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Cycloaddition of singlet carbene to 2-vinylpyridine studied by laser flash photolysis of 3-(biphenyl-4-yl)-3-chlorodiazirine

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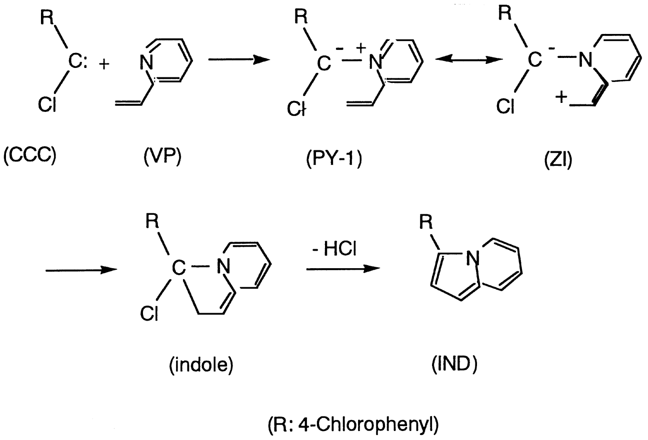
Abstract

The laser flash photolyses (LFPs) of 3-(biphenyl-4-yl)-3-chlorodiazirine (BCD) were carried out in the presence of 2-vinylpyridine (VP) in 2,2,4-trimethylpentane. Immediately after the flash, the absorption spectrum of (biphenyl-4-yl)chlorocarbene (BCC) was recorded ($\lambda_{max} = 360$ nm). Corresponding to the decrease in the BCC band, a new band formed by first-order kinetics in the wavelength range from 440 to 620 nm ($\lambda_{max} = 540$ nm). This band is assigned to a pyridinium ylide (PY) produced by the addition of BCC with VP. The PY formation rate was equal to the BCC decay rate. Because PY has a 1,5-zwitter ion (ZI) structure as a contributing resonance form, this species decayed by the intramolecular cyclization of the ZI ($\tau = 43\ \mu$s). Also the rates of the BCC decay, the PY formation and the PY decay increased with increasing 2,3-dimethyl-2-butene (TME) concentration, suggests that the BCC was in equilibrium with PY. The equilibrium constant was roughly estimated to be 80 dm^3 mol^{-1}. The photoreaction of BCD in the presence of VP produced the indolizine (IND) derivative (56%) and cyclopropane compounds (total yield, 12%). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Laser flash photolysis; Singlet carbene; Pyridinium ylide; 1,5-Zwitter ion; Equilibrium constant

1. Introduction

Cyclopropane formation is the most interesting reaction of a carbene with an olefin [1,2]. On the other hand, singlet carbene reacts with pyridine to yield a pyridinium ylide (PY) [3]. The latter reaction is also important for the detection of invisible carbenes during laser flash photolysis (LFP). In the reaction with 2-vinylpyridine (VP), the carbene seems to react both with the vinyl group to yield cyclopropanes and with the nitrogen atom of the pyridine ring to yield PY. Liu and Romashin [4] reported that the reaction of chloro(4-chlorophenyl)carbene (CCC) with VP gave the indolizine (IND) derivative, a very interesting heterocyclic compound. This compound must be produced by an intramolecular cyclization of the 1,5-zwitter ion (ZI) intermediate, that is a resonance form of the CCC–VP ylide (PY-1), and a subsequent dehydrochlorination reaction of the cyclized products, pyrrolidine derivatives (Eq. (1)). They reported that the dehydrochlorination proceeded simultaneously with the cyclization. Although CCC seemed to yield PY-1 completely, the isolated yield of IND was very low (11%) [5].



(1)

Recently, we examined a long-lived singlet carbene (biphenyl-4-yl)chlorocarbene (BCC, 24.8 ms in 2,2,4-trimethylpentane (i-Oc)) (Eq. (2)) and its reactions with ether and nitrile substrates by the 355 nm LFP of (biphenyl-4-yl) chlorodiazirine (BCD) [6–8]. In those studies, we formed

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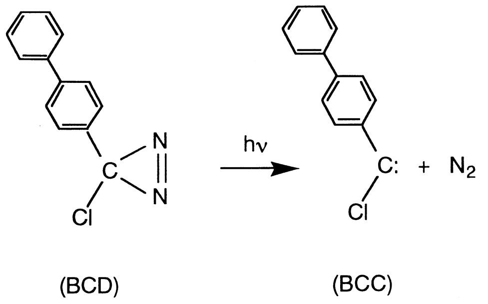
BCC–pyridine ylide (PY-2) [6]. On the basis of those results, we further studied in detail the reaction mechanism of IND formation in the LFPs of BCD in the presence of VP.



