

Formation of nitrile ylides in the addition of singlet carbene to nitrile compounds—laser flash photolysis of (biphenyl-4-yl)-chlorodiazirine in the presence of nitrile compounds



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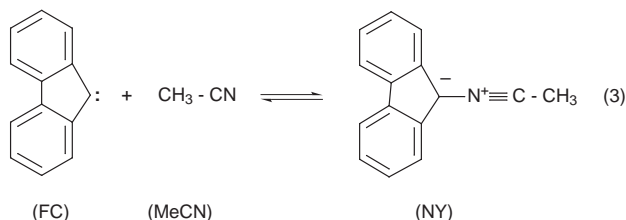
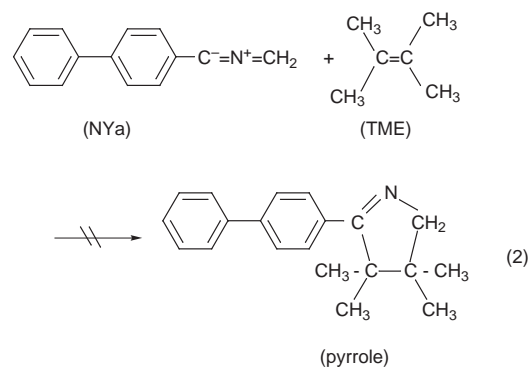
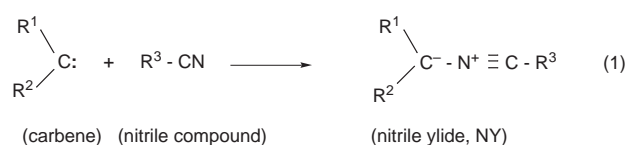
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Formation of a nitrile ylide (NY) by addition of a singlet carbene to a nitrile compound was studied by laser flash photolysis (LFP) of (biphenyl-4-yl)chlorodiazirine (BCD) in the presence of nitrile compounds. Although the generated (biphenyl-4-yl)chlorocarbene (BCC) forms a NY by addition to a nitrile compound in an equilibrium reaction, the absorption spectrum of the NY can be measured only in the LFP of BCD in the presence of 2,4,6-trimethoxybenzonitrile. The equilibrium constants for the NY formation in the addition of BCC to propionitrile or pivalonitrile were determined to be 0.45 and 0.37 M⁻¹ at 295 K, respectively. The reactivity of NY towards olefins seems to be substantially lower than those of BCC. The reaction of BCC with 2,3-dimethylbut-2-ene was carried out in 2,2,4-trimethylpentane and propionitrile in the temperature range of *ca.* 170 to 300 K. In both solvents, the rate constants increased with decreasing temperature and the maximum value appeared at around 210 K. Using the difference in the rate constants, the free energy difference for the equilibrium constant was also estimated to be *ca.* 4.2 kJ mol⁻¹.

Introduction

Reactions of methylene with electron-deficient olefins, such as fumaronitrile, acrylonitrile, dimethyl acetylenedicarboxylate, were reported in detail to yield pyrrole derivatives in acetonitrile (MeCN).¹ It is concluded that these reactions proceed *via* a nitrile ylide (NY) intermediate formed by the addition of methylene to the nitrile solvent, as shown in eqn. (1). The reactions of 1-naphthylcarbene (NC),² 2-naphthylcarbene,³ fluoren-9-ylidene (FC)⁴ and cyclopentadienyliidene⁵ in MeCN were also reported to proceed by way of a NY because the rate constants determined in the reaction of carbene with electron-deficient olefins in MeCN agreed with those of the reactions of NY formed from 2*H*-azirine and these olefins. Moreover, NC was reported to form the corresponding NY by addition to benzonitrile (PhCN) or 2,2-dimethylpropionitrile (t-BuCN).^{2b} These NYs formed from NC were also reported to react with electron-rich olefins such as 2,3-dimethylbut-2-ene (TME).^{2b} The NY formed from 3-(biphenyl-4-yl)-2*H*-azirine (NYa), however, is a relatively stable species ($\tau = 12$ ms in cyclohexane) and does not react with TME [eqn. (2)].⁶ Moreover, FC in MeCN was reported to yield 2*H*-azirine (in the absence of a scavenger), pyrrole (in the presence of dimethylmaleic anhydride), and cyclopropane (in the presence of 2-methylbut-2-ene).^{4a} The former two products were obtained by way of the NY formed by the addition of FC to MeCN. The last product was also obtained by the direct addition of FC to the olefin even in MeCN. Thus, it seems that there is an equilibrium reaction between FC and MeCN, as shown in eqn. (3). These carbenes are triplets in their ground state. On the other hand, phenylchlorocarbene (PCC), a typical singlet carbene, was reported not to form a NY,⁷ but a small solvent effect was reported in the reaction of PCC with TME.⁸ NY was detected spectrometrically only in the reaction of (4-nitrophenyl)chlorocarbene with MeCN.⁹



