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Ylide formation of singlet carbene with carbonyl compound—laser flash photolysis of (biphenyl-4-yl)chlorodiazirine in propanone

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Abstract

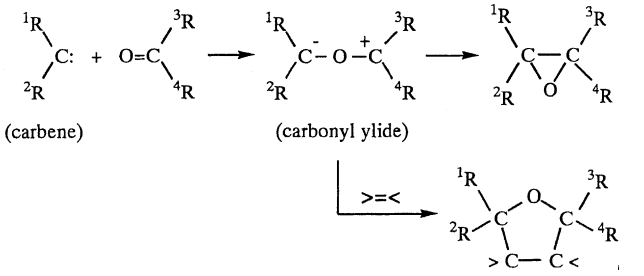
The ylide formation between a singlet carbene and a carbonyl compound has been studied by laser flash photolysis (LFP) of (biphenyl-4-yl)chlorodiazirine (BCD) in propanone and cyclopentanone, and by product analyses. (Biphenyl-4-yl)chlorocarbene (BCC) adds to the carbonyl compound to yield an equilibrium amount of the carbonyl ylide (CY) which has an absorption maximum around 490 nm. The rate constants of CY formation and dissociation have been determined. CY decays by unimolecular and bimolecular mechanisms. In the photoreaction of BCD with propanone, an aryl olefinic ketone and aryl α-hydroxy ketone were obtained. In the presence of dimethyl fumarate, the photoreaction of BCD in propanone gives a dihydrofuran derivative. The measured ratios of reaction products are in good agreement with ratios calculated from measured rate constants, which indicates that the rate constants are reliable.

Keywords: Laser flash photolysis; Carbonyl ylide; Equilibrium constant; 1,3-Dipolar addition

1. Introduction

Carbenes are one of most reactive species and often yield interesting products [1]. Many carbene reactions proceed by the way of ylide intermediates [2][1]. In the presence of a carbonyl compound, a carbene yields a carbonyl ylide (CY), i.e. a kind of 1,3-dipole, as shown in Eq. (1). Because these species are generated easily by photoirradiation of oxiranes, 1,3-dipolar additions have been well studied for the syntheses of heterocyclic compounds [3].

Although CY formation from triplet carbene has been studied by many in the past [1], CYs from singlet carbene have been rather difficult to detect. Liu and coworkers reported transient absorptions of CY from reactions of singlet chloro(4-substituted phenyl)carbenes with propanone [4]. Bounneau and Liu [5] also reported kinetic parameters of CY formation from chlorophenylcarbene with propanone by means of a computer fitting method using oscilloscope traces in the 400–580 nm region. Unfortunately, they did not mention 1,3-dipolar additions of CY with carbonyl compounds. Because propanone acts as a dipolarophile in the 1,3-dipolar addition of 3-(biphenyl-4-yl)-nitrile ylide [6], CY from singlet carbene should react with propanone.



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Recently, we detected a long-lived singlet carbene (biphenyl-4-yl)chlorocarbene [BCC, λ_{max} = 360 nm, τ = 24.8 μs in 2,2,4-trimethylpentane (i-Oc)] by 355 nm laser flash photolysis (LFP) of (biphenyl-4-yl)chlorodiazirine (BCD), as shown in Eq. (2) [7]. We established the formation of oxonium ylide [7], nitrile ylide [8], and pyridinium ylide [9] in reactions of BCC with ethers, nitrile compounds, and 2-vinylpyridine, respectively. We clarified that these ylides were in equilibrium with BCC. In those studies, we reported a method of determining the equilibrium constant for the reaction of BCC using a typical singlet

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[1] For fluorenylidene, see [2a,2c], diphenylcarbene [2b], 1-naphthylcarbene [2d], 4-oxocyclohexadiene [2f] and cyclopentadienylidene [2g].

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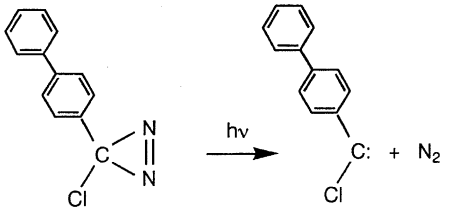
carbene scavenger, 2,3-dimethyl-2-butene (TME). In this study, we investigated in detail the formation of 1,3-dipole CY in the reaction of BCC with proapnone using a dipolarophile. To make clear the results, the reaction of BCC with cyclopentanone (CP) was also studied.



(BCD) (BCC) (2)

2. Experimental

2.1. Materials

(Biphenyl-4-yl)chlorodiazirine (BCD) was prepared from 4-cyanobiphenyl via the corresponding amidine hydrochloride salt (vide infra) [6]. White crystals: UV (2,2,4-trimethylpentane) λ_{max} = 358 nm (ε = 4.2 × 10^3 dm^2 mol^{-1}), 376 nm (6.2 × 10^3 dm^2 mol^{-1}) and 395 nm (5.2 × 10^3 dm^2 mol^{-1}).