(2)

2. Experimental

2.1. Materials

The synthesis and purification of 3-(biphenyl-4′-yl)-3-chlorodiazirine (BCD, $\lambda_{\max} = 358$ nm ($\varepsilon = 4.2 \times 10^3$ dm^2 mol^{-1} in i-Oc), 376 nm ($\varepsilon = 6.2 \times 10^3$ dm^2 mol^{-1}), 395 nm ($\varepsilon = 5.2 \times 10^3$ dm^2 mol^{-1}) were reported previously [6]. Spectroscopic grade i-Oc and methylene chloride were used without further purification. VP was used immediately after two distillations under a low nitrogen pressure. 2,3-Dimethyl-2-butene (TME) was purified by two distillations after drying over calcium hydride.

2.2. Laser flash photolysis

The i-Oc solutions of BCD (ca. 6×10^{-4} mol dm^{-3}, $d_{355\text{ nm}}$ = ca. 0.6) with VP were put into 10 mm rectangular quartz cells. Degassing or argon bubbling of the solution were not carried out. Laser flash photolyses (LFPs) of BCD were carried out in the presence of VP in i-Oc at 293 K by using a Continuum YAG laser apparatus Power Light type 9010 (355 nm, ca. 6 ns, ca. 60 mJ per flash). The transient absorptions were monitored by a digitizer and were analyzed using a personal computer.

2.3. Photoirradiation

Mixed solutions of BCD and VP were sealed in pyrex ampoules after several freeze-thaw degassing cycles ((a) [BCD] = 1.62×10^{-4} mol, [VP] = 1.01×10^{-2} mol in 5.00×10^{-2} dm^3 of i-Oc; (b) [BCD] = 1.57×10^{-4} mol, [VP] = 2.02×10^{-2} mol in 5.00×10^{-2} dm^3 of i-Oc). The photoreactions of BCD with VP were carried out by irradiation with 366 nm light for 3 h at room temperature (ca. 295 K). The products were isolated by flash chromatography (silica gel/95% hexane–5% ethyl acetate). Six kinds of low molecular weight products were obtained, i.e. 3-(biphenyl-4′-yl)-indolizine (Rf = 0.67; yields, 37 (a), 56% (b) determined by weight), *Z*-1-(biphenyl-4′-yl)-1-chloro-2-(2″-pyridinyl)cyclopropane (Rf = 0.36; yields, 14 (a), 8% (b)), *E*-1-(biphenyl-4′-yl)-1-chloro-2-(2″-pyridinyl)cyclopropane (Rf = 0.25; yields, 8 (a), 4% (b)), two unknown products (Rf < 0.2; total yield, 8% (b)) and a third unknown product ($C_{20}H_{16}NO_2$) (Rf < 0.1; yield, 11% (b)).

Spectral data: 3-(biphenyl-4′-yl)-indolizine, mp 401–403 K, ^{1}H NMR (CDCl$_3$, TMS) $\delta = 6.51$ ppm (ddd, 1H, $J = 7.2, 6.3, 1.2$ Hz, 5H), 6.56 ppm (d, 1H, $J = 3.9$ Hz, 1H), 6.70 ppm (ddd, 1H, $J = 6.3, 9.0, 0.9$ Hz, 6H), 6.92 ppm (d, 1H, $J = 3.9$ Hz, 2H), 7.35–7.50 ppm (m, 4H, biphenyl), 7.65–7.73 ppm (m, 6H, 7H + biphenyl), 8.35 ppm (dd, 1H, $J = 7.2, 0.9$ Hz, 4H); ^{13}C NMR (CDCl$_3$, TMS) $\delta = 99.9$, 110.7, 114.2, 116.9, 119.6, 122.3, 1250, 126.9, 127.3, 127.5, 128.8, 131.5, 134.0, 139.6, 140.6 ppm; El-MS: *m/z* 269 (M$^+$).

