Bull. Chem. Soc. Jpn., **72**, 103—113 (1999)

Behavior of Biradicals Generated from a Norrish Type-I Reaction of 2,2-Diphenylcycloalkanones. Chain-Length Dependence and Magnetic Field Effects

Itsuko Suzuki, Ryoko Tanaka, Akinori Yamaguchi, Shin-ichiro Maki, Hiroaki Misawa,# Katsumi Tokumaru, Ryoichi Nakagaki,†, ## and Hirochika Sakuragi*

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571

†Institute for Molecular Science, Myodaiji, Okazaki 444-8585

(Received September 7, 1998)

The reaction course of acyl-diphenylmethyl biradicals (α-oxo-ω, ω-diphenyl-α,ω-alkanediyl biradicals), $\mathrm{O{=}C^{\uparrow}{-}(CH_2)_{n-2}{-}C^{\uparrow}Ph_2}$ (^{3}BR-*n*), generated from the Norrish type-I reaction of 2,2-diphenylcycloalkanones (CK-*n*) with various ring sizes in methanol, is switched from intramolecular disproportionation (n = 6, 7), giving a diphenylalkenal, to acyl-phenyl recombination ($n \geq 9$), affording a cyclophane derivative. The behavior of ^{3}BR-9 derived from CK-9 was studied in detail; the photolysis of CK-9 afforded an open-chain and a cyclic decarbonylation product together with an unsaturated aldehyde and a 4-methylene-2,5-cyclohexadienyl ketone (a pre-cyclophane). The photolysis of this ketone gave the same products that arose from the photolysis of CK-9, presenting the possibility that the decarbonylation products and a part of the aldehyde are formed as secondary products during irradiation.

The magnetic field dependence of the lifetimes of ^{3}BR-*n* (n = 12 and 13) generated from CK-12 and 13, respectively, was measured in methanol by means of a pulsed-laser excitation technique. The rate constants for intersystem crossing showed a maximum at a relatively low field strength, which decreased with increasing the field strength to level off to an asymptotic value at > 1.5 kG. The results show that the role of hyperfine coupling in intersystem crossing is less important in these systems, presumably because of the presence of a carbonyl oxygen and the absence of a hydrogen atom at the radical center.

Photochemical α-cleavage (Norrish type-I reaction) of cyclic ketones is among the most documented reactions, and usually proceeds from ketone triplets to generate triplet biradicals, which afford, after intersystem crossing (ISC), disproportionation and/or cyclization products.[1—5] Much attention has been focused on the nature of ISC and the chain dynamics of the intermediate biradicals.[6] The lifetime of triplet biradicals in fluid solutions corresponds to the efficiency of ISC,[6,7] which is governed by the spin-orbit coupling (SOC) and hyperfine coupling (HFC).[6] For ISC of acyl-alkyl biradicals (α-oxo-α,ω-alkanediyl biradicals) SOC plays the main role;[6,8] however, the HFC mechanism is involved in the triplet biradicals with a long methylene chain, as revealed by CIDNP[9—14] and magnetic field effects.[15—17] Recent interest has been directed to an evaluation of exchange interactions between the radical termini in long-chain biradicals.[18,19]

In a previous communication,[20] we reported that the reaction course of triplet biradicals, $\mathrm{O{=}C^{\uparrow}{-}(CH_2)_{n-2}{-}C^{\uparrow}Ph_2}$ (^{3}BR-*n*), generated from an α-cleavage of *n*-membered 2,2-diphenylcycloalkanones (CK-*n*), was switched from disproportionation (n = 6 and 7) to acyl-phenyl cyclization ($n \geq 9$). Thus, the photolysis of 2,2-diphenylcycloheptanone (CK-7) gave exclusively an unsaturated aldehyde in a manner similar to that of 2,2-diphenylcyclohexanone (CK-6);[7] however, 2,2-diphenylcyclododecanone (CK-12) and 2,2-diphenylcyclotridecanone (CK-13) afforded oxoparacyclophanes together with decarbonylated cyclophanes; there were no significant amounts of unsaturated aldehydes.

In this paper, we give a full account of our work concerning the behavior of a series of triplet acyl-diphenylmethyl biradicals with different lengths of the methylene chain combining the radical termini. In particular, we describe the photochemistry of 2,2-diphenylcyclononanone (CK-9) and the magnetic field dependence of the lifetime of triplet biradicals with a rather longer methylene chain.

Results and Discussion

1. Absorption Spectra of 2,2-Diphenylcycloalkanones. The absorption spectra of 2,2-diphenylcycloheptanone (CK-7) and 2,2-diphenylcyclotridecanone (CK-13) are shown in Fig. 1 and the spectral features of the cyclic ketones are summarized in Table 1. As expected, the 2,2-diphenylcycloalkanones (CK-*n*) employed in this work showed very similar absorption spectra, independent of the ring size, exhibiting an n–π^* band at around 300 nm (ε 210—280 cm^2 mmol^{-1}).

Present address: Department of Ecosystem Engineering, Graduate School of Engineering, the University of Tokushima, Minamijyosanjima, Tokushima 770-8506.

Present address: Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920-0934.

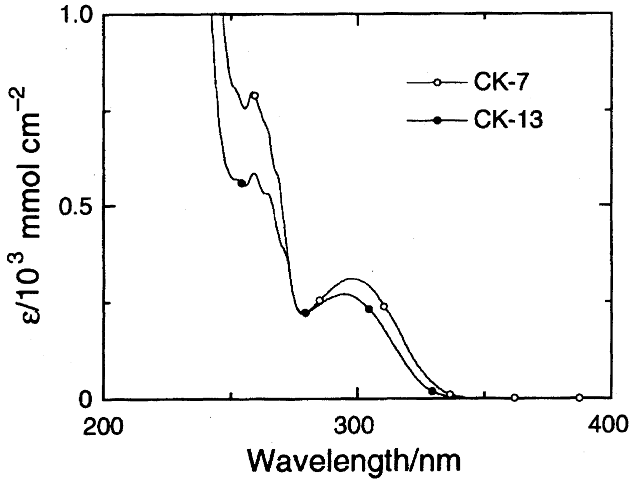


Fig. 1. Absorption spectra of CK-7 and CK-13 in methanol.

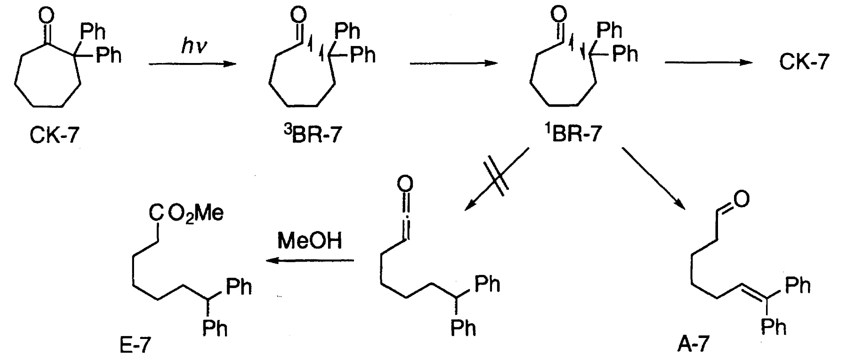
Table 1. Spectral Features of 2,2-Diphenylcycloalkanones, CK-*n*

n in CK-*n*	λ_{max}/nm (ε/cm^2 mmol^{-1})	
7	259 (800)	297 (310)
9	259 (500)	300 (270)
11	259 (570)	298 (230)
12	260 (450)	298 (210)
13	259 (590)	295 (270)

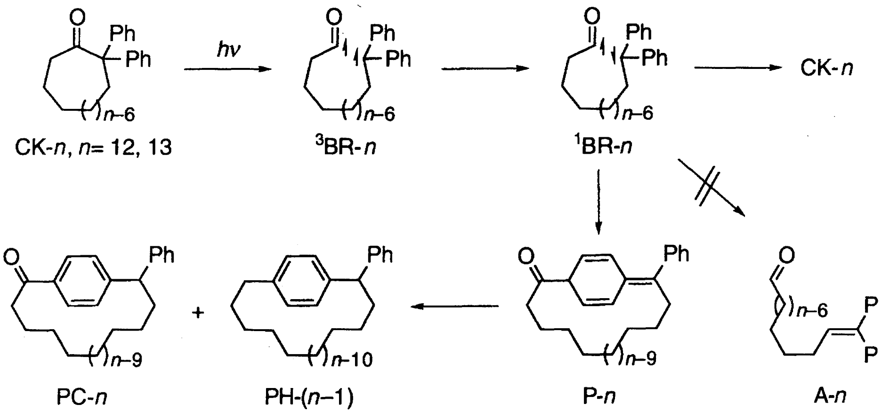
This band was irradiated in the following measurements with a 313-nm mercury line or 308-nm XeCl excimer laser.