Spectroscopic grade 2,2,4-trimethylpentane (i-Oc) and propanone were used without further purifications. Cyclopentanone (CP) and 2,3-dimethyl-2-butene (TME) were purified twice by distillations under N_2. Dimethyl fumarate was purified twice by recrystallizations from ethanol.

2.2. Laser flash photolysis

The laser flash photolysis (LFP) of BCD was carried out 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 analyzed using a PC.

2.3. Photoreaction of BCD in propanone

Mixed solutions of propanone (0.10 dm^3), 2,2,4-trimethylpentane (0.10 dm^3), and BCD (220.4 mg) were sealed into pyrex ampoules after several freeze-thaw degassing cycles. The photoirradiations of BCD solutions were carried out for 3 h at room temperature using a 300 W high pressure Hg lamp. Filters were not used. After the reaction, the solvent was evaporated and the products (217.7 mg) were isolated by using a high pressure liquid chromatography (silica gel/ethyl acetate) and a GPC apparatus [poly(styrene-divinylbenzene) beads/chloroform]. Six products were obtained, i.e., 1-(biphenyl-4-yl)-2-hydroxy-2-methyl-1-propanone (**1**, yield 24.8%), 1-(biphenyl-4-yl)-2-methyl-2-propen-1-one (**2**, 50.9%), 4-biphenylcarboxylic acid (**3**, 6.3%), (biphenyl-4-yl)chloroketooxime dimer (**4**, 4.1%) and 1,2-di(biphenyl-4-yl)-1,2-dichloroethene (**5**, 2.8%), and an unidentified product (small amount).

Spectral data: 1-(biphenyl-4-yl)-2-hydroxy-2-methyl-1-propanone (**1**), ^{1}H NMR ($CDCl_3$, TMS) δ = 1.55 (s, 6H, CH_3), 5.12 (s, 1H, OH), 7–8 ppm (m, 9H, aromatic H); El-MS: *m*/*z* 240 (M^+).

1-(Biphenyl-4-yl)-2-methyl-2-propen-1-one (**2**), ^{1}H NMR ($CDCl_3$, TMS) δ = 1.47 (q, 3H, CH_3), 4.39 (dq, 1H, *cis*-H), 4.39 (dq, 1H, *trans*-H), 7–8 ppm (m, 9H, aromatic H); El-MS: *m*/*z* 222 (M^+).

4-Biphenylcarboxylic acid (**3**), ^{1}H NMR ($CDCl_3$, TMS) δ = 3.52 (s, 1H, OH), 7–8 ppm (m, 9H, aromatic H); El-MS: *m*/*z* 198 (M^+).

(Biphenyl-4-yl)chloromethylketooxime dimer (**4**), ^{1}H NMR ($CDCl_3$, TMS) δ = 7–8 ppm (m, 18H, aromatic H); El-MS *m*/*z* 428 (M^+)].

1,2-Di(biphenyl-4-yl)-1,2-dichloroethene (**5**), ^{1}H NMR ($CDCl_3$, TMS) δ = 7–8 ppm (m, 18H, aromatic H); El-MS: *m*/*z* 400 (M^+).

2.4. Photoreaction of BCD in propanone the presence of dimethylfumarate

BCD (200.2 mg) and dimethyl fumarate (794.0 mg) were dissolved in a mixture of propanone (0.120 dm^3) and 2,2,4-trimethylpentane (0.120 dm^3). The mixed solution was sealed in a pyrex ampoule after several freeze-thaw degassing cycles. Photoirradiation of the solution was carried out for 3 h at room temperature using the 300 W high pressure Hg lamp. After the reaction, the solvent was evaporated and the products (914.7 mg) were isolated using the liquid chromatography (silica gel/ethyl acetate) and the GPC equipment [poly(styrene-divinylbenzene) beads/chloroform] cyclically operated. Six products were obtained, i.e., **1** (15.9%), **2** (34.5%), **4** (2.8%), 5-(biphenyl-4-yl)-3,4-dicarbomethoxy-2,3-dihydro-2,2-dimethylfuran (**6**, 27.4%), 1-(biphenyl-4-yl)-1-chloro-2,3-dicarbomethoxycyclopropane (**7**, 4.4%), and unidentified products (small amounts).