Z-1-(Biphenyl-4′-yl)-1-chloro-2-(2″-pyridinyl)cyclopropane; mp 350–351 K; ^{1}H NMR (CDCl$_3$, TMS) $\delta = 1.99$ ppm (dd, 1H, $J = 6.6, 9.9$ Hz, 3c-H), 2.42 ppm (dd, 1H, $J = 6.6, 7.2$ Hz, 3t-H), 3.18 ppm (dd, 1H, $J = 9.9, 7.2$ Hz, 2c-H), 6.94 ppm (ddd, 1H, $J = 7.8, 4.5, 0.9$ Hz, pyridinyl-H), 7.04 ppm (d, 1H, $J = 7.8$ Hz, pyridinyl-H), 7.29–7.52 ppm (m, 10H, biphenylyl-H), 8.24 ppm (d, 1H, $J = 4.5$ Hz, pyridinyl-H); El-MS: *m/z* 305 (M$^+$), 270 (M$^+$–Cl).

E-1-(Biphenyl-4′-yl)-1-chloro-2-(2″-pyridinyl)cyclopropane; ^{1}H NMR (CDCl$_3$, TMS) $\delta = 1.89$ ppm (dd, 1H, $J = 6.6, 9.8$ Hz, 3t-H), 2.30 ppm (dd, 1H, $J = 6.6, 7.8$ Hz, 3c-H), 2.91 ppm (dd, 1H, $J = 9.8, 7.8$ Hz, 2t-H), 7.23 ppm (dd, 1H, $J = 7.5, 4.8$ Hz, pyridinyl-H), 7.36–7.52 ppm (m, 5H, biphenylyl and pyridinyl-H), 7.58–7.71 ppm (m, 6H, biphenylyl and pyridinyl-H), 8.64 ppm (d, 1H, $J = 4.8$ Hz, pyridinyl-H); El-MS: *m/z* 305 (M$^+$), 270 (M$^+$–Cl).

Third unknown product: mp 398–400 K; ^{1}H NMR (CDCl$_3$, TMS) $\delta = 4.61$ ppm (d, 1H, $J = 5.0$ Hz), 4.69 ppm (d, 1H, $J = 5.0$ Hz), 7.15 ppm (ddd, 1H, $J = 7.7, 5.0, 1.2$ Hz), 7.36–7.48 ppm (m, 6H), 7.98 ppm (d, 2H, $J = 8.4$ Hz), 8.45 ppm (ddd, 1H, $J = 5.0, 1.5, 0.9$ Hz); ^{13}C NMR (CDCl$_3$, TMS) $\delta = 59.2$, 60.3, 121.3, 123.4, 127.2, 127.4, 128.4, 128.8, 129.0, 133.9, 136.6, 139.6, 146.5, 149.1, 153.1, 191.3 ppm; El-MS: *m/z* 301 (M$^+$), 285 (M$^+$–O).

3. Results and discussion

3.1. Transient species

We carried out the LFPs of 3-(biphenyl-4-yl)-3-chlorodiazirine (BCD) at 295 K in the presence of VP (2.10×10^{-2} mol dm^{-3}) in i-Oc using a YAG-laser apparatus ($\lambda_{\text{ex}} = 355$ nm). An absorption maximum due to BCC, was recorded at 360 nm immediately after the flash [6]. Corresponding to the decay of BCC, a new absorption band formed in the wavelength range from 440 to 620 nm. The new band has an absorption maximum ($\lambda_{\max}$) at 540 nm. Fig. 1 shows typical digitizer traces monitored at 370 nm

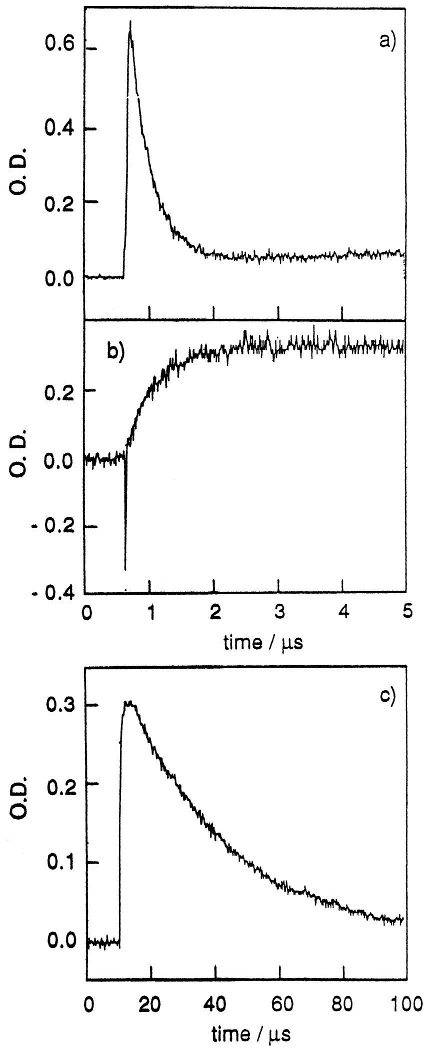


Fig. 1. Typical digitizer traces monitored in the LFP of BCD in the presence of VP in i-Oc. [BCD] = 6.0×10^{-4} mol dm^{-3}, [VP] = 2.10×10^{-2} mol dm^{-3}, monitored at 370 nm (a), 540 nm (b) and (c).