The photoreaction of (biphenyl-4-yl)chlorodiazirine (BCD) yielded a long-lived singlet carbene, (biphenyl-4-yl)chlorocarbene [BCC, $\lambda_{\text{max}} = 360$ nm, $\tau = 24.8$ μs in 2,2,4-trimethylpentane (i-Oc)] as shown in eqn. (4).¹⁰ Recently, we measured the IR spectrum assigned to the heterocumulene structure

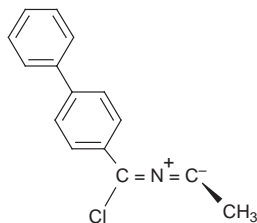


Fig. 1 Heterocumulene structure of NY formed by the addition of BCC to MeCN.

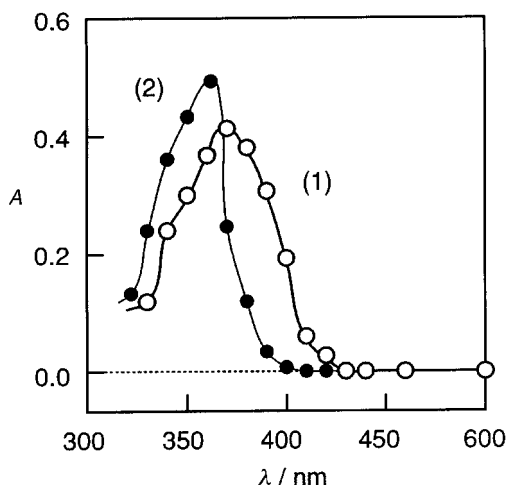
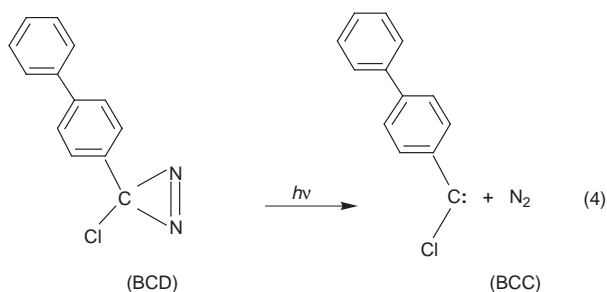


Fig. 2 Transient absorption spectra of BCC measured in MeCN (1) and *i*-Oc (2) *ca.* 80 ns after the flash. [BCD] = *ca.* 6×10^{-4} mol dm $^{-3}$.



($>C=N^+=C^-$) formed by the addition of BCC to MeCN in an argon matrix at 10 K, as shown in Fig. 1.¹¹ In this regard, we have studied the formation of NYS from BCC and various types of nitrile compounds by means of laser flash photolysis (LFP) of BCD.

Results and discussion

Transient absorption spectrum

Laser flash photolysis (LFP) of (biphenyl-4-yl)chlorodiazirine (BCD) was carried out in acetonitrile (MeCN) at 295 K to detect the nitrile ylide (NY) directly. A transient spectrum measured immediately after the flash exhibits only one absorption maximum at $\lambda = 370$ nm, as shown in Fig. 2. Fig. 2 also shows the absorption spectrum of (biphenyl-4-yl)chlorocarbene (BCC) in 2,2,4-trimethylpentane (*i*-Oc). The shape of the spectrum did not change during *ca.* 10 μ s after the flash (the delayed measuring time). Decay profiles of the absorption at 370 nm obeyed first-order kinetics. The decay rate ($\tau^{-1} = 7.94 \times 10^4$ s $^{-1}$) was independent of the measured wavelength. It is unclear whether these transient spectra belong to BCC or its NY yielded by the addition of BCC to MeCN.