5-(Biphenyl-4-yl)-3,4-dicarbomethoxy-2,3-dihydro-2,2-dimethylfuran (**6**), ^{1}H NMR ($CDCl_3$, TMS) δ = 1.46 (s, 3H, t-CH_3), 1.59 (s, 3H, c-CH_3), 3.71 (s, 3H, 4-CO_2CH_3), 3.80 (s, 3H, 3-CO_2CH_3), 3.92 (s, 1H, 3-H), 7–8 ppm (m, 9H, aromatic H); ^{13}C NMR ($CDCl_3$, TMS) δ = 23.5 (1C, 2c-CH_3), 29.4 (1C, 2t-CH_3), 51.1 (1C, 3-CH_3O), 52.0 (1C, 3-CH_3O), 59.5 (1C, 3-C), 86.5 (1C, 2-C), 101.8 (1C, 4-C), 126.3 (2C, 3,5-biphenyl), 127.2 (2C, 2,6-biphenyl), 127.7 (1C, 4′-biphenyl), 128.4 (1C, 4-biphenyl), 128.8 (2C, 2′,6′-biphenyl), 129.9 (2C, 3′,5′-biphenyl), 140.4 (1C, 1-biphenyl), 143.5 (1C, 1′-biphenyl), 165.9 (1C, 4-CO), 171.8 ppm (1C, 3-CO); El-MS: *m*/*z* 366 (M^+).

1-(Biphenyl-4-yl)-1-chloro-2,3-dicarbomethoxycyclopropane (**7**), ^{1}H NMR ($CDCl_3$, TMS) δ = 3.19(d, 1H, t-H, J = 7.2 Hz), 3.21 (d, 1H, c-H, J = 7.2 Hz), 3.66 (s, 3H,

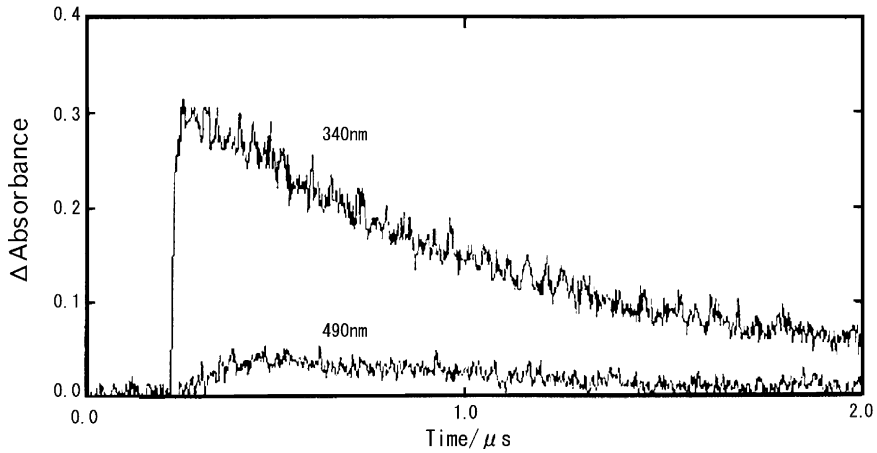


Fig. 1. Typical digitizer traces monitored at 340 (a) and 490 nm (b) in the LFP of BCD in propanone at 293 K. The latter trace was the average of 16 runs. [BCD] = 6×10^{-4} mol dm^{-3}.

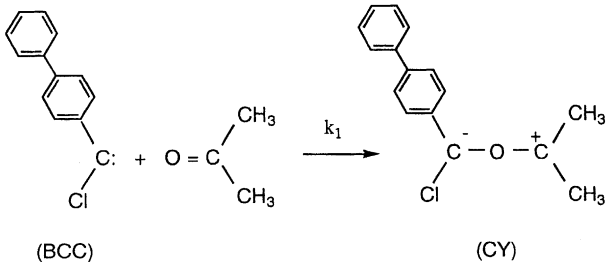
t-CO_2CH_3), 3.87 (s, 3H, c-CO_2CH_3), 7–8 ppm (m, 9H, aromatic H); ^{13}C NMR ($CDCl_3$, TMS) δ = 35.3 (2C, 2,3-C), 51.1 (1C, 1-C), 52.5 (1C, 2t-CH_3O), 52.8 (1C, 3c-CH_3O), 127.2 (2C, 3,5-biphenyl), 127.5 (2C, 2,6-biphenyl), 127.7 (1C, biphenyl), 128.8 (2C, 2′6′-biphenyl), 129.0 (2C, 3′,5′-biphenyl), 167.1 ppm (1C, 2-CO), 173.0 ppm (1C, 2-CO); El-MS: *m*/*z* 344 (M^+), 346 $\{(M+2)^+\}$.

3. Results and discussion

3.1. Detection of CY

We carried out the 355 nm LFP of BCD in propanone to detect CY. An absorption maximum at 360 nm, due to BCC, was recorded in propanone at about 70 ns after the start of the flash. Although BCC does not have absorption bands at wavelengths longer than 420 nm in any solvent, we detected a new small absorption band in the wavelength range 460–540 nm. Fig. 1 shows typical oscilloscope traces monitored at 340 and 490 nm (the trace is the average from 16 runs). Corresponding to the decay of BCC, the new band formed around 500 nm. The maximum optical density of the latter trace was obtained around 250 ns after the flash. After 250 ns, the optical density decreased with increasing the measured delay time after the flash. These traces indicate clearly that the new band is due to a new intermediate formed in the reaction of BCC with the carbonyl compound.