(decay of BCC (a)) and 540 nm (formation (b) and decay (c) of the new band). The absorbance of the new band initially increased with the increasing measured delay time after the flash. The maximum optical density ($d_{\max}$ = ca. 0.3) was obtained around 3 μs after the flash. After 3 μs, the optical density of the new band decreased with the increasing measured delay time after the flash. With increasing VP concentration, the delay time to attain the maximum optical density became shorter and the maximum optical density increased. Fig. 2 shows the time-resolved absorption spectra measured in the LFP of BCD in the presence of VP (2.10×10^{-2} mol dm^{-3}). Because the new band is not detected in the absence of VP, it must due to a new species formed by the reaction of BCC with VP.

The decay of BCC, and the formation and decay of the new band obey first-order kinetics ($\tau^{-1} = 7.2 \times 10^6$, 9.1×10^6 and 2.2×10^4 s^{-1}, respectively, at [VP] = 2.10×10^{-2} mol dm^{-3}). These rates are independent of the monitoring wavelength. The formation rate of the new species is the same as the decay rate of BCC. Although the decay rate of the new species was independent of the VP concentration, the decay rate of BCC and the formation rate of the new band linearly increased with increasing VP concentration, as shown in Fig. 3. The rate constant determined from the BCC decay (3.3×10^8 dm^3 mol^{-1} s^{-1}) agreed with the value determined using the new band formation (4.1×10^8 dm^3 mol^{-1} s^{-1}). In the LFPs of BCD with VP in dichloromethane, similar results were obtained.[1] Therefore, it is concluded that the new intermediate species is formed by the reaction of BCC and VP.

Because VP is an electron-rich olefin, the cycloaddition of the singlet carbene with the vinyl group of VP is rapid. Turro and coworkers [9–11] reported a complex upon the addition reaction of a singlet carbene with an olefin. This complex is reported to be spectrometrically undetectable. Based on its similarity to the spectrum of PY-2 (Eq. (3)), the new band is assigned to the BCC–VP ylide (PY-3). The agreement of the rate for the BCC decay with that for the PY-3 formation indicates that the PY-3 formation proceeded quantitatively.

$$\text{BCC} + \text{VP} \rightarrow \text{PY-3} \tag{3}$$

Scheme 1 shows the structures of the PYs. There are some differences between PY-2 and PY-3 in their spectra, in the rate constants of the ylide formation, and in the life times of the ylide, as listed in Table 1. The reported results of PY-1 [4] are also listed in this table. The rate constant of the PY-3 formation (3.3×10^8 dm^3 mol^{-1} s^{-1}) is about a half of the value of PY-2 (8.3×10^8 dm^3 mol^{-1} s^{-1}) [5]. This difference seems to be acceptable for the steric hindrance effect of the 2-substituent on the pyridine ring. Although these spectra have an absorption maximum around 520 nm (520 nm (PY-1) [4], 500 nm (PY-2) [6] and 540 nm (PY-3)), the $\varepsilon_{\max}$ value of PY-3 was estimated to be only one-third to one-half of the value for PY-2.[2] The life time of PY-3 is very much shorter than that of PY-2 (species stable during the measurement: ~200 μs). PY-3 has also a ZI structure as a resonance structure, as reported by Liu and coworkers [4,5] (Eq. (1), R = biphenyl-4-yl). ZI is assumed to cyclize easily by the intramolecular addition. Therefore, the short life time and the small absorption band of PY-3 seem to be caused by the contribution of the ZI structure.

3.2. Addition effect of TME

Alkyl halides (R–Cl), such as carbon tetrachloride and trichloroacetonitrile, are typical carbene scavengers

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[1] The LFPs of BCD were carried out in the presence of VP (3.4×10^{-2} and 4.8×10^{-2} mol dm^{-3}) in dichloromethane. A few different results were obtained, as (1) the solutions did not become turbid in CH_2Cl_2, and (2) the formation of IND was not detected in the LFP.

[2] I. Naito estimated that the $\varepsilon_{\max}$ value for PY-2 was roughly equal to the value for BCC. The value for PY-3 is one-third to one-half that for BCC.