2. Photochemistry of 2,2-Diphenylcycloalkanones. The photochemistry of CK-*n* was expected to proceed through triplet biradicals generated from a Norrish type-I cleavage. The reaction course of the intermediate biradicals was found to switch from hydrogen transfer (disproportionation) in a seven-membered ketone to cyclophane formation (recombination) in twelve- and thirteen-membered ketones. Thus, the irradiation of CK-7 with 313-nm light in methanol at ambient temperature gave exclusively an unsaturated aldehyde (A-7) in 76% yield, but neither cyclophane-type products nor methyl ester (E-7), which would be expected from the methanolysis of a ketene, was detected (Scheme 1). The photochemistry of CK-7 is very similar to that of CK-6.[7] The triplet biradicals 7-oxo-1,1-diphenyl-1,7-heptanediyl (^{3}BR-7), after intersystem crossing (ISC) into the singlet biradicals (^{1}BR-7), undergo intramolecular hydrogen-transfer to afford A-7 or cyclization to regenerate CK-7.

The irradiation of 2,2-diphenylcyclododecanone (CK-12) and CK-13 under similar conditions afforded oxoparacyclophanes (PC-*n*, *n* = 12 and 13; 50 and 27% yield, respectively) together with decarbonylated cyclophanes (PH-(*n* − 1), *n* = 12 and 13; 27 and 37%, respectively); no significant amounts of aldehydes (A-*n*) were detected (Scheme 2). The product distributions are summarized in Table 2. In these cases, the triplet biradicals, *n*-oxo-1,1-diphenyl-1,*n*-alkanediyl (^{3}BR-*n*), after ISC, undergo para-coupling of the acyl terminus in competition with the regeneration of CK-*n*. The



Scheme 1.



Scheme 2.

Table 2. Yields of Products from Irradiation of Cyclic Ketones in Methanol[a)]

n in CK-*n*	A-*n*	L-*n*	PC-*n*	PH-(*n* − 1)	C-(*n* − 1)	P-(*n* − 1)
7	76					
9	31	23			33	+
11	+	+	74	14		+
12			50	27		
13			32	37		

a) Symbol '+' refers to detection as products though their yields were not determined.

formed 4-methylene-2,5-cyclohexadienyl ketones (P-*n*) may be stabilized by a proton shift to give oxocyclophanes PC-*n*. For the formation of decarbonylated cyclophanes (PH-(*n* − 1)), some possibilities can be postulated, as described below.

The photochemistry of 2,2-diphenylcyclononanone (CK-9) and 2,2-diphenylcycloundecanone (CK-11) is rather complicate, but informative. Prolonged irradiation of CK-9 with 313-nm light in methanol afforded an open-chain (L-8; 23%) and a cyclic decarbonylation product (C-8; 33%) together with aldehyde A-9 (31%); however, a work-up of the sample solution at early stages gave a 4-methylene-2,5-cyclohexadienyl ketone (P-9) and A-9 (Scheme 3, Table 2).

The time development of the products was monitored by HPLC during the photolysis of CK-9 in methanol. Figure 2 shows time profiles of the disappearance of CK-9 and the formation of products upon the irradiation of CK-9 in methanol. As the starting ketone was consumed, P-9 was rapidly formed during the early stage, but decreased with time, and other products (A-9, C-8, and L-8) increased slowly. Moreover, photolysis of the isolated P-9 with 313-nm light in methanol gave A-9, C-8, and L-8 in a similar ratio; no significant amount of CK-9 was detected (Scheme 4, Fig. 3). These results show that P-9 is photochemically unstable, and decomposes under the reaction conditions to give not only decarbonylation products, such as C-8 and L-8, but also the aldehyde, A-9. No evidence for cyclophane formation was reported in the photolysis of 2-phenylcyclononanone, though the photolysis of the corresponding cyclodecanone through cyclododecanone and cyclopentadecanone resulted in the formation of cyclophanes.[21)]

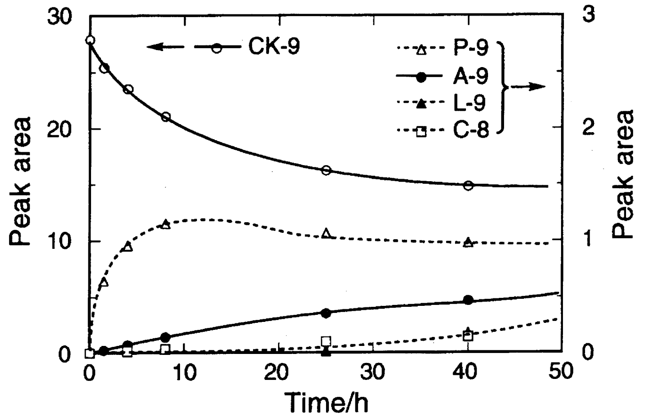


Fig. 2. Time profiles of CK-9 disappearance and product formation. The ordinate shows the relative peak area of an HPLC chart monitored at 260 nm.

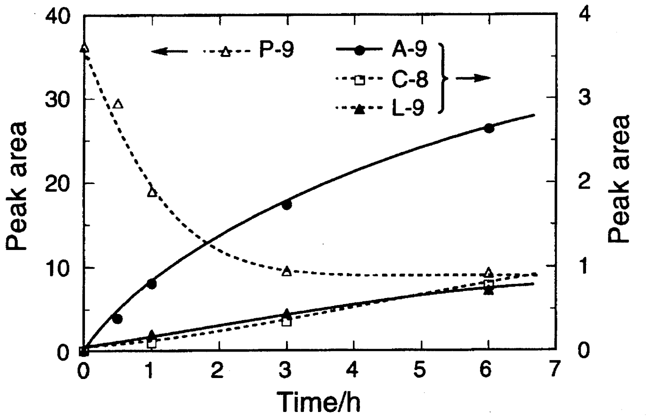
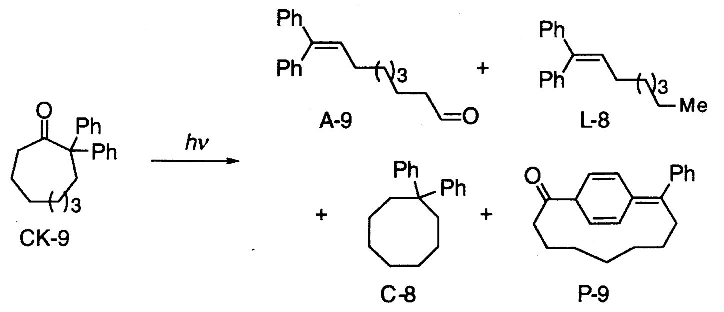
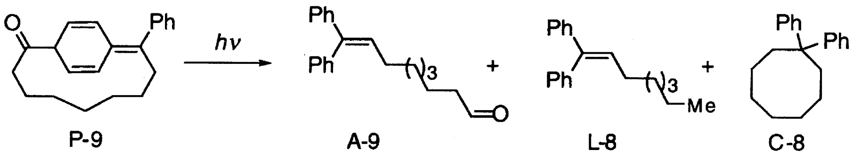


Fig. 3. Time profiles of P-9 disappearance and product formation. The ordinate shows the relative peak area of an HPLC chart monitored at 260 nm.



Scheme 3.



Scheme 4.

Similar studies on CK-11 indicated that a 4-methylene-2, 5-cyclohexadienyl ketone (P-11) was a primary product,[22] which was thermally converted to PC-11 or photolyzed into PH-10, A-11, and L-10 (Scheme 5, Fig. 4). Prolonged irradiation of CK-11 afforded PC-11 (74%) and PH-10 (14%) together with small amounts of A-11 and L-10.[23] P-11 was stable at low temperature in solution, as monitored by absorption-spectrum measurements, but easily collapsed to PC-11 on silica gel for chromatography.

On the basis of the above observations, we propose that the primary products in the photolysis of CK-*n* ($n \geq 9$) are the para-coupling products of biradicals, 4-methylene-2,5-cyclohexadienyl ketones (P-*n*), which are converted thermally to PC-*n* (for n = 11—13), or photolyzed to give decarbonylation products upon prolonged irradiation (for n = 9, 11—13).

3. Quantum Yields for the Disappearance of Cyclic Ketones. The quantum yields for disappearance of CK-*n* ($\phi_{\text{-CK}}$) were determined at low conversion by irradiating their methanol solutions with 313-nm light at ambient temperature; they are listed in Table 3. The quantum yields for CK-9, CK-11, and CK-13 were nearly 0.4, and rather higher than those for the others examined. The addition of isoprene, a triplet quencher, reduced the quantum yields. Stern–Volmer plots of the quenching data gave quenching constants (K_{SV}) of the ketone triplets, as summarized in Table 3. The triplet lifetimes of CK-*n* were estimated to be less than 1 ns from the K_{SV} values.