Fig. 2 shows time-resolved absorption spectra measured in the LFP of BCD in propanone. We concluded that the new band had an absorption maximum around 500 nm based on the spectra measured at 0.5, 1.0, and 2.0 μs after the flash.[2] In CP, a new band was also detected around 500 nm corresponding to the decay of BCC. Liu and coworkers reported the absorption maxima of chlorophenylcarbene-propanone CY (λ_{max} = 450 nm) [5], of chloro(4-chlorophenyl)carbene-propanone CY (480 nm), and of chloro(4-trifluoromethylphenyl)carbene-propanone CY (480 nm) [4]. Therefore, we assigned the new band to the CY shown in Eq. (3). In Eq. (3), k_1 is the rate constant of CY formation.



(3)

3.2. Effect of propanone concentration

The BCC decay rate was determined from the decay trace measured at 380 nm in the time range between about 1 μs and about 10 μs after the flash.[3] The BCC decay rate increases linearly with increasing propanone concentration, as shown in Fig. 3. The rate constant was determined to be 8.1×10^4 dm^3 mol^{-1} s^{-1} (CP: 3.1×10^5 dm^3 mol^{-1} s^{-1}). On the other hand, the formation and decay rates of CY were determined by means of an average of 16 oscilloscope traces measured at 480 nm in i-Oc. Both rates increase linearly with increasing propanone concentration, as shown in Fig. 4. The rate constants of the formation and decay of CY are 8.6×10^5 and 7.3×10^4 dm^3 mol^{-1} s^{-1}, respectively (CP: 1.6×10^6 and 2.8×10^5 dm^3 mol^{-1} s^{-1}, respectively).

[2] Since the absorption maximum was not detected around 500 nm at 250 ns after the flash, we assumed that the results contained noises in the measurements of the shorter wavelength.

[3] Before 1 μs, the traces did not obey first-order kinetics. We estimated that the equilibrium was not attained until 1 μs after the flash.

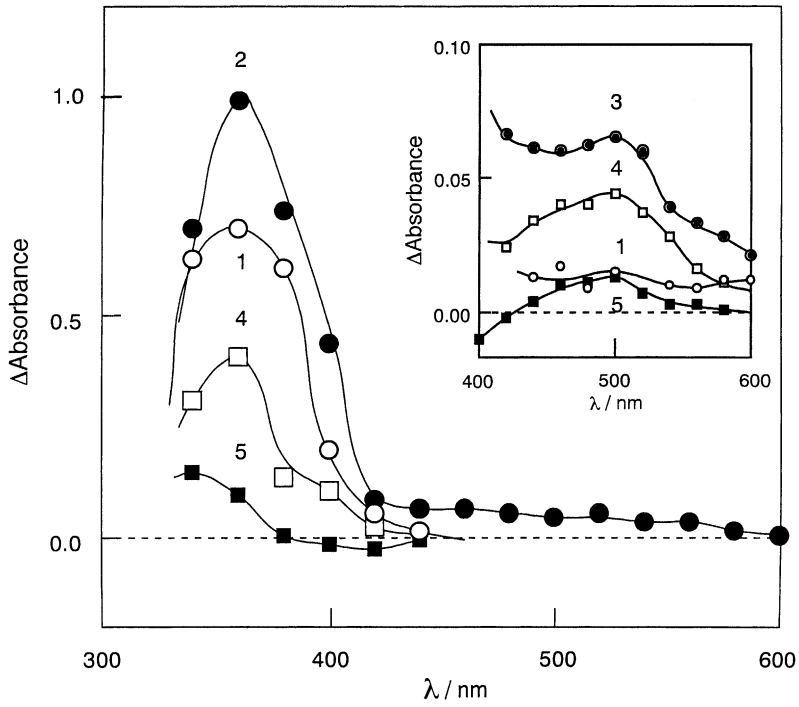


Fig. 2. Time-resolved absorption spectra measured in the LFP of BCD in propanone at 20 ns (1), 70 ns (2), 480 ns (3), 1 μs (4), and 2 μs (5) from the start of the flash. The oscilloscope traces were averages of 16 runs at 293 K. [BCD] = 8×10^{-4} mol dm^{-3}.

Although the rate constant determined by means of BCC decay rate was one order of magnitude smaller than it for the CY formation, that rate constant agreed with the value for CY decay rate. When BCC is in equilibrium with CY, the decay of CY must proceed according to the decay of BCC. Either way, the k_1 value must be as determined for the CY formation, listed in Table 1.