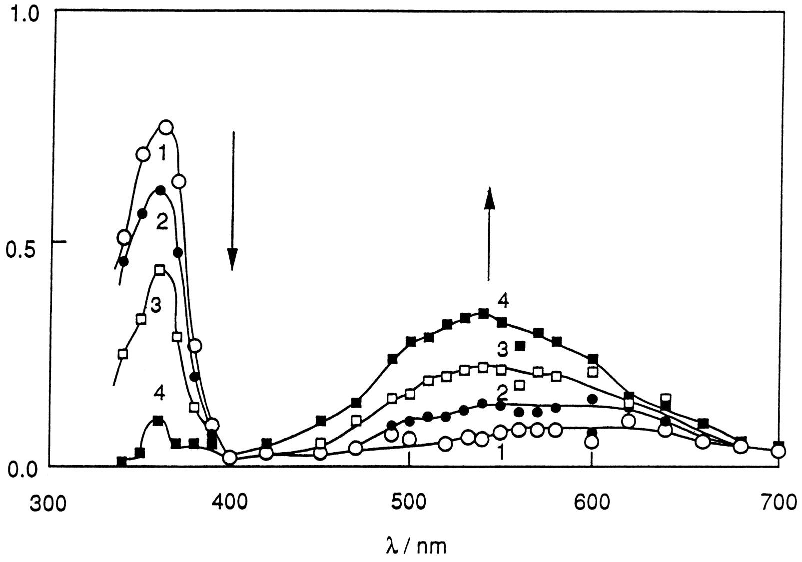


Fig. 2. Time-resolved absorption spectra measured in the LFP of BCD in the presence of VP. Monitored at 0.10 (1), 0.21 (2), 0.42 (3), and 2.4 μs after the flash (4), [BCD] = 6×10^{-4} mol dm^{-3}, [VP] = 2.10×10^{-2} mol dm^{-3} in i-Oc.

[12,13]. Platz and coworkers [13] reported that the observed carbene–pyridine ylide formation rate (k_{obs}) increased with increasing R–Cl concentration as shown in Eq. (4).

$$k_{\mathrm{obs}} = k_{\mathrm{o}} + k_{\mathrm{py}}[\text{pyridine}] + k_{\mathrm{RCl}}[\text{R–Cl}] \qquad (4)$$

where k_{o} is the sum of the rate constants of all first-order and pseudo-first-order processes of the carbene. The symbols, k_{py} and k_{RCl}, are the rate constants of the ylide formation and trapping reaction by R–Cl, respectively.

2,3-Dimethyl-2-butene is a typical singlet carbene scavenger like R–Cl and seems hardly to react with PY. The formation rate of PY-3 can also be expected to increase with increasing TME concentration. We studied the effects of TME concentration on the decay rate of BCC ($k_{\mathrm{obs\,1}}$) and the formation rate ($k_{\mathrm{obs\,2}}$) of PY-3 ([VP] = 2.10×10^{-2} mol dm^{-3} in i-Oc). Both rates increased with increasing TME concentration as shown in Fig. 4 ([VP] = 2.10×10^{-2} mol dm^{-3} in i-Oc). The rate constant determined for PY-3 formation (k =

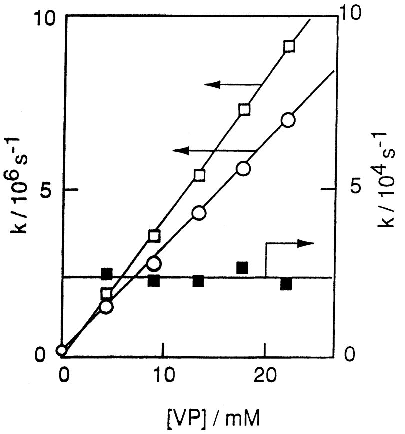
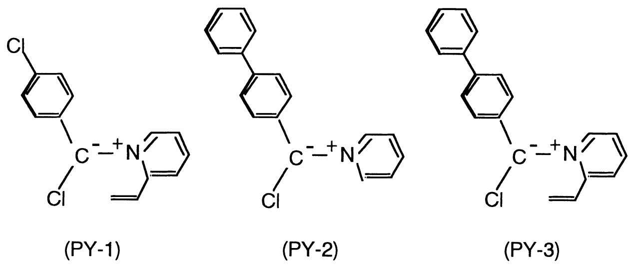


Fig. 3. Effects of VP on the decay rate of BCC, the formation rate and decay rate of the new band. The decay rates of BCC (○) and the new band (■) and the formation rate of the new band (□) are plotted against VP concentration. The LFPs of BCD were carried out in i-Oc ([BCD] = 6.0×10^{-4} mol dm^{-3}).