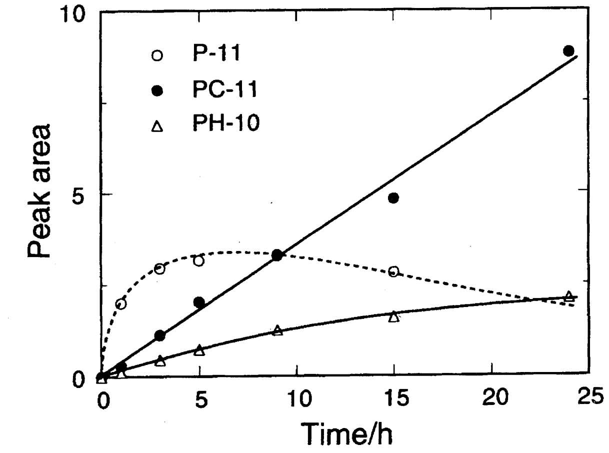


Fig. 4. Time profiles of product formation from CK-11.

Table 3. Quantum Yields for Disappearance of Cyclic Ketones (CK-*n*) and Quenching Constants (K_{SV}) of the Ketone Triplet by Isoprene

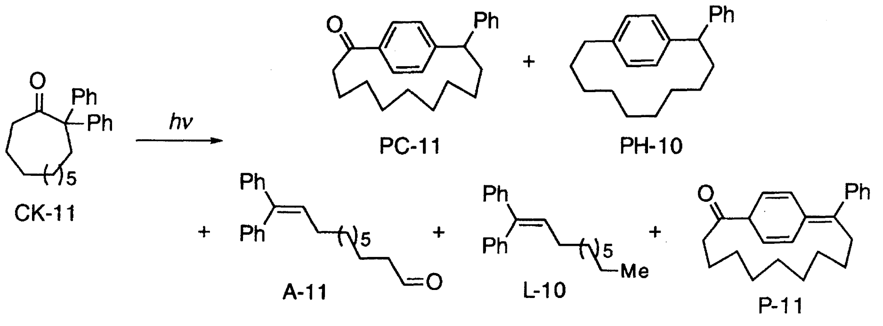
n in CK-*n*	$\phi_{\text{-}CK}$	$K_{\text{SV}}/\text{mol}^{-1}\,\text{dm}^3$	$\tau_{\text{T}}/\text{ps}$ [a]
6[b]	0.27		[c]
7	0.21	1.3	260
9	0.39	0.21	40
11	0.36	0.18	40
12	0.14	0.08	20
13	0.41	0.13	30

a) The quenching rate constant, k_{q} was assumed as 5×10^9 $\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$. b) Ref. 7. c) The triplet lifetime of 2-phenylcyclohexanone is reported to be 3 ns; Ref. 22.

4. Transient Absorption Spectra of the Cyclic Ketones. The behavior of the triplet biradicals was directly observed by means of the laser-flash photolysis of CK-*n*. Pulsed-laser excitation of CK-*n* at 308 nm in methanol exhibited a transient absorption at around 335 nm. The spectrum decayed according to first-order kinetics. Figure 5 shows the transient-absorption spectra observed for CK-7 and CK-13, as examples. These absorptions can be ascribed to triplet biradicals with a diphenylmethyl radical terminus;[25] their spectral shape and wavelength are very similar to those from CK-6, ^{3}BR-6.[7] The lifetime of the absorption from CK-7 was not affected by a replacement with deuterium of the hydrogen that might be transferred (CK-7D: 2,2-diphenylcycloheptanone-3,3,7,7-d_4), as observed in CK-6.[7] This confirms that the intersystem crossing precedes the reactions of the biradicals. All of the ketones (CK-*n*) employed in this work exhibited similar transient absorptions with lifetimes of ca. 100 ns (see below).

The transient-absorption spectra observed for CK-9 are shown in Fig. 6, where the band due to ^{3}BR-9 at around 355 nm decayed with a lifetime of 123 ns, and a new band appeared 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 that of ^{3}BR-9 in spectral shape and lifetime (130 ns, Fig. 7) upon pulsed-laser excitation at 308 nm. These observations indicate that the photolysis of P-9 also proceeds through α-cleavage to generate an intermediate similar to BR-9.

P-9 has a rigid structure because of its linked para substituent, which prohibits isomerization to an oxocyclophane (PC-9). The excitation of P-9 may result in a Norrish I-



Scheme 5.

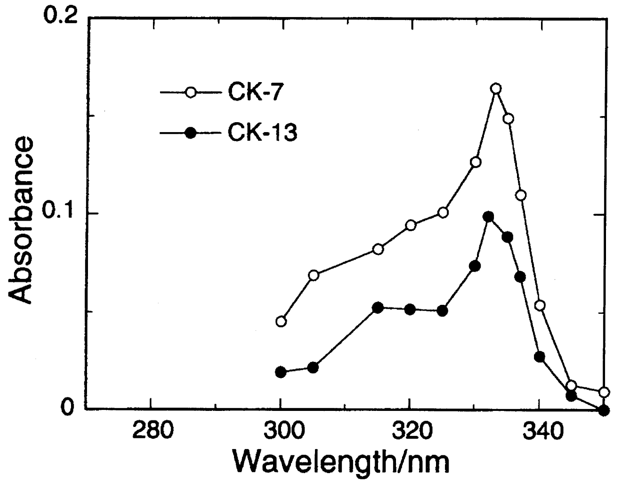


Fig. 5. Transient absorption spectra observed on 308-nm laser excitation of CK-7 (63 ns after laser pulse) and CK-13 (55 ns) in methanol.

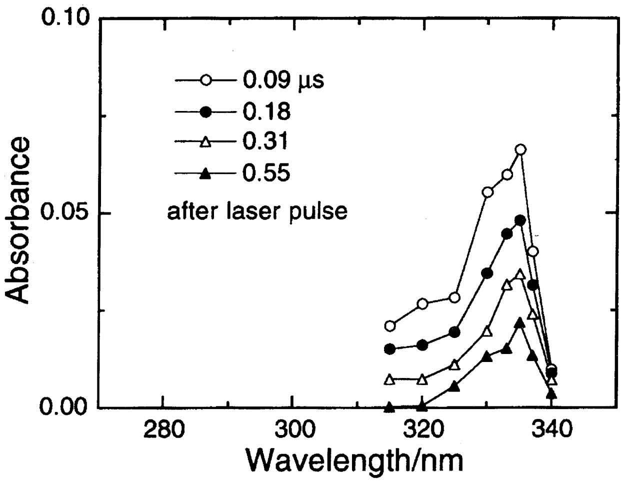


Fig. 7. Transient absorption spectra observed on 308-nm laser excitation of P-9 in methanol.

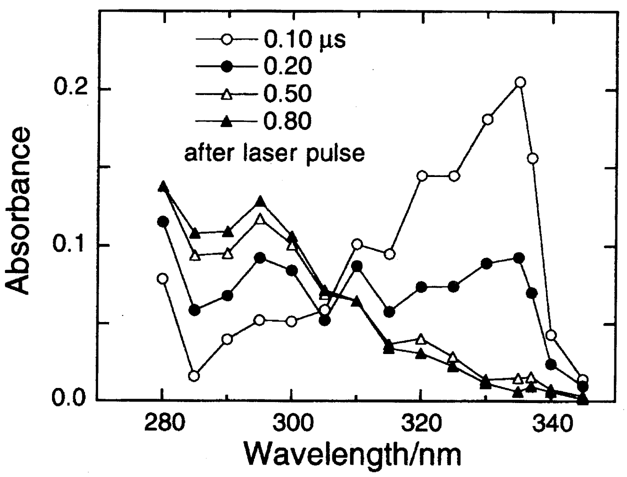
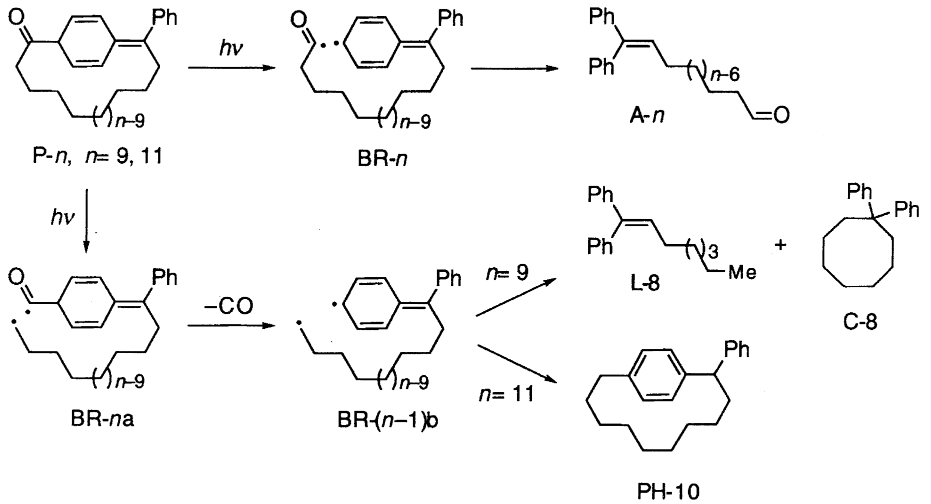


Fig. 6. Transient absorption spectra observed on 308-nm laser excitation of CK-9 in methanol.

type cleavage at the α-position to give a biradical, BR-9 or BR-9a (Scheme 6). The former gives A-9 and the latter undergoes decarbonylation to give another biradical, BR-8b, which produces L-8 by way of an intramolecular hydrogen shift or cyclizes to C-8; for BR-8b cyclization at the *para*-position is sterically prohibited.