Because the plots of the CY decay (Fig. 4b) have intercepts (ca. 5×10^4 s^{-1}; CP, ca. 5×10^4 s^{-1}), the CY decay seems to proceed through unimolecular and bimolecular mechanisms, as shown in Eqs. (4) and (5),

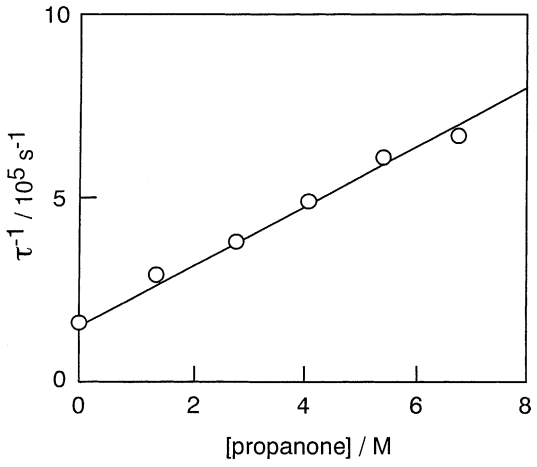


Fig. 3. Effect of propanone concentration on the decay rate of the transient absorption measured at 380 nm. The LFPs of BCD were carried out in i-Oc in the presence of propanone at 293 K. [BCD] = 8×10^{-4} mol dm^{-3}.

$$\mathrm{CY} \xrightarrow{k_2} \text{products} \tag{4}$$

$$\mathrm{CY} + \text{propanone} \xrightarrow{k_3} \text{products} \tag{5}$$

where k_2 and k_3 are the rate constants of the unimolecular and bimolecular decay processes of CY, respectively.

In the reaction of dichlorocarbene with benzaldehyde, Martin and coworkers reported the formation of a dioxirane via 1,3-dipolar addition of the dichlorocarbene-benzaldehyde CY with benzaldehyde [10]. Similarly, Bekhazi and Warkentin reported that dimethylcarbene in propanone yielded 2,2,4,4,5,5-hexamethyl-1,3-dioxirane via 1,3-dipolar addition of the dimethylcarbene-propanone CY with propanone [11]. These reports strongly suggest that the BCC-propanone CY reacts with propanone. Without 1,3-dipolar addition of CY with propanone, there are no bimolecular decay processes of CY. We carried out the LFP of BCD in propanone in the presence of dimethyl fumarate, as a typical dipolarophile. The decay rate of CY accelerated by the addition of dimethyl fumarate [$k = 3.4 \times 10^7$ (in propanone), 1.5×10^7 dm^3 mol^{-1} s^{-1} (in CP)]. In the photoirradiation of BCD in the presence of dimethyl fumarate in propanone, we obtained a 1,3-dipolar addition product, described later. A different type of 1,3-dipole, nitrile ylide produced in the photoreaction of a 2H-azirine, reacts with propanone ($k = 2.5 \times 10^3$ dm^3 mol^{-1} s^{-1} in cyclohexane) [6]. Therefore, we propose that the bimolecular mechanism

of the CY decay is due to 1,3-dipolar addition of CY with propanone.

3.3. Addition effect of singlet carbene scavenger

Many types of ylides are in equilibrium with carbenes [7–9]. Furthermore, CYs formed by the cleavage reaction of oxiranes are reported to be in equilibrium with carbenes [12]. The agreement of the BCC decay rate with the CY decay rate suggests that CY and BCC are in equilibrium, as shown in Eq. (6),

$$\mathrm{BCC} + \mathrm{propanone} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{CY} \tag{6}$$

where k_{-1} is the rate constant of the CY dissociation.

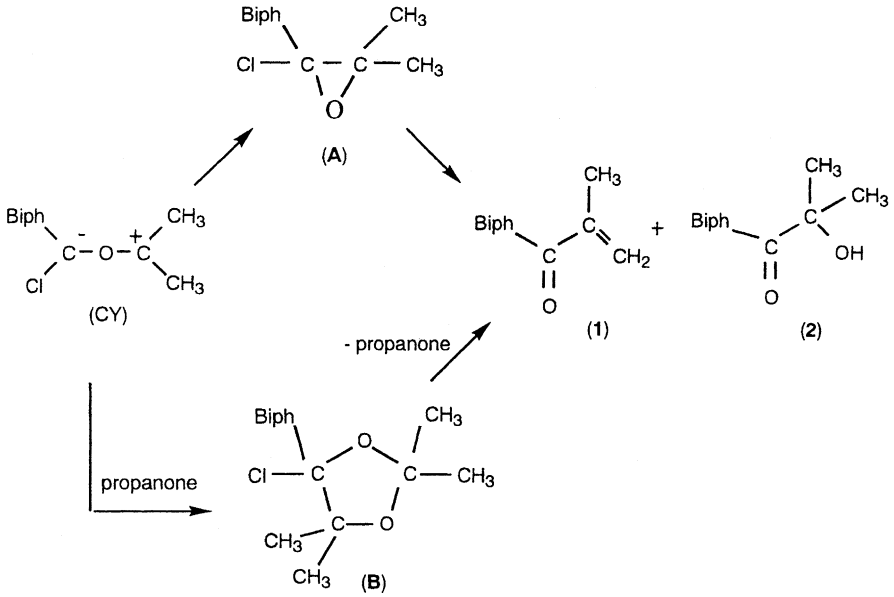
Bounneau and Liu reported that CY is in equilibrium with carbene by analyzing oscilloscope traces [5]. There are some difficulties in determining parameters by this method, however, and results have relatively large errors. However, we have already reported an easy method for estimating an equilibrium constant ($K = k_1/k_{-1}$) by using a typical singlet carbene scavenger, 2,3-dimethyl-2-butene (TME) as shown in Eq. (7) [6,7]; CY hardly reacts with such electron rich olefins [13],