Scheme 1. PY structures.

Table 1
Results of PY[a]

PY	k of PY formation (dm^3 mol^{-1} s^{-1})	Life time (μs)	$\lambda_{\max}$ (nm)	$\varepsilon_{\max}$ (dm^2 mol^{-1})
PY-1[a]	2.0×10^8	32	520	–
PY-2[b]	8.3×10^8	~200	500	Large[c]
PY-3	3.3×10^8	45	540	Small[d]

[a] [3].

[b] [5].

[c] The $\varepsilon_{\max}$ value for PY is estimated to be roughly equal to the value for BCC.

[d] This value is about one-third to one-half the value for BCC.

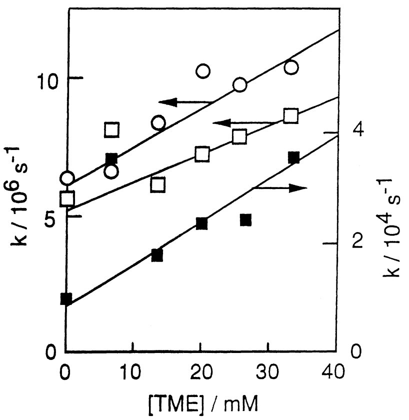


Fig. 4. Effects of TME on the decay rate of BCC, the formation rate and decay rate of the new band. The decay rates of BCC (○) and the new band (■) and the formation rate of the new band (□) are plotted against TME concentration. The LFPs of BCD were carried out in the presence of VP in i-Oc ([BCD] = $6.0 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$, [VP] = $2.10 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$).

$1.03 \times 10^8\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$) agrees with the value for the BCC decay rate ($k_{\mathrm{TME}} = 1.39 \times 10^8\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$). Thus, the increase in the $k_{\mathrm{obs}\,2}$ value depends on the increase in the $k_{\mathrm{obs}\,1}$ value. The decay rate of PY-3 ($k_{\mathrm{obs}\,3}$) also increased with increasing TME concentration (slope of the plots = $7.9 \times 10^5\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$).

Many types of ylides are in equilibrium with carbenes [6,7,14–16]. When PY-3 formation is in equilibrium with a carbene, the rates of both the PY-3 formation and decay must also increase with increasing the carbene scavenger concentration. This equilibrium was also supported by the yields of products, described below. Because PY-3 gives cyclized products, the reaction of BCC with VP can be written by Eq. (5)

$$\mathrm{BCC} + \mathrm{VP} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{PY-3} \xrightarrow{k_2} \text{cyclization products} \tag{5}$$

where k_1, k_{-1}, and k_2 are the rate constants of the formation, dissociation, and cyclization reactions of PY-3, respectively.

The decay rate of PY-3 ($k_{\mathrm{obs}\,3}$) is defined by Eq. (6)

$$\frac{-\mathrm{d}[\text{PY-3}]}{\mathrm{d}t} = -k_1[\mathrm{BCC}][\mathrm{VP}] + (k_{-1} + k_2)[\text{PY-3}] \tag{6}$$

In the equilibrium, the formation rate of PY-3 (k_1[BCC][VP]) is equal to the dissociation rate of PY-3 (k_{-1}[PY-3]). So, Eq. (6) may be simplified to Eq. (7) which includes the BCC concentration

$$\frac{-\mathrm{d}[\text{PY-3}]}{\mathrm{d}t} = k_2[\text{PY-3}] = k_2K[\mathrm{BCC}][\mathrm{VP}] \tag{7}$$

and, K is the equilibrium constant ($=k_1/k_{-1}$). Because the initial formation rate of PY-3 is the same as the decay rate of BCC ($k_{\mathrm{obs}\,1} = k_{\mathrm{o}} + k_1[\mathrm{VP}] + k_{\mathrm{TME}}[\mathrm{TME}]$) as reported by Platz and coworkers [13] (Eq. (4)), the decay rate of PY-3 ($k_{\mathrm{obs}\,3}$) is written by Eq. (8)

$$k_{\mathrm{obs}\,3} = \frac{k_2 k_{\mathrm{obs}\,1}}{k_{-1}} = \left(\frac{k_2}{k_{-1}}\right)(k_{\mathrm{o}} + k_1[\mathrm{VP}] + k_{\mathrm{TME}}[\mathrm{TME}]) \tag{8}$$