P-11 may behave similarly upon excitation; biradicals BR-10b can undergo cyclization at the *para*-positions (Scheme 6). Decarbonylation is assumed to be unimportant as a collapsing process of BR-*n*, since the temperature dependence of the lifetime of BR-7 and BR-13 showed extremely small activation energies (5.3 and 3.8 kJ mol^{-1}, respectively; see below) compared with that for the decarbonylation of phenylacetyl radicals (29 kJ mol^{-1}).[26] A similar phenomenon was observed in the Norrish type-I reaction of a tetrahydrodiphenylbenzo[7]annulenone.[27]

5. Lifetimes of Triplet Biradicals as Reaction Intermediates. Usually, the lifetime (τ_{BR}) of triplet biradicals is determined by intersystem crossing (ISC) to the singlet biradicals; reactions in the latter are much faster than ISC.[7,28] ISC in triplet biradicals containing an acyl terminus results from spin-orbit coupling (SOC), and the radicals undergo ISC in conformations with small end-to-end distances, as



Scheme 6.

discussed before.[29] The lifetimes of triplet biradicals ^{3}BR-*n* (n = 6, 7, 9, 11—13) depended on the chain length (n), and showed a maximum at n = 9, ^{3}BR-9, in methanol and 1,2-ethanediol (Fig. 8). 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 having chain lengths of 8 to 10 compared to those of shorter and longer chain lengths (difficulty in medium-sized ring closure).[30,31] Therefore, the above results indicate that ISC takes place predominantly in cyclic conformers, which are preferable for product formation, although the observed ISC rate ($k_{\mathrm{isc}} = \tau_{\mathrm{BR}}^{-1}$) is the mean of all the individual ISC rates of conformers in equilibrium ($k_{\mathrm{isc}} = \sum_i f_i k_{\mathrm{isc}}{}^i$, where f_i and $k_{\mathrm{isc}}{}^i$ are the fraction and ISC rate constant of conformer i).[6] These observations, when combined with switching of the reaction course, indicate that the most favorable conformation for ISC is different between the short- and long-chain biradicals.

The solvent viscosity affected the biradical lifetimes; as the viscosity was increased by adding 1,2-ethanediol to methanol, the lifetimes of BR-7 and BR-13 gradually increased (Fig. 9). The increase in the lifetime can be explained by a decrease in the fractions of the cyclic conformers with a large ISC rate. The different behavior in viscosity dependence between BR-7 and BR-13 indicates that the conformational distributions might be affected by structural factors of the biradicals, such as the chain length.

The temperature dependence of the biradical lifetimes was also examined for CK-7, CK-7D, and CK-13 in the temperature range 50—−90 °C. Arrhenius plots for the decay of the biradicals derived therefrom in methanol provided different activation parameters in the higher (50—20 °C) and lower (−50—−90 °C) temperature ranges (Figs. 10 and 11). CK-7 and CK-7D showed identical behavior. The results are summarized in Table 4. The extremely low activation energies and the sizable ones in the higher and lower temperature range, respectively, indicate that ISC and the chain dynamics are the rate-determining steps for the biradical decay in the respective temperature ranges.[32]

The activation parameters for biradical decay were also measured in 1,2-ethanediol in the higher temperature range (Fig. 12, Table 4). In this case the temperature dependence of the solvent viscosity may be included in the apparent activation energies.

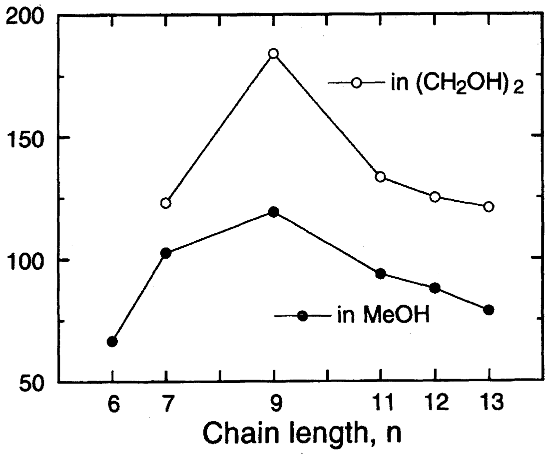


Fig. 8. Lifetimes of triplet biradicals derived from CK-*n*.

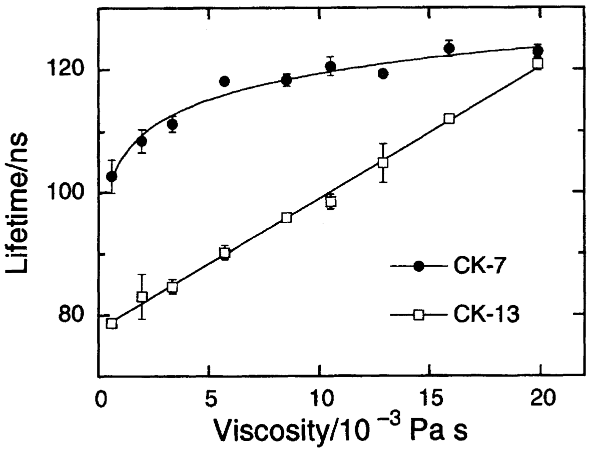


Fig. 9. Solvent viscosity dependence of biradical lifetimes at 20 °C.

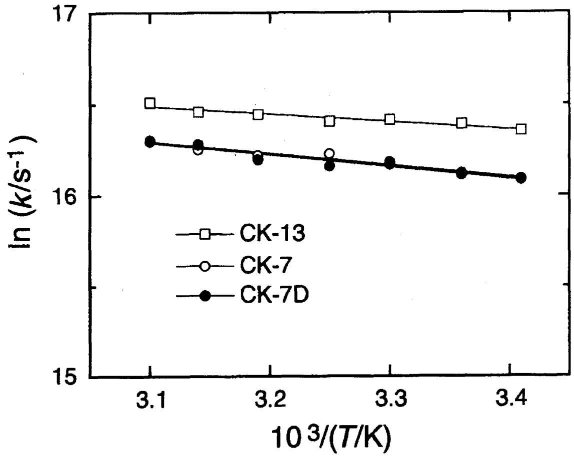


Fig. 10. Arrhenius plots of biradical disappearance in the higher temperature range in methanol.

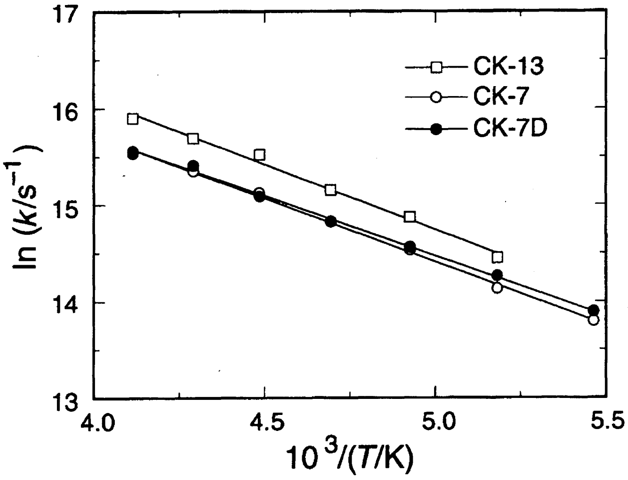


Fig. 11. Arrhenius plots of biradical disappearance in the lower temperature range in methanol.