$$\frac{k_{\mathrm{TME},0}}{k_{\mathrm{TME}}} = 1 + K[\mathrm{propanone}] \tag{7}$$

where $k_{\mathrm{TME},0}$ and k_{TME} are rate constants of the reaction of BCC with TME in the absence and presence of propanone, respectively. The effect of propanone concentration on the rate constant of the reaction of BCC with TME (k_{TME}) was studied in i-Oc. At each propanone concentration, a good linear relationship was obtained between the decay rate of BCC and TME concentration. The k_{TME} value decreased with increasing concentration of carbonyl compound (in the absence of propanone, $k_{\mathrm{TME},0} = 8.13 \times 10^8\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ [7]). When the ratios of the rate constants ($k_{\mathrm{TME},0}/k_{\mathrm{TME}}$) were plotted against propanone concentration, a good linear relationship was obtained, as shown in Fig. 5. The K value, the slope of the plots, was estimated to be roughly $0.4\ \mathrm{dm^3\ mol^{-1}}$ (CP: $0.4\ \mathrm{dm^3\ mol^{-1}}$ in i-Oc). Thus, the k_{-1} value was estimated to be $2.1 \times 10^6\ \mathrm{s^{-1}}$ in i-Oc (CP: $k_{-1} = 3.9 \times 10^6\ \mathrm{s^{-1}}$). Bounneau and Liu reported the k_{-1} value of chlorophenylcarbene-propanone CY to be $7.5 \times 10^5\ \mathrm{s^{-1}}$ in i-Oc [5]. Table 2 listed the k_{-1} values. Our measured value for k_{-1}, therefore, is reasonable.

3.4. Photoreaction of BCD in propanone

In the reaction of carbene with excess amounts of carbonyl compounds, oxiranes and dioxiranes were obtained by way of CY formation [10,14][4]. Photoirradiations of BCD in mixtures of i-Oc and propanone (50%, ca. $6.7\ \mathrm{mol\ dm^{-3}}$) yielded α-hydroxyketone (**1**, 24.8%), olefinic ketone (**2**, 50.9%), carboxylic acid (**3**, 6.3%), ketooxime dimer (**4**, 4.1%), small amounts of a carbene dimer (**5**, 2.8%), and an unknown compound. We could not detect the oxirane, 2-(biphenyl-4-yl)-2-chloro-3,3-dimethyloxirane (**A**), and the dioxirane, 4-(biphenyl-4-yl)-4-chloro-2,2,5,5-tetramethyldioxirane (**B**). Even in the absence of dimethyl fumarate, the 1,3-dipolar addition product, dioxirane (**B**) must be the major product of the reaction between BCC and an excess of propanone, because the decay of CY proceeds mainly through bimolecular mechanism as demonstrated in Fig. 4b. Chlorooxirane (**A**) has been reported to decompose easily to α-chloroketone and olefinic ketone [15]. Halodioxirane (**B**) is now concluded to decompose to olefinic ketone (**1**), α-chloroketone and/or α-hydroxyketone (**2**), as shown in Eq. (8).



(8)

[4] For aldehyde, see [14a], and ketone [14d].

