLC chart monitored at 260 nm.

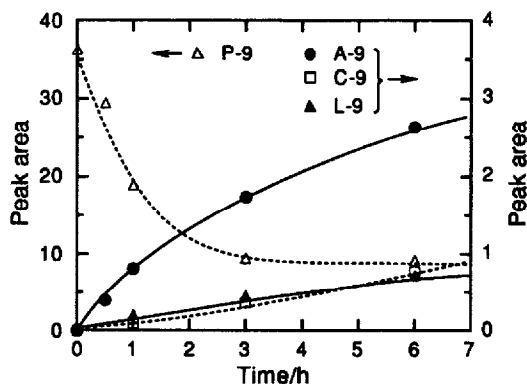


Fig. 2. Time Development of P-9 Disappearance and Product Formation. The ordinate is relative peak area of HPLC chart monitored at 260 nm.

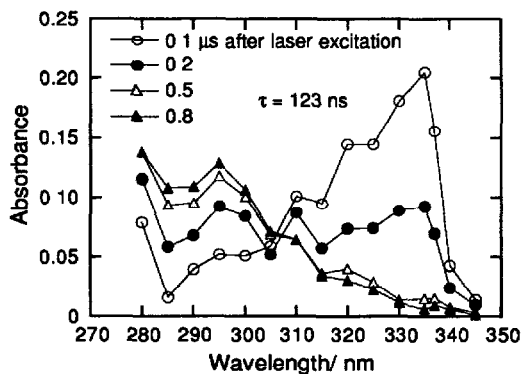


Fig. 3. Transient absorption spectra observed on 308-nm laser excitation of CK-9 in methanol.

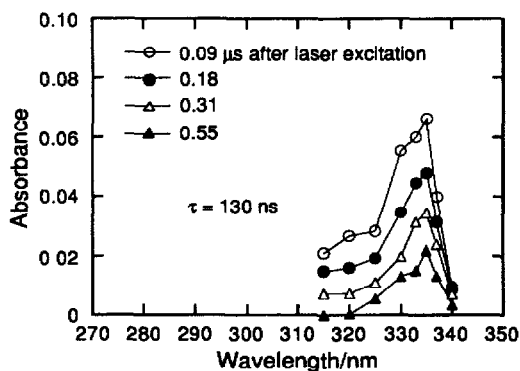
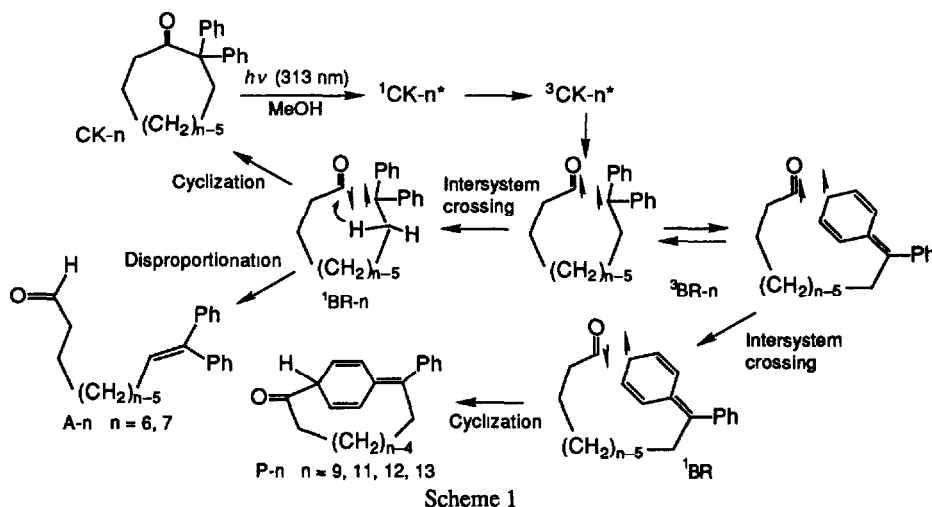


Fig. 4. Transient absorption spectra observed on 308-nm laser excitation of P-9 in methanol.



transient absorptions can be ascribed to the corresponding triplet biradicals.² In Fig. 3 a new absorption band grows up in the shorter wavelength region. This band is ascribed to a permanent product, P-9. The isolated P-9 also exhibited a transient absorption similar to the 335-nm band from CK-9 in the spectral shape and lifetime (130 ns, Fig. 4). These observations indicate that photolysis of P-9 generates the same intermediate as the biradical from CK-9.

The lifetime of triplet biradicals ${}^3\text{BR-}n$ ($n=6, 7, 9, 11-13$) depends on the chain length n , and shows a maximum at $n=9$, ${}^3\text{BR-}9$. This feature is in good agreement with the reactivity profile of cyclization reactions of chain molecules with two reaction centers at each end; the cyclization is less efficient for molecules of the chain length of 8 to 10 compared to those of shorter and longer chain lengths (difficulty in medium-sized ring closure).¹² These results indicate that the intersystem crossing takes place predominantly in the cyclic conformers preferable for product formation, since the lifetime of ${}^3\text{BR-}n$ is governed by intersystem crossing to ${}^1\text{BR-}n$ ² due to dominant spin-orbit coupling,³ and under the present reaction conditions ${}^3\text{BR-}n$ is in conformational equilibrium among various conformers. Therefore, the switching of reaction courses means that the most favorable conformation for intersystem crossing is different between short-chain and long-chain biradicals.

It is concluded that photolysis of CK-*n* gives the aldehyde through disproportionation of biradical intermediates when the ring size of CK-*n* is as small as 6 or 7, and, when the ring size is as large as 9 through 13, the biradicals cyclize mainly at the phenyl group to give the methylenecyclohexadienyl ketones. The intersystem crossing of the triplet biradicals takes place in their cyclic conformations that are favorable for giving cyclization or disproportionation products in the singlet biradicals.

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4. 2,2-diphenylcycloalkanones (CK-*n*, 9×10^{-4} mol dm⁻³) were irradiated for several hours under nitrogen with a 400-W high-pressure mercury lamp through a K₂CrO₄-Na₂CO₃ filter solution. The products were isolated and their structure was determined on the basis of various spectral data. The yields of products were determined with GLPC or HPLC.
5. Ketone P-9 was isolated with repeated chromatography on silica gel and identified based on spectral data.
6. No significant amount of CK-9 was detected.
7. P-11 was stable at low temperature in solution but easily collapsed to PC-11 on silica gel for chromatography.
8. The multiplicity of excited state responsible for the photolysis of P-*n* is now under investigation.
9. A minor contribution of pathways of their direct formation from CK-*n* through triplet or singlet biradicals cannot be ruled out.
10. Laser flash photolyses of CK-*n* and P-9 were performed with 308-nm laser pulses from an excimer laser (Lambda Physik EMG-101) as an exciting light source and a pulsed xenon arc (Wacom KXL-151) as a monitoring light source. The details of the apparatus for laser flash photolysis have been described elsewhere.¹¹
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