Table 4. Activation Energies (E_a/kJ mol^{-1}) and Pre-exponential Factors (A/s^{-1}) for Decay of Biradicals in Methanol

Temperature	CK-7		CK-7D		CK-13	
range	E_a	log$A$	E_a	log$A$	E_a	log$A$
In methanol						
High	5.3	7.9	5.5	8.0	3.4	7.7
Low	11.0	9.1	10.4	9.0	11.3	9.4
In 1,2-ethanediol						
High	6.9	8.1	7.0	8.2	12.3	9.1

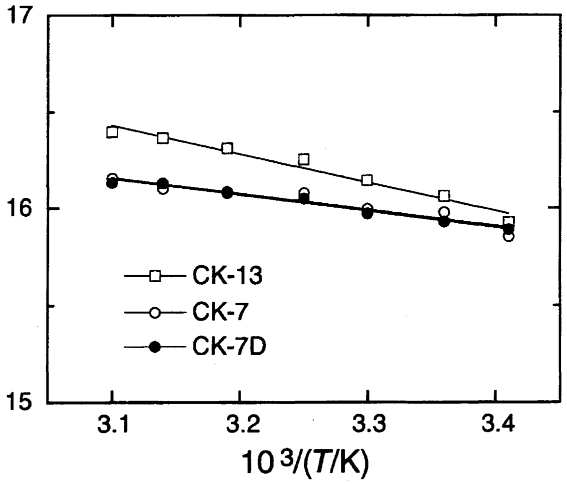


Fig. 12. Arrhenius plots of biradical disappearance in 1,2-ethanediol.

6. Magnetic Field Effects on Biradical Lifetime. The magnetic field dependence of the biradical lifetimes was observed by various techniques.[10,12,15—17] For acyl-benzyl biradicals SOC plays a major role in their ISC; however, for those with large end-to-end distances a sizable contribution of the hyperfine coupling (HFC) was reported based on the magnetic field dependence.[15—17] The lifetimes of triplet biradicals from CK-12 and CK-13 were measured in applied magnetic fields, 0 (earth's field) to 2 kG (0.2 T). Figure 13 shows plots of the decay rates ($= \tau_{BR}^{-1}$) of the triplet biradicals in various applied magnetic fields (k_{isc}^{H}) relative to that at the zero magnetic field strength (k_{isc}^{0}). In both cases the relative rate showed a maximum at a low magnetic field, followed by a decrease to an asymptotic value at high field (k_{isc}^{∞}). This local maximum of the ISC rate arises from a T_{-1}–S degeneracy due to the Zeeman splitting of the triplet sublevels, T_{+1}, T_0, and T_{-1} (Fig. 14), since the singlet usually lies below the triplet in the acyl-alkyl biradicals.[10,33] The decrease in the ISC rate and reaching an asymptotic value results from separation of the S level from T_{-1} and T_{+1}, leaving only S–T_0 ISC. This kind of magnetic field effect can arise from the HFC mechanism. The asymptotic values of the relative rate are ca. 0.88 and 0.82 for CK-12 and CK-13, respectively, and correspond to the sum of ISC due to SOC mechanism and one third of that due to HFC mechanism. From these values we can estimate the contribution of the HFC mechanism to ISC at the zero magnetic field strength as being 18 and 27% for CK-12 and CK-13, respectively. The contribution of HFC in the present system seems to be lower compared to the 2-phenylcycloalkanone system reported by Zimmt et al.[15] The difference could be attributed to the absence of a hydrogen atom at the diphenylmethyl terminus in our system.

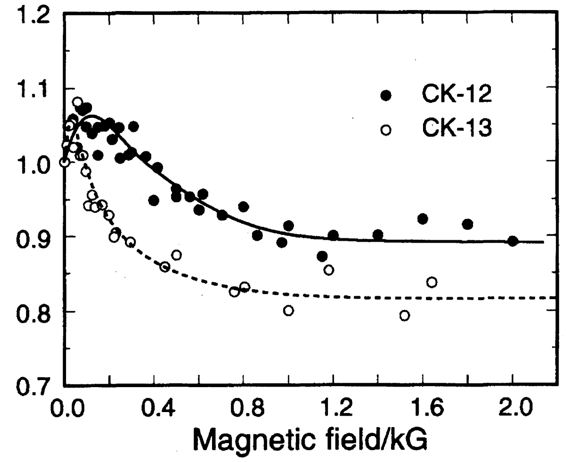


Fig. 13. Magnetic field dependence of the decay rates of triplet biradicals generated from CK-12 and CK-13.

7. Chain-Length Dependence of the Reaction Course of Triplet Biradicals (Conclusions). The α-cleavage of CK-n took place in the triplet state to generate triplet biradicals (^{3}BR-n), whose absorption spectra appeared at around 335 nm. Their lifetimes were dependent upon the chain length (n), and the maximum value was given at $n = 9$, which was in the region of 'difficulty in medium-sized ring closure'.

The reaction course of the intermediate biradicals switched at ^{1}BR-9 from intramolecular hydrogen transfer to acyl-phenyl recombination; ^{1}BR-6 and ^{1}BR-7 formed unsaturated aldehydes and ^{1}BR-11 through ^{1}BR-13 produced methylenecyclohexadienyl ketones (Scheme 7). The singlet biradicals ^{1}BR-9 derived from CK-9 by way of ^{3}BR-9 are assumed to competitively undergo hydrogen transfer and acyl-phenyl recombination, giving P-9, which is, however, so photolabile that it gives rise to secondary products under the reaction conditions (Scheme 7; $n = 9$). Photolysis of the isolated P-

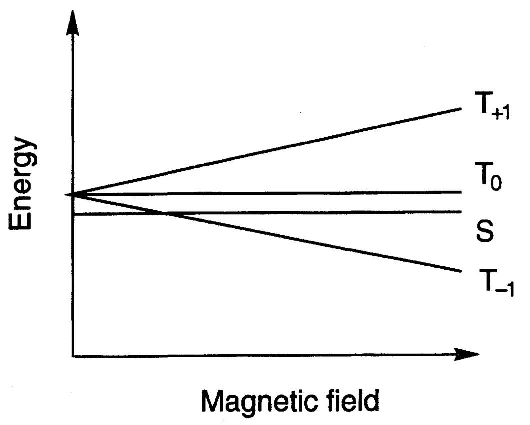
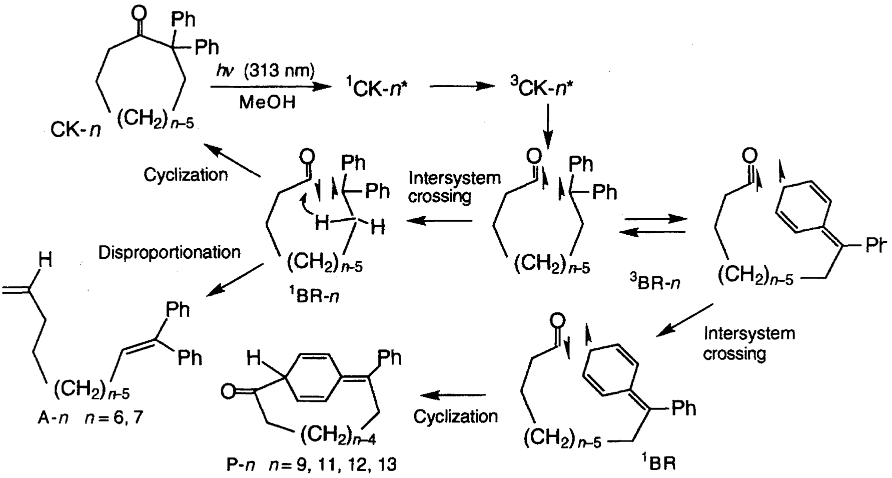


Fig. 14. Energy level diagram for a biradical in a magnetic field.



Scheme 7.

9 gave the same products as those obtained directly from CK-9. The formation of decarbonylated products from CK-*n* was assumed to be due to the photolability of the P-*n*-type primary products.

It is suggested that ISC of the triplet biradicals takes place predominantly in their cyclic conformations, which are favorable for giving cyclization or disproportionation products in the singlet biradicals. An external magnetic field effect was observed for the lifetimes of triplet biradicals from CK-12 and CK-13. The contribution of the HFC mechanism to intersystem crossing was smaller in the present 2,2-diphenylcycloalkanone series than in the corresponding monophenylcycloalkanone series.

Experimental

General. UV absorption and fluorescence spectra were measured using a JASCO Ubest-660 or Ubest 55 spectrophotometer and a Hitachi F-4000 spectrofluorimeter, respectively. Proton and carbon 13 NMR spectra were recorded on a JEOL FX-100 (100 and 25 MHz, respectively) or FX-500 (500 and 125 MHz, respectively) spectrometer. Mass spectra were measured with a Shimadzu GC-MS-QP2000A mass spectrometer. Solvent viscosities were measured with an Ubbelohde viscometer in comparison with 1,2-ethanediol ($\eta = 19.9\times10^{-3}$ Pa s at 20 °C)[34] as a standard.

Materials. Solvent methanol (Dojin, spectrograde) and 1,2-ethanediol (Wako, special grade) were used as received.