LFP of BCD was also carried out in the presence of a variety of nitrile compounds [benzonitrile (solvent), 4-methoxybenzonitrile, 2,4,6-trimethoxybenzonitrile (TMB), 4-cyanobiphenyl, and 1-naphthonitrile in MeCN]. A weak absorption was

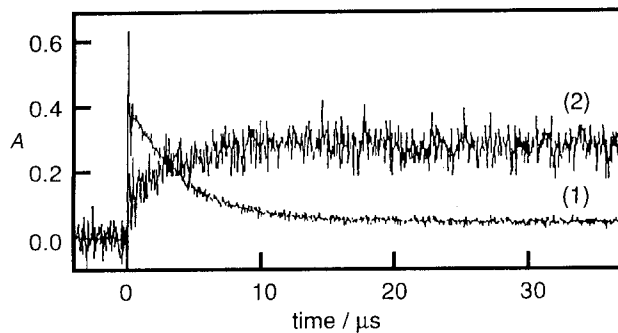


Fig. 3 Typical digitizer traces monitored in the LFP of BCD in the presence of TMB. $\lambda_{\text{moni}} = 390$ (1) and 440 nm (2). [BCD] = *ca.* 6×10^{-4} mol dm $^{-3}$, [TMB] = 6.7×10^{-1} mol dm $^{-3}$ in MeCN.

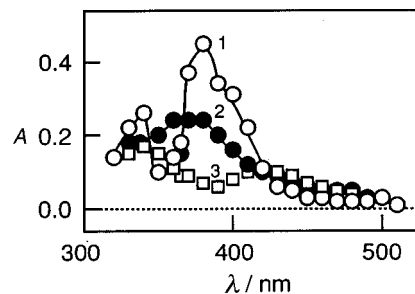
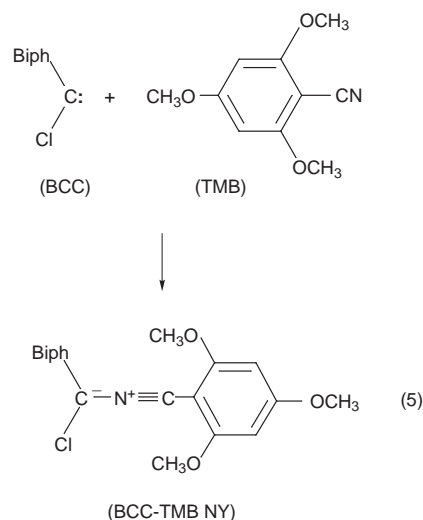


Fig. 4 Time-resolved transient absorption spectrum measured in the LFP of BCD in the presence of TMB. Monitored at 0.5 (1), 3.4 (2) and 37.1 μ s (3), [BCD] = *ca.* 6×10^{-4} mol dm $^{-3}$, [TMB] = 6.7×10^{-1} mol dm $^{-3}$ in MeCN.

observed only in the presence of TMB in the wavelength range from 420 to 490 nm, which was formed in accordance with the decay of the absorption at $\lambda = 370$ nm. The spectrum seems to exhibit a maximum at around 440 nm. Figs. 3 and 4 show typical digitizer traces monitored at 390 nm (decay of BCC) and 440 nm (formation of the new band), and time-resolved absorption spectra ([TMB] = 0.67 M in MeCN), respectively. The formation rate of the absorption at 440 nm (3.5×10^5 s $^{-1}$) agrees with the decay rate of BCC (2.6×10^5 s $^{-1}$). Thus, the new band is assigned to the NY formed by the addition of BCC to TMB, as shown in eqn. (5).



Effects of addition of nitrile compounds on rate constants

In the reaction of carbenes with ethers, the formation of oxonium ylides (OY) has been studied by measuring the rate constants of the typical carbene reactions, because the absorption spectra of OY cannot be measured.¹⁰ Because the absorption spectrum of NY seems to overlap with that of BCC, the formation and reactivity of NY were studied by analyzing the

Table 1 Rate constants ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) of the reactions of BCC with TME, MF and pyridine^a

Solvent	TME			MF			pyridine		
	$k/10^7$	$k'/10^{7b}$	Ratio ^c	k	$k'/10^{6b}$	Ratio ^c	$k/10^8$	$k'/10^{8b}$	Ratio ^c
i-Oc	18.3	—	1.00	1.50×10^7	—	1.00	8.24	—	1.00
MeCN	6.75	4.8	0.26	2.20×10^6	1.6	0.11	2.95	2.1	0.26
EtCN	5.55	5.0	0.27	2.32×10^6	2.1	0.14	2.75	2.5	0.30
i-PrCN	6.15	6.3	0.34	2.53×10^6	2.6	0.17	2.65	2.7	0.33
t-BuCN	6.30	8.4	0.46	3.05×10^6	4.1	0.27	2.41	3.2	0.39
ClMeCN	2.47	2.6	0.14	9.50×10^5	1.0	0.07	1.11	1.2	0.14