Thus, when we plotted the $k_{\mathrm{obs}\,3}$ value against TME concentration, a linear relationship was observed as shown in Fig. 4, and the slope of the relation must be the term, $k_2k_{\mathrm{TME}}/k_{-1}$. We estimated the dissociation rate constant (k_{-1}) to be ca. $4 \times 10^6\,\mathrm{s^{-1}}$ by means of the slope of the linear relation in Fig. 4 (slope = $7.9 \times 10^5\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$) and the k_2 and k_{TME} values ($k_2 = 2.3 \times 10^4\,\mathrm{s^{-1}}$, $k_{\mathrm{TME}} = 1.4 \times 10^8\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$). Therefore, we estimate the equilibrium constant (K) to be about $80\,\mathrm{dm^3\,mol^{-1}}$.

3.3. Decay process of PY-3

In the reaction of CCC and VP, indolizine ($\lambda < 400\,\mathrm{nm}$) was reported to form immediately after the decay of PY-1 [4]. In this reaction, we expect that the formation of IND proceeds in a stepwise manner. Initially, the intramolecular cyclization of ZI gave pyrrolidine derivatives. The dehydrochlorination reaction of these compounds then proceeds to give IND. The BCD and VP solution (<ca. $3.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$) became turbid after only one laser shot for the photolysis. The increase of the absorption (λ = 320–400 nm) could be undetected at low VP concentrations in i-Oc (>ca. $1 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$) or in methylene chloride. The time-resolved absorption spectra 10 μs after the flash were measured ([VP] = $2.10 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ in i-Oc), as shown in Fig. 5. At 40 μs after the flash, although the concentration of PY-3 decreased to one-half of its value at ca. 10 μs, the large absorption increase was undetected in the wavelength range from 320 to 400 nm. At 100 μs after the flash, the absorption dramatically increased. The time-resolved absorption spectra clearly showed that these pyrrolidine derivatives do not absorb light in the wavelength range measured.

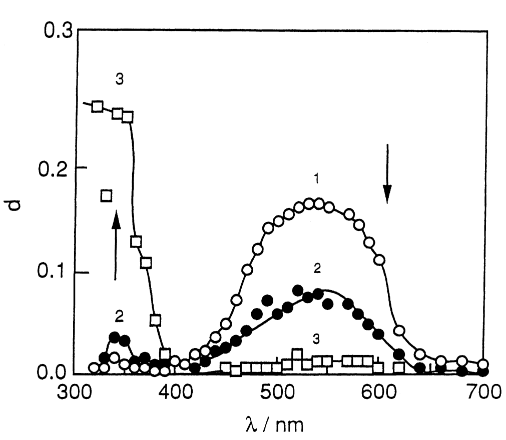


Fig. 5. Time-resolved absorption spectra measured in the LFP of BCD in the presence of VP. Monitored at 10.1 (1), 38.0 (2), and 99 μs after the flash (3), [BCD] = $6 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$, [VP] = $2.10 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ in i-Oc.

Table 2
Photoreactions of BCC in the presence of VP[a]

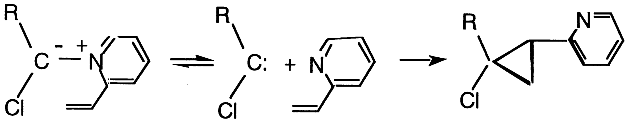
Run no.	[BCC] (mol dm^{-3})	[VP] (mol dm^{-3})	Products (%)		
			IND	*E*-CP	*Z*-CP
1	3.22×10^{-3}	2.02×10^{-1}	37	14	6
2	3.08×10^{-3}	4.04×10^{-1}	56	8	4

[a] The photoreactions were carried out in i-Oc with irradiation of 366 nm light at room temperature.