2,2-Diphenylcycloheptanone (CK-7). 2,2-Diphenylcycloheptanone was prepared from cyclohexanone with a reference procedure which was employed to prepare 2,2-diphenylcyclohexanone.[35] Cyclohexanone was converted to 1-hydroxycyclohexanecarbonitrile with sodium cyanide in the presence of sodium hydrogensulfite. The hydroxy carbonitrile was hydrolyzed with hydrochloric acid and esterified with methanol in the presence of sulfuric acid to give methyl 1-hydroxycyclohexanecarboxylate. Treatment of the hydroxy ester with three molar amounts of phenylmagnesium bromide afforded a diol, 1-[hydroxy(diphenyl)methyl]-1-cyclohexanol; this diol was rearranged to CK-7 upon heating in acetic acid in the presence of iodine; mp 89—91 °C (crystallized from methanol; lit, 92—94 °C);[36] ^{1}H NMR (CDCl$_3$) δ = 7.32—7.14 (m, 10H), 2.66—2.59 (m, 4H), 1.79—1.53 (m, 6H); ^{13}C NMR (CDCl$_3$) δ = 212.4, 144.4, 128.7, 128.0, 126.5, 65.1, 42.4, 37.4, 30.6, 26.5, 24.9. Found: C, 86.24; H, 7.65%. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63%.

2,2-Diphenylcycloheptanone-3,3,7,7-*d*₄ (CK-7D). Cyclohexanone-2,2,6,6-*d*$_4$ (5.4 g, 0.053 mol) was prepared by stirring cyclohexanone twice with deuterium oxide (30 ml) containing potassium carbonate[35] (8 g, 0.058 ml) for 5 d and coupled reductively with benzophenone (9 g, 0.050 mol) in 1,2-dimethoxyethane (450 ml) in the presence of titanium(0) prepared from anhydrous titanium(III) chloride (50 g, 0.25 mol) and lithium wire (8 g, 1.1 mol).[37] The crude product was subjected to column chromatography of silica gel eluted with hexane to give (diphenylmethylene)-cyclohexane-2,2,6,6-*d*$_4$ (3.9 g, 30%).

(Diphenylmethylene)cyclohexane-2,2,6,6-*d*$_4$ (3.9 g, 0.015 mol) was converted to the corresponding epoxide by treating with *m*-chloroperoxybenzoic acid (3.5 g, 0.020 mol) in chloroform. The epoxide was purified by crystallization from hexane (1.7 g, 42%).

The epoxide was rearranged to CK-7D upon heating in acetic acid in the presence of iodine; the crude product was purified by column chromatography of silica gel eluted with hexane–ethyl acetate (19 : 1) (0.32 g, 19%). GC-MS and ^{1}H-NMR analyses showed that more than 70% of the product contains four deuterium atoms.

2,2-Diphenylcyclononanone (CK-9). (Diphenylmethylene)-cyclooctane was prepared by the McMurry's method[37] of reductive coupling of cyclooctanone (6.3 g, 0.05 mol) and benzophenone (9.1 g, 0.05 mol) in 1,2-dimethoxyethane (550 cm^3) in the presence of titanium(0) prepared from anhydrous titanium(III) chloride (50 g, 0.25 mol) and lithium wire (8 g, 1.1 mol). The crude product was subjected to column chromatography of silica gel eluted with hexane to give (diphenylmethylene)cyclooctane (5.4 g, 41%); IR (KBr) 1622 (C=C), 1599, 1491, 760, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 7.36—7.04 (m, 10H), 2.27 (t, J = 5.9 Hz, 4H), 1.58 (m, 10H); ^{13}C NMR (CDCl$_3$) δ = 143.8, 140.1, 128.9, 128.1, 125.8, 32.3, 26.4, 26.2.

(Diphenylmethylene)cyclooctane (2.2 g, 0.008 mol) was converted to the epoxide by treating with *m*-chloroperoxybenzoic acid (1.7 g, 0.010 mol) in chloroform. The epoxide was purified by silica-gel column chromatography (chloroform/hexane (1 : 1)) and crystallization from methanol (1.8 g, 79%); mp 70.0—71.5 °C; IR (KBr) 1599, 1491, 787, 752, 704 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 7.54—7.10 (m, 10H), 1.77—1.27 (m, 14H); ^{13}C NMR (CDCl$_3$) δ = 128.1, 127.0, 126.9, 72.6, 70.1, 31.5, 26.8, 25.0, 23.5.

The epoxide (0.74 g) was treated with concentrated sulfuric acid (15 cm^3) at 0 °C and the mixture was poured onto ice water. The precipitate was subjected to silica-gel column chromatography (benzene/hexane (3 : 1)) and crystallized from methanol to give CK-9 (0.19 g, 26%); mp 85.5—86.0 °C; ^{1}H NMR ($CDCl_3$) δ = 7.34—7.19 (m, 10H), 2.60 (t, J = 5.54 Hz, 2H), 2.32 (m, 2H), 1.80 (quint, J = 6.65 Hz, 2H), 1.59—1.44 (m, 8H); ^{13}C NMR ($CDCl_3$): δ = 212.7, 143.0, 129.1, 128.0, 126.6, 64.7, 38.1, 33.3, 24.7, 24.2, 24.0. Found: C, 85.96; H, 8.30%. Calcd for $C_{21}H_{24}O$: C, 86.26; H, 8.27%.

2,2-Diphenylcycloundecanone (CK-11), 2,2-Diphenylcyclododecanone (CK-12), and 2,2-Diphenylcyclotridecanone (CK-13) were prepared in a similar manner from cyclodecanone, cycloundecanone, and cyclododecanone, respectively.

(Diphenylmethylene)cyclodecane, 49%; 2,2-diphenyl-1-oxaspiro[2.9]dodecane, 74%; 2,2-diphenylcycloundecanone (CK-11); 87—88 °C; 44%; ^{1}H NMR ($CDCl_3$) δ = 1.1—1.9 (m, 14), 2.15—2.35 (m, 2), 2.35—2.65 (m, 2), 7.15—7.45 (m, 10); ^{13}C NMR ($CDCl_3$) δ = 22.0, 23.1, 24.1, 25.4, 25.8, 26.4, 27.1, 34.8, 37.9, 64.6, 126.4, 127.9, 128.9, 143. 6, 211.0. Found: C, 86.10; H, 8.78%. Calcd for $C_{23}H_{28}O$: C, 86.20; H, 8.81%.

(Diphenylmethylene)cycloundecane, 46%; 2,2-diphenyl-1-oxaspiro[2.10]tridecane, 63%; 2,2-diphenylcyclododecanone (CK-12); 124—125.5 °C, 64%. Found: C, 86.00; H, 9.09%. Calcd for $C_{24}H_{30}O$: C, 86.18; H, 9.04%.

(Diphenylmethylene)cyclododecane, mp 120—127 °C, 18%; 2,2-diphenyl-1-oxaspiro[2.11]tetradecane, 134—136 °C, 79%; 2,2-diphenylcyclotridecanone (CK-13), mp 79.5—80 °C, 62%; ^{1}H NMR ($CDCl_3$) δ = 1.17—1.63 (m, 18), 2.29—2.34 (t, 2), 2.31—2.43 (m, 2), 7.16—7.26 (m, 10); ^{13}C NMR ($CDCl_3$) δ = 22.4, 22.6, 24.6, 25.1, 25.7, 25.9, 26.4, 26.9, 27.3, 36.5, 37.9, 64.6, 126.4, 127.9, 129.0, 143.8, 210.4; MS m/z 348 (M$^+$). Found: C, 86.20; H, 9.30%. Calcd for $C_{25}H_{32}O$: C, 86.15; H, 9.25%.

Photolysis of CK-7. A solution of CK-7 (90 mg) in methanol (100 cm^3) was irradiated for 5 h at ambient temperature with 313-nm light isolated from a 400-W high-pressure mercury lamp through a filter solution of K_2CrO_4 (0.27 g dm^{-3}) and Na_2CO_3 (1.0 g dm^{-3}) in water. After evaporation of the solvent the residue (84 mg) was separated by preparative TLC (silica gel, hexane/ethyl acetate (7 : 1)) to give a product (30 mg), which was identified as 7,7-diphenyl-6-heptenal (A-7).

A-7: ^{1}H NMR ($CDCl_3$) δ = 9.5 (t, 1H), 7.3 (m, 10H), 6.1 (t, 1H), 2.2 (m, 2H), 1.6 (m, 6H); IR (KBr) 2700, 1725 (CHO), 1600, 1500, 1450, 1360, 760, 705 cm^{-1}; Mass m/z 264 (M$^+$), 235 (M$^+$ − CHO).

Photolysis of CK-9. A solution of CK-9 (95 mg) in methanol (100 cm^3) was irradiated for 5 h at ambient temperature with a 400-W high-pressure mercury lamp. After evaporation of the solvent, the residue was separated by column chromatography (silica gel, hexane/ethyl acetate (7 : 1)) to give a mixture (62 mg) of products A and B, product C (36 mg), and a mixture (8 mg) of A, B, and C. Preparative TLC (hexane) followed by Lobar-column separation (Merck, LiChroprep Si60, hexane) of the first fraction afforded A and B (about 10 mg each). These products were assigned to 1,1-diphenyl-1-octene (L-8) and 1,1-diphenylcyclooctane (C-8), respectively, on the basis of the spectral data. Product C afforded spectral data similar to those of A-7, and was identified as 9,9-diphenyl-8-nonenal (A-9).