^a Measured at 295 K. ^b Value corrected by means of solvent viscosity. ^c $k'_{\text{RCN}}/k_{\text{i-Oc}}$.

typical reactions of a singlet carbene BCC in the presence of nitrile compounds (RCN) [reactions with 2,3-dimethylbut-2-ene (TME, an electron-rich olefin), dimethyl fumarate (MF, an electron-deficient olefin) and pyridine (Py)]. MeCN, propionitrile (EtCN), methylpropionitrile (i-PrCN) and dimethylpropionitrile (t-BuCN) were used as the nitrile solvents, because there are no big differences in their viscosities. Chloroacetonitrile (ClMeCN), which has an electron-withdrawing alkyl group, was also used as a solvent. The decay profiles of the transient absorption obeyed pseudo-first order kinetics. The measured decay rates were independent of the monitored wavelengths. Rate constants (k values) of the reaction were determined from the slope of the linear plots of the decay rate *versus* scavenger concentration, and are listed in Table 1.

Barcus *et al.* reported that the rate constant for the reaction of NY formed from NC and MeCN with an electron-deficient olefin is substantially larger than the k value of the reaction of the same NY with TME.^{2b} Griller *et al.* reported similar results for the reaction of NY formed from FC and MeCN,^{4b} and we have also reported that NYa, yielded from 3-(biphenyl-4-yl)-2H-azirine, reacts well with electron-deficient olefins ($k \sim 10^6$ – $10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) but not with electron-rich olefins such as TME.^{12a} The logarithmic rate constant ($\log k$) increased linearly with increasing ionization potential of the olefin^{12a} or carbonyl compound.^{12b} If BCC forms a NY in a nitrile solvent, a larger k value is expected in the reaction with the electron-deficient olefin MF. The determined rate constants for the reaction in i-Oc ($k_{\text{i-Oc}}$), however, were the maximum even in the reaction with MF.

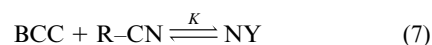
Because it is well-known that the rate constant depends on the diffusion constant, the k values in nitrile solvents (k_{RCN}) were corrected for the difference in viscosity relative to the rate constants measured in i-Oc by means of eqn. (6) (corrected value

$$k'_{\text{RCN}} = (\eta_{\text{RCN}}/\eta_{\text{i-Oc}}) k_{\text{RCN}} \quad (6)$$

k'_{RCN}), where the symbols η_{RCN} and $\eta_{\text{i-Oc}}$ are the viscosities of the nitrile solvent and i-Oc¹³ ($\eta_{\text{i-Oc}} = 5.04 \times 10^{-1} \text{ g m}^{-1} \text{ s}^{-1}$). In any reaction, the k'_{RCN} value in ClMeCN was the minimum, and it increased in other solvents as follows; ClMeCN < MeCN < EtCN < i-PrCN < t-BuCN. The ratios $k'_{\text{RCN}}/k_{\text{i-Oc}}$ are also listed in Table 1 to show the effect of the alkyl groups. The ratio for the reaction with MF is lower than that for the reaction with TME in each nitrile solvent. The ratio for the reaction with pyridine was similar to that for the reaction with TME in each nitrile solvent. Jones *et al.* reported the effect of the solvent relative permittivity on the rate constants for the reaction of phenylchlorocarbene (PCC) with pyridine to be small^{14a} and with trichloroacetonitrile to be large.^{14b} BCC produced NY with MeCN in a 10 K argon matrix.¹¹ They are convinced that some solvents react with a singlet carbene, even if the transient signals are undetectable. Thus, it is concluded that the NY formed by the addition of BCC to a nitrile solvent, hardly reacts with olefins and pyridine and that the ylide can be most effectively formed in ClMeCN.