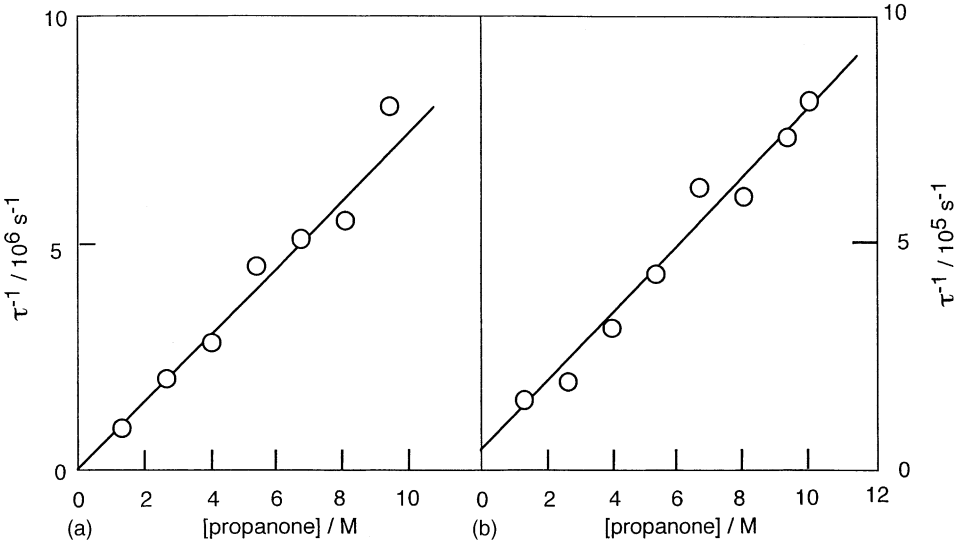


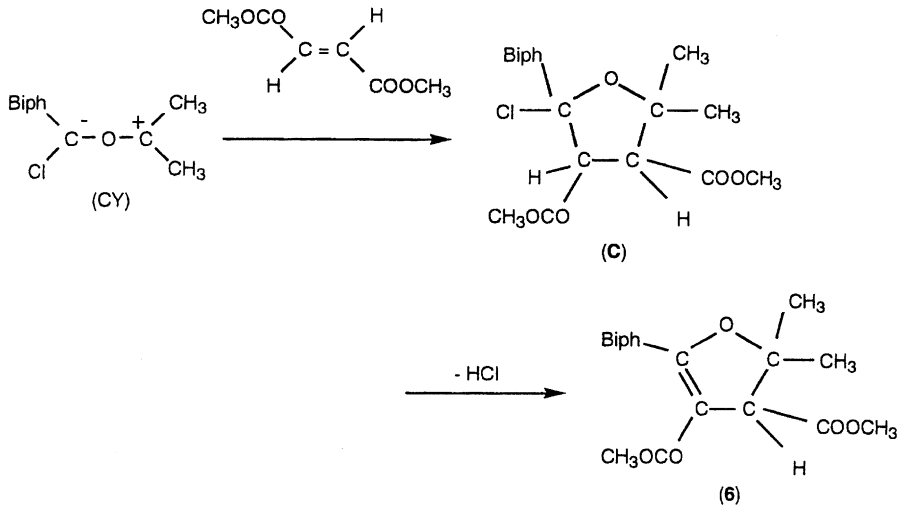
Fig. 4. Effects of propanone concentration on the formation (a) and decay rates (b) of CY. The LFPs of BCD were carried out in i-Oc at 293 K. [BCD] = 8×10^{-4} mol dm^{-3}.

Table 1
Rate constants of CY formation of chloro(4-substituted phenyl) carbene

Substituent	Carbonyl compound	Solvent	λ_{ma} (nm)	k_1 (dm^3 mol^{-1} s^{-1})	Remarks
Phenyl (BCC)	Propanone	i-Oc[a]	500	8.6×10^5	This work
Phenyl (BCC)	CP	i-Oc	500	1.6×10^6	This work
H	Propanone	i-Oc	450	2.0×10^5	[4a]
Cl	Propanone	Tolune	480	4.81×10^6	[4b]
CF_3	Propanone	Tolune	480	1.56×10^7	[4b]
NO_2	Propanone	i-Oc		3.5×10^7	[4b]

[a] 2,2,4-Trimethylpentane.

In the presence of dimethyl fumarate (2.30×10^{-2} mol dm^{-3}), we obtained dihydrofuran (**6**, 27.4%), and cyclopropane (**7**, 4.4%) with the former products [**1** (15.9%), **2** (34.5%), and **4** (2.8%)]. Product **6** was formed by dehydrochlorination of the 1,3-dipolar addition product of CY with dimethyl fumarate, 5-(biphenyl-4-yl)-5-chloro-3,4-dicarbomethoxy-2,2-dimethyl-tetrahydrofuran (**C**), as shown in Eq. (9). Thus, CY must react with propanone. Product **7** was formed by the addition of BCC with dimethyl fumarate, as shown in Eq. (10).



(9)

Table 2
Determined rate constants of BCC with carbonly compound in i-Oc

Carbonyl compound	k_1 ($dm^3\,mol^{-1}\,s^{-1}$)	k_{-1} (s^{-1})	k_2 (s^{-1})	k_3 ($dm^3\,mol^{-1}\,s^{-1}$)
Propanone	8.6×10^5	2.1×10^6	5×10^4	7.3×10^4
CP	1.6×10^6	3.9×10^6	5×10^4	2.8×10^5