L-8: ^{1}H NMR ($CDCl_3$) δ = 7.1—7.4 (m, 10H), 6.11 (t, J = 7.4 Hz, 1H), 2.13 (bt, J = 7.4 Hz, 2H), 1.7—1.1 (m, 8H), 0.88 (t, J = 5.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ = 130.4, 129.9, 128.1, 127.2, 126.7, 31.7, 30.0, 29.8, 29.0, 22.7; IR (KBr) 1600, 1500, 1450, 760, 703 cm^{-1}; Mass m/z 264 (M$^+$).

C-8: ^{1}H NMR ($CDCl_3$) δ = 7.3—7.2 (m, 10H), 2.5—2.3 (m, 4H), 1.7—1.3 (m, 10H); ^{13}C NMR ($CDCl_3$) δ = 150.0, 127.8, 125.4, 49.9, 34.2, 28.7, 25.2, 22.8; IR (KBr) 2931, 1600, 1500, 1480, 1450, 760, 700 cm^{-1}; Mass m/z 264 (M$^+$).

A-9: ^{1}H NMR ($CDCl_3$) δ = 9.74 (t, J = 1.7 Hz, 1H), 7.4—7.1 (m, 10H), 6.06 (t, J = 7.4 Hz, 1H), 2.38 (td, J = 6.6, 1.7 Hz, 2H), 2.11 (bq, J = 7.4 Hz, 2H), 1.75—1.1 (m, 8H); ^{13}C NMR ($CDCl_3$) δ = 202.7, 129.9, 128.0, 127.1, 126.7, 43.8, 29.7, 29.6, 28.9, 22.0; IR (KBr) 2720, 1730 (CHO), 1600, 1500, 760, 700 cm^{-1}; Mass m/z 292 (M$^+$).

A solution of CK-9 (36 mg) in methanol (25 cm^3) was placed in eight Pyrex tubes and irradiated for 6 h at ambient temperature in a merry-go-round-type reactor with 313 nm light isolated from a 400-W high-pressure mercury lamp through a filter solution of K_2CrO_4 (0.09 g dm^{-3}) and Na_2CO_3 (0.03 g dm^{-3}) in water. After evaporation of the solvent, the residue was separated with a Lobar column (Merck, LiChroprep Si60, hexane/ethyl acetate (99 : 1)) to give a new product (2 mg). This was identified as 10-phenylbicyclo[9.2.2]pentadeca-10,12,14-trien-2-one (P-9) on the basis of spectral data.

P-9: ^{1}H NMR (C_6D_6/CCl_4) δ = 7.25—7.13 (m, 5H), 6.76 (d, J = 9.74, 1H), 6.35 (dd, J = 9.81, 1.33 Hz, 1H), 5.73 (ddd, J = 9.69, 5.55, 1.61 Hz, 1H), 5.59 (ddd, J = 9.78, 5.37, 1.61 Hz, 1H), 3.84 (t, J = 5.15 Hz, 1H), 3.06—3.00 (m, 1H), 2.82 (td, J = 12.88, 3.45 Hz, 1H), 2.35 (dt, J = 13.27, 3.81 Hz, 1H), 1.61—1.13 (m, 11H); ^{13}C NMR (C_6D_6/CCl_4) δ = 205.2, 141.1, 138.5, 129.7, 129.1, 128.6, 128.1, 127.9, 127.7, 127.5, 126.9, 125.5, 124.6, 57.3, 34.4, 33.5, 27.2, 26.9, 26.8, 25.7, 25.1; Mass m/z 292 (M$^+$), 264 (M$^+$ − CO).

Photolysis of CK-11. A solution of CK-11 (150 mg) in methanol (100 cm^3) was irradiated for 6 h at ambient temperature with a 400-W high-pressure mercury lamp. After evaporation of the solvent, the residue was separated by column chromatography (silica gel, hexane/benzene (1 : 1) and benzene) to give products D and E. These products were assigned to a paracyclophane, 1-phenyl[10]paracyclophane (PH-10) and an oxoparacyclophane, 1-oxo-11-phenyl[11]paracyclophane (PC-11) on the basis of spectral data.

PH-10: ^{1}H NMR ($CDCl_3$) δ = 7.31—7.21 (m, 9H), 3.85 (dd, J = 12, 4.6 Hz, 1H), 2.63 (t, J = 6.1 Hz, 2H), 2.52—0.59 (m, 16H); ^{13}C NMR ($CDCl_3$) δ = 129.6—125.3, 41.4, 35.5—22.5; IR (KBr) 1600, 1500 cm^{-1}; Mass m/z 292 (M$^+$).

PC-11: ^{1}H NMR ($CDCl_3$) δ = 7.75—7.19 (m, 9H), 3.89 (m, 1H), 3.11—2.58 (m, 2H), 2.26 (m, 2H), 1.94—0.75 (m, 14H); ^{13}C NMR ($CDCl_3$) δ = 205.5, 149.7, 144.1, 138.0, 130.4, 128.7, 128.4, 128.2, 128.1, 127.8, 127.7, 126.4, 51.7, 38.4, 34.2, 28.7, 27.9, 26.9, 25.1; IR (KBr) 1680 (C=O), 1610, 1500, 760, 710 cm^{-1}.

Photolysis of CK-12. A solution of CK-12 (150 mg) in methanol (100 cm^3) was irradiated for 4 h at ambient temperature with a 400-W high-pressure mercury lamp. After evaporation of the solvent, the residue was separated by preparative TLC (silica gel, hexane/ethyl acetate (9 : 1)) to give products F and G. These products were assigned to 1-phenyl[11]paracyclophane (PH-11) and 1-oxo-12-phenyl[12]paracyclophane (PC-12) on the basis of resemblance of spectral data to those of PH-10 and PC11, respectively.

PH-11: ^{1}H NMR ($CDCl_3$) δ = 7.32—7.02 (m, 9H), 3.71 (dd, J = 11.3, 3.5 Hz, 1H), 2.58 (m, 2H), 2.40 (m, 2H), 2.25—0.81 (m, 16H); ^{13}C NMR ($CDCl_3$) δ = 145.7, 142.8, 140.9, 129.7, 129.2, 129.0, 128.2, 127.6, 125.8, 51.5, 35.6, 34.3, 28.9, 28.2, 27.2, 26.9, 26.5, 25.3; IR (KBr) 1600, 1500, 760, 740 cm^{-1}; Mass m/z 306 (M$^+$).

PC-12: ^{1}H NMR ($CDCl_3$) δ = 7.62 (d, J = 8.7 Hz, 2H), 7.2—7.0 (m, 7H), 3.89 (dd, J = 12, 4.3 Hz, 1H), 2.82 (m, 2H), 2.6—0.6 (m, 18H).

Photolysis of CK-13. A solution of CK-13 (150 mg) in methanol (100 cm^3) was irradiated for 4.5 h at ambient temperature with a 400-W high-pressure mercury lamp. After evaporation of the solvent, the residue was separated by column chromatography (silica gel, hexane/benzene (1 : 1) and benzene) to give products H and I. These products were assigned to 1-phenyl[12]paracyclophane (PH-12) and 1-oxo-13-phenyl[13]paracyclophane (PC-13) on the basis of resemblance of spectral data to those of PH-10 and PH-11, and PC-11 and PC-12, respectively.

PH-12: ^{1}H NMR ($CDCl_3$) δ = 7.5—7.1 (m, 9H), 3.81 (dd, 1H), 2.68 (m, 2H), 2.52 (m, 2H), 2.10—0.80 (m, 18H); Mass *m/z* 320 (M^+).

PC-13: ^{1}H NMR ($CDCl_3$) δ = 7.81 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.27 (m, 5H), 3.92 (dd, *J* = 11, 5 Hz, 1H), 2.91 (m, 2H), 2.08 (m, 2H), 1.9—0.8 (m, 18H); ^{13}C NMR ($CDCl_3$) δ = 203.4, 150.0, 144.8, 136.0, 128.9, 128.4, 127.4, 126.2, 51.4, 38.6, 34.9, 28.5, 28.4, 27.8, 27.7, 26.9, 26.4.

Time Profiles in Photocleavage of Cyclic Ketones. Several degassed methanol solutions (3 cm^{-3}) of CK-9, CK-11, and P-9 in methanol were irradiated with 313-nm light isolated from a 400-W high-pressure mercury lamp through a filter solution of K_2CrO_4 (0.09 g dm^{-3}) and Na_2CO_3 (0.03 g dm^{-3}) in water. After a given period of irradiation, the reaction mixture was analyzed by HPLC (Waters 600 multisolvent delivery system/Waters 490 programmable multiwavelength detector; column: 5-ODS-H (Chemosorb), eluent: methanol : water = 99 : 1).