Because NY absorbs light in the same wavelength range as that of BCC, the measured rate constant depends on the concentration of free BCC. The ratio of rate constants ($k_{\text{RCN}}/k_{\text{i-Oc}}$) is assumed to be a parameter of the fraction of BCC ($f = [\text{BCC}]/([\text{BCC}] + [\text{NY}])$). Thus, the fraction of NY ($1 - f$) increased as follows, t-BuCN < i-PrCN < EtCN < MeCN < ClMeCN. There are two probable effects of the solvent alkyl group on the determination of the NY ratio, *i.e.* the inductive and steric effects. When we compare the order of the steric parameters¹⁵ with that of the f value, it is easily concluded that the steric effect is not a dominant factor determining the NY ratio. On the other hand, the order of the f value agreed with that of Taft's σ^* value for the solvent alkyl group.¹⁵ It is concluded that the formation rate of NY increases with increasing inductive effect of the solvent alkyl groups, because this effect increases the electron density on the nitrogen atom. The fraction of NY, however, decreased with the decreasing inductive effect of the alkyl groups. IR bands of the BCC–MeCN NY in an argon matrix at 10 K indicate that NY assumes the heterocumulene structure shown in Fig. 1.¹⁰ With nitrile compounds which contain more electron-withdrawing alkyl groups in the nitrile compounds, there is greater stabilization of the negative charge on NY thus favoring the heterocumulene structure. Thus, it is concluded that the of NY increases with decreasing electron-donating inductive effect of the alkyl group of the solvent.

Jones *et al.* studied the pyridinium ylide (PY) formation reaction of PCC in the presence of trichloroacetonitrile.^{14b} The formation rate of PY increased even with increasing trichloroacetonitrile concentration, reflecting the PCC decay rate. NY hardly reacts with TME.¹⁶ When BCC is in equilibrium with NY in the reaction of FC with MeCN, the formation rate and the decay rate of NY must be accelerated by the addition of TME. The addition effects of TME on the formation and decay rates of BCC–TMB NY were also studied in MeCN ([TMB] = $0.714 \text{ mol dm}^{-3}$). The decay rate of BCC and the formation rate of the NY increased with increasing TME concentration, which strongly suggests that the NY is in equilibrium with BCC and TMB. Indeed, the rate constant determined by means of the NY formation rate ($7.6 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $\lambda_{\text{moni.}} = 440 \text{ nm}$) agreed roughly with the value determined by means of the BCC decay rate ($5.58 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $\lambda_{\text{moni.}} = 380 \text{ nm}$). Because the formation of NY depends on the concentration of free BCC, the formation rate of NY must reflect the concentration of TME. In MeCN, the photo-reactions of BCD with TME yielded neither azirines nor pyrroles which were products from NY.¹⁶ It is concluded that there is an equilibrium reaction between BCC and NY, as shown in eqn. (7).



In a constant viscosity solvent, the equilibrium constant (K) of eqn. (7) depends on the dissociation rate constant of NY because the formation rate constant of NY is controlled by the solvent viscosity. In this equilibrium, the electron-withdrawing

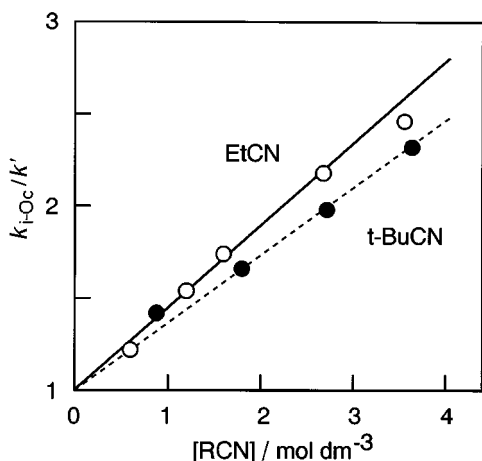


Fig. 5 Change in the ratio of the rate constants, k_{i-Oc}/k' , with RCN concentration. The LFP of BCD in the presence of TME was carried out at 295 K with EtCN (○) or t-BuCN (●) in i-Oc solution (every 5 TME concentrations for each solvent mixture). $[BCD] = ca. 6 \times 10^{-4} \text{ mol dm}^{-3}$.

alkyl groups of the solvent will decrease the dissociation rate constant of NY due to the stabilization of negative charge. However, although the NY decay rate seemed to increase slightly with the addition of TME, the rate constant could not be determined.

Effects of addition of nitrile compounds on the reaction of BCC with TME

The free BCC concentration depends on the concentration of RCN. Using EtCN and t-BuCN as typical nitrile compounds, the effect of addition of RCN on the reaction of BCC with TME was studied in i-Oc.¹⁷ The rate constants were found to decrease with increasing nitrile concentration. In the presence of RCN, the measured rate constant (k') must be proportional to free BCC concentration, because the reaction of NY with TME is negligible.¹⁶ The fraction of BCC [$f = [BCC]/([BCC] + [NY])$] can be obtained using the equilibrium constant K obtained from $f = (1 + K[RCN])^{-1}$. Thus, the k' value can be expressed using the k value in i-Oc (k_{i-Oc}) and the K value, as shown in eqn. (8).

$$k' = f k_{i-Oc} = (1 + K[RCN])^{-1} k_{i-Oc} \quad (8)$$

When the ratios of the rate constants in the absence and in the presence of RCN (k_{i-Oc}/k') are plotted against RCN concentration, good linear relationships were obtained, as shown in Fig. 5. The K values were determined to be 0.45 M^{-1} (EtCN) and 0.36 M^{-1} (t-BuCN) from the slopes of the plots. These K values also support the belief that the fraction of NY increases with the decreasing electron-donating inductive effect of the alkyl group of RCN.