3.4. Photoirradiation of BCD in the presence of VP

In the photoreaction of 3-chloro-3-(4′-chlorophenyl)diazirine with VP, only 11% of IND was obtained, although the LFP results indicated that CCC quantitatively produced PY-1 [4,5,17]. It seems that there are other dominant routes for PY-1 deactivation. To clarify the low IND yield, the photoreactions of BCD were carried out in i-Oc in the presence of VP with irradiation of 366 nm light ([BCD] $= 3.22 \times 10^{-3}$ mol dm^{-3}, [VP] $= 2.02 \times 10^{-1}$ mol dm^{-3}). The products and their yields are listed in Table 2. IND (37%) was obtained as the main product. Thus, this compound was obtained by dehydrochlorination of pyrrolidine derivatives, i.e. the intramolecular cyclization products, as reported by Liu and coworker [4,5] (Eq. (1), R = biphenyl-4-yl), although pyrrolidine derivatives were undetected. Cyclopropane products were also obtained (14 (*E*-isomer, *E*-CP) and 6% (*Z*-isomer, *Z*-CP)), although BCC seemed to produce PY-3 quantitatively as seen by the results of the LFP. When we used twice the molar amount of VP ([BCD] $= 3.08 \times 10^{-3}$ mol dm^{-3}, [VP] $= 4.04 \times 10^{-1}$ mol dm^{-3}), the yield of IND increased (56%) but those of the cyclopropanes decreased (8 (*E*-isomer) and 4% (*Z*-isomer)). Three unidentified products were also obtained (total yield ca. 20%).

A small fraction of BCC reacts with VP to produce cyclopropanes. Because the LFP results indicate that BCC produces PY-3 quantitatively, the cyclopropanes were mainly produced by the reaction of BCC regenerated by the dissociation reaction of PY-3 (Eq. (9)) and by the reaction of BCC generated by photoirradiation. Because increasing the VP concentration decreases the BCC concentration in the equilibrium, there is no large difference in the formation rate of cyclopropanes. At high VP concentration (ca. 0.4 mol dm^{-3}), VP also acts as a solvent. The ZI structure must be stabilized in a polar solvent. We assume that the difference in the yields of IND and cyclopropanes depends on the solvent.



(PY-3) (BCC) (VP) (cyclopropane)

(R: biphenyl-4-yl)

(9)

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References

[1] R.A. Moss, The application of relative reactivity studies to carbene olefin addition reaction, in: M. Jones, R.A. Moss (Eds.), Carbenes, Wiley, New York, 1973, 153 pp.

[2] M. Regitz, et al., Carbene, in: K.H. Büchel, J. Falbe, H. Hagemann, M. Hanack, D. Klamann, R. Kreher, H. Krope, M. Regitz, E. Schaumann (Eds.), Methoden der Organishen Chemie, Band E19b, Teil 1 und 2, Georg Thieme Verlag, Stuttgart, 1989, 58 pp.

[3] J.E. Jackson, N. Soundararajan, M.S. Platz, M.T.H. Liu, J. Am. Chem. Soc. 110 (1988) 5595.

[4] M.T.H. Liu, Y. Romashin, R. Bonneau, Chem. Kinet. 26 (1994) 1179.

[5] R. Bonneau, Y.N. Romashin, M.T.H. Liu, S.E. MacPherson, J. Chem. Soc., Chem. Commun. (1994) 509.

[6] I. Naito, A. Oku, N. Otani, Y. Fujiwara, Y. Tanimoto, J. Chem. Soc., Perkin Trans. 2 (1996) 725.

[7] I. Naito, A. Oku, Y. Fujiwara, Y. Tanimoto, J. Chem. Soc., Perkin Trans. 2 (1999) 1051.

[8] I. Naito, K. Nakamura, T. Kumagai, K. Matsuda, H. Iwamura, A. Oku, J. Phys. Chem. A103 (1999) 8187.

[9] N.J. Turro, G.F. Lehr, J.A. Butcher, R.A. Moss, W. Guo, J. Am. Chem. Soc. 104 (1982) 1754.

[10] I.G. Gould, N.J. Turro, J. Butcher Jr., C. Doubleday Jr., N.P. Hacker, G.F. Lehr, R.A. Moss, D.P. Cox, W. Guo, R.C. Munjal, L.A. Perez, M. Fedorynski, Tetrahedron 41 (1985) 1887.

[11] R.A. Moss, W. Lawrynowicz, N.J. Turro, I.R. Gould, Y. Cha, J. Am. Chem. Soc. 108 (1986) 7028.

[12] W.H. Urry, J.R. Eiszner, J.W. Wilt, J. Am. Chem. Soc. 79 (1957) 918.

[13] M.B. Jones, V.M. Maloney, M.S. Platz, J. Am. Chem. Soc. 114 (1992) 2163.

[14] P.B. Grasse, B.-E. Brauer, J.J. Zupancic, K.J. Kaufmann, G.B. Schuster, J. Am. Chem. Soc. 105 (1983) 6833.

[15] P.C. Wong, J.C. Scaiano, J. Am. Chem. Soc. 104 (1982) 6631.

[16] Z. Huan, J.A. Landgrebe, K. Peterson, J. Org. Chem. 48 (1983) 4519.

[17] M.T.H. Liu, Personal communication.