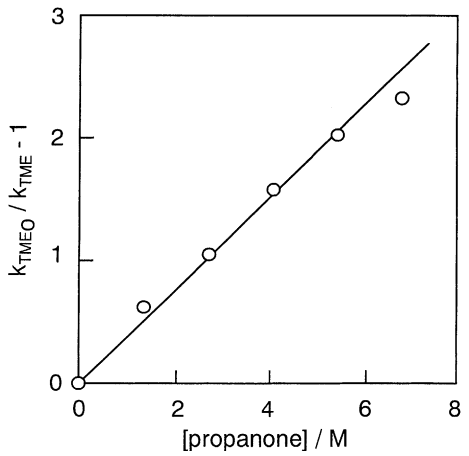
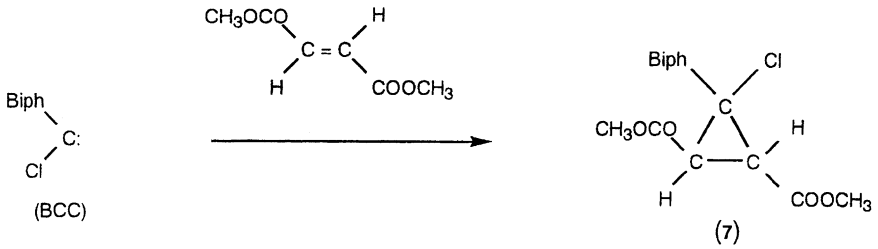


Fig. 5. Plots of the ratios of the rate constants in the absence ($k_{TME,0}$) and in the presence of propanone (k_{TME}) vs. propanone concentration.



(10)

In the presence of the dipolarophile, the relative reactivities, i.e. the ratio of the rate constants, can be compared from the ratio of the products ([**6**]/[**7**]) using Eq. (11),

$$\frac{[\text{dihydrofuran, } \mathbf{6}]}{[\text{cyclopropane, } \mathbf{7}]} = \frac{\int d[\mathbf{6}]\,dt}{\int d[\mathbf{7}]\,dt} = \frac{f_1 k_4[\mathbf{CY}][\text{dimethyl fumarate}]}{k_5[\mathbf{BCC}][\text{dimethyl fumarate}]} = f_1 k_4 k_5^{-1} K[\text{propanone}] \quad (11)$$

where k_4 and k_5 are the rate constants of the reactions of CY and BCC with dimethyl fumarate, respectively. The parameter f_1 is the fraction of the dehydrochlorination reaction of the 1,3-dipolar addition product to yield dihydrofuran. The value of k_4 was determined to be $3.4 \times 10^7\,dm^3\,mol^{-1}\,s^{-1}$ in propanone. The k_5 value has been reported to be $1.5 \times 10^7\,dm^3\,mol^{-1}\,s^{-1}$ in i-Oc [7]. Thus, the measured product ratio (6.2) agrees well with the ratio estimated from known rate constants (6.1), when the dehydrochlorination proceeded quantitatively ($f_1 = 1$).

Both products **1** and **2** were formed by decomposition of **A** and of **B**. The formation of **B** is a reaction parallel with the formation of **C**. When the successive reactions proceeded quantitatively, the ratio of the products [**6**/(**1** + **2**)] can be estimated from of the measured rate constants, as in Eq. (12),

$$\frac{[\text{dihydrofuran, } \mathbf{6}]}{[\text{olefinic ketone, } \mathbf{1}] + [\alpha\text{-hydroxyketone, } \mathbf{2}]} = \frac{f_1 \int d[\mathbf{C}]\,dt}{f_2 \int d[\mathbf{A}]\,dt + f_3 \int d[\mathbf{B}]\,dt} = \frac{\int f_1 k_4[\mathbf{CY}][\text{dimethyl fumarate}]\,dt}{\int (f_2 k_2[\mathbf{CY}] + f_3 k_3[\mathbf{CY}][\text{propanone}])\,dt} = \frac{f_1 k_4[\text{dimethyl fumarate}]}{f_2 k_2 + f_3 k_3[\text{propanone}]} \quad (12)$$

where f_2 and f_3 are parameters (analogous to f_1) relating to the reactions of both oxirane **A** and dioxirane **B** to yield products **1** and **2**. Assuming $f_2 = 1.0$ and $f_3 = 1.0$, the ratio was estimated to be 0.33 by means of Eq. (12). This ratio is about two thirds of the measured product ratio (0.54). But because the difference between the ratios is within the error limits, the derived rate constants are acceptable.

4. Conclusion

LFP of BCD was carried out in propanone or in CP for the study of CY formation of the singlet carbene BCC with carbonyl compounds. BCC reacted with carbonyl compounds to yield the 1,3-dipole CY. CY has an absorption band around 500 nm and is in equilibrium with BCC ($K = 0.4\,dm^3\,mol^{-1}$). The rate constants for CY formation and dissociation, and its subsequent reactions were determined. In the absence of a dipolarophile, aryl olefinic ketone and aryl hydroxy ketone were obtained by the way of oxirane and dioxirane, which were formed by additions of BCC and CY with the carbonyl compound, respectively. Although it is very difficult to clarify the bimolecular reaction of CY, the ratio of the products is good evidence of the 1,3-dipolar addition of CY with carbonyl compound. In the presence of dimethyl fumarate, the dihydrofuran derivative was obtained. Comparison of ratios of products obtained with ratios

estimated from measured rate constants indicate that the determined rate constants are reasonable.

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