Effects of temperature on the reaction of carbene with TME

The reaction of BCC with TME is one of the most typical reactions of a singlet carbene. The effect of temperature on the NY formation was studied by comparison of the reaction rate constants in EtCN with those in i-Oc. Fig. 6 shows Arrhenius plots of the reaction of BCC with TME in both solvents. The rate constants increased with decreasing temperature. The maximum rate constants were measured at around 210 K. Below 210 K, the rate constants decreased with decreasing temperature. Arrhenius activation energies (E_a) in i-Oc were determined to be $ca. -6.3 \text{ kJ mol}^{-1}$ ($ca. -5.9 \text{ kJ mol}^{-1}$ in EtCN) for the temperature range from 210 to 297 K and 4.2 kJ mol^{-1} for the range from 179 to 210 K. Liu and Subramanian reported the E_a value of the reaction of benzylbromocarbene with TME in i-Oc to be -6.3 kJ mol^{-1} in the temperature range from 275 to 374 K.¹⁸

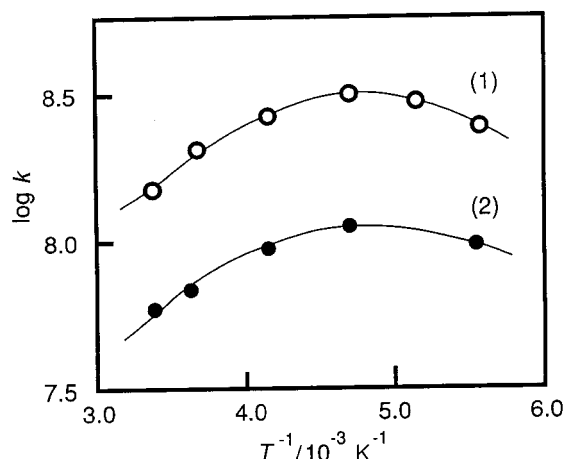


Fig. 6 Arrhenius plots for the reaction of BCC with TME in i-Oc (1) and in EtCN (2).

Moss *et al.* reported the E_a values of the reactions of phenylhalocarbenes with TME in i-Oc, e.g., for PCC: -7.1 kJ mol^{-1} (263–310 K) and 3.3 kJ mol^{-1} (200–250 K).¹⁹ Our determined E_a values for BCC agree well with the reported values.

Turro *et al.* reported that the addition of a carbene to an olefin proceeds by way of a carbene–olefin complex intermediate.^{8,19,20} They proposed that a part of the complex yields the product and another part dissociates to carbene and olefin, as shown in eqn. (9), where k_1 , k_{-1} and k_2 are the rate constants for



complex formation, dissociation of the complex and product formation, respectively. The overall rate constant k was defined as shown below in eqn. (10).

$$k = k_1 k_2 / (k_{-1} + k_2) \quad (10)$$

When the k_1 value is equal to the diffusion constant, the ratio of the rate constants, k_{-1}/k_2 , was calculated $[(k_1 - k)/k]$. When the logarithmic ratio of the rate constants $[\log(k_{-1}/k_2)]$ was plotted against the reciprocal temperature (T^{-1}), a good linear relationship was obtained in the reaction in i-Oc, as shown in Fig. 7. From the slope of the linear relation, the thermodynamic parameters, $\Delta\Delta G^\ddagger$ ($=\Delta G^\ddagger_{\text{product}} - \Delta G^\ddagger_{\text{dissociation}}$), $\Delta\Delta H^\ddagger$, and $\Delta\Delta S^\ddagger$, were determined to be 15.9 kJ mol^{-1} , $-12.6 \text{ kJ mol}^{-1}$ and $-96 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. These parameters agreed well with the reported values for the reactions of PCC with TME ($\Delta\Delta G^\ddagger = 9.2 \text{ kJ mol}^{-1}$, $\Delta\Delta H^\ddagger = -18.4 \text{ kJ mol}^{-1}$, and $\Delta\Delta S^\