Quantum Yield Measurements. Cyclic ketones CK-*n* (1—2$\times10^{-3}$ mol dm^{-3}) were irradiated under argon with 313-nm light isolated from a 400-W high-pressure mercury lamp through a Toshiba UV-D-33S glass filter and a filter solution of K_2CrO_4 (0.9 g dm^{-3}) and Na_2CO_3 (0.33 g dm^{-3}) in water. The quantum yields were determined by potassium tris(oxalato)ferrate(III) actinometry[38] or in comparison with the values for ring closure of a flugide, (*E*)-2-[2-(2,5-dimethyl-3-furyl)ethylidene]-3-isopropylidenebutanedioic anhydride (0.20 at 313 and 366 nm).[39] Consumption of the starting ketones was monitored by GLPC (Shimadzu GC-4CM; column OV-17 1.5 m) or HPLC (Shimadzu LC-6A/Otsuka Densi MCPD-350PC; column: 5CN-R (Chemco Pak), eluent: hexane : ethyl acetate = 200 : 1).

In quenching experiments, solutions of CK-*n* in methanol containing isoprene (0—0.2 mol dm^{-3}) were degassed by freeze-pump-thaw cycles and irradiated with 313-nm light isolated from a 1 kW high-pressure mercury lamp.

Laser-Flash Photolyses. Laser-flash photolyses were performed by using an excimer laser (Lambda Physik EMG101, XeCl, 308 nm, 10-ns fwhm, 70 mJ/pulse) and a pulsed xenon arc (Wacom KXL-151, 150 W) as a monitoring light source. The monitoring beam obtained from the xenon lamp was oriented perpendicularly to the exciting laser beam, passed through a sample cell and a grating monochromator (JASCO CT-25C), and detected with a photomultiplier (Hamamatsu Photonix R928). The amplified signal was recorded as the time profile of a transmittance change on a storage oscilloscope (Iwatsu TS-8123), transferred to a personal computer (NEC PC-9801VX21), and accumulated for 3—5 times to be averaged. The system was computer-controlled and the decay curves were analyzed by this computer system. The details of the apparatus for laser-flash photolysis have been described elsewhere.[40]

The temperature of sample cells was controlled with a thermostated cell holder and a circulating water bath (Haake F3-K) or with a cryostat (Oxford Instruments DN1704).

Magnetic Field Effects. For measurements of magnetic field effects, sample solutions in quartz cells were placed between the pole pieces of an electromagnet (Tokin SEE-9). The magnetic field strength was controlled by a current-regulated power supply. The residual magnetic field was canceled by a counter current to be lower than 0.3 mT for measurements at the zero magnetic field strength. Laser-flash photolyses were performed with 308-nm laser pulses from an excimer laser (Lambda Physik EMG-50E) as an exciting light source and a xenon flash lamp (EG&E FX-200) as a probe light source. The details of the apparatus have been described elsewhere.[41]

References

1) J. C. Dalton, K. Dawes, N. J. Turro, D. S. Weiss, J. A. Barltrop, and J. D. Coyle, *J. Am. Chem. Soc.*, **93**, 7213 (1971).

2) A. A. Baum, *Tetrahedron Lett.*, **1972**, 1817.

3) P. J. Wagner and T. J. Stratton, *Tetrahedron*, **37**, 3317 (1981).

4) X. G. Lei, C. Doubleday, Jr., and N. J. Turro, *Tetrahedron Lett.*, **27**, 4675 (1986).

5) N. Han, X. Lei, and N. J. Turro, *J. Org. Chem.*, **56**, 2927 (1991).

6) C. Doubleday, Jr., N. J. Turro, and J.-F. Wang, *Acc. Chem. Res.*, **22**, 199 (1989), and references cited therein.

7) R. A. Caldwell, H. Sakuragi, and T. Majima, *J. Am. Chem. Soc.*, **106**, 2471 (1984).

8) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).

9) G. L. Closs, R. J. Miller, and O. D. Redwine, *Acc. Chem. Res.*, **18**, 196 (1985).

10) G. L. Closs and C. E. Doubleday, *J. Am. Chem. Soc.*, **95**, 2735 (1973).

11) G. L. Closs and R. J. Miller, *J. Am. Chem. Soc.*, **103**, 3586 (1981).

12) C. Doubleday, Jr., *Chem. Phys. Lett.*, **85**, 65 (1982).

13) N. J. Turro, K. C. Hwang, V. P. Rao, and C. Doubleday, Jr., *J. Phys. Chem.*, **95**, 1872 (1991).

14) K. C. Hwang, N. J. Turro, and C. Doubleday, Jr., *J. Am. Chem. Soc.*, **113**, 2850 (1991).

15) M. B. Zimmt, C. Doubleday, Jr., and N. J. Turro, *J. Am. Chem. Soc.*, **107**, 6726 (1985).

16) J. Wang, C. Doubleday, Jr., and N. J. Turro, *J. Phys. Chem.*, **93**, 4780 (1989).

17) J. Wang, V. P. Rao, C. Doubleday, Jr., and N. J. Turro, *J. Phys. Chem.*, **94**, 1144 (1990).

18) M. D. E. Forbes and G. R. Schulz, *J. Am. Chem. Soc.*, **116**, 10174 (1994).

19) N. I. Avdievich and M. D. E. Forbes, *J. Phys. Chem.*, **99**, 9660 (1995).

20) R. Tanaka, I. Suzuki, A. Yamaguchi, H. Misawa, H. Sakuragi, and K. Tokumaru, *Tetrahedron Lett.*, **33**, 3651 (1992).

21) X.-G. Lei, C. E. Doubleday, Jr., M. B. Zimmt, and N. J. Turro, *J. Am. Chem. Soc.*, **108**, 2444 (1986).

22) The formation of P-11 was identified by appearance of an absorption spectrum similar to that of P-9 in HPLC analyses using a multi-channel detector.

23) The multiplicity of excited state responsible for the photolysis of P-*n* has not been determined.

24) P. J. Wagner and R. W. Spoerke, *J. Am. Chem. Soc.*, **91**, 4437 (1969).

25) R. A. Caldwell, T. Majima, and C. Pac, *J. Am. Chem. Soc.*, **104**, 629 (1982).

26) L. Lunazzi, K. U. Ingold, and J. C. Scaiano, *J. Phys. Chem.*, **87**, 529 (1983).

27) R. Tanaka, Y. Kuriyama, H. Itoh, H. Sakuragi, and K. Tokumaru, *Chem. Lett.*, **1993**, 1447.

28) J. C. Scaiano, E. A. Lissi, and M. V. Encinas, *Res. Chem. Intermed.*, **2**, 139 (1978), and references therein.

29) M. B. Zimmt, C. Doubleday, Jr., I. R. Gould, and N. J. Turro, *J. Am. Chem. Soc.*, **107**, 6724 (1985).

30) M. A. Winnik, *Chem. Rev.*, **81**, 491 (1981).

31) R. Nakagaki, H. Sakuragi, and K. Mutai, *J. Phys. Org. Chem.*, **2**, 187 (1989).

32) M. B. Zimmt, C. Doubleday, Jr., and N. J. Turro, *J. Am. Chem. Soc.*, **108**, 3618 (1986).

33) G. L. Closs and C. E. Doubleday, *J. Am. Chem. Soc.*, **94**, 9248 (1973).

34) S. L. Murov, I. Carmicael, and G. L. Hug, "Handbook of Photochemistry," 2nd ed, Revised and Expanded, Marcel Dekker, New York (1993), p. 285.

35) C. J. Fortin, M. Forest, C. Vaziri, D. Gravel, and Y. Rousseau, *Can. J. Chem.*, **51**, 3445 (1973).

36) R. E. Lyle and G. G. Lyle, *J. Am. Chem. Soc.*, **74**, 4059 (1952).

37) J. E. McMurry, M. P. Fleming, K. L. Kees, and L. R. Krepski, *J. Org. Chem.*, **43**, 3255 (1978).

38) S. L. Murov, I. Carmicael, and G. L. Hug, "Handbook of Photochemistry," 2nd ed, Revised and Expanded, Marcel Dekker, New York (1993), p. 299.

39) H. G. Heller and J. R. Langan, *J. Chem. Soc., Perkin Trans. 2*, **1981**, 341.

40) H. Furuuchi, T. Arai, Y. Kuriyama, H. Sakuragi, and K. Tokumaru, *Chem. Phys. Lett.*, **162**, 211 (1989).

41) R. Nakagaki, M. Hiramatsu, T. Watanabe, Y. Tanimoto, and S. Nagakura, *J. Phys. Chem.*, **89**, 3222 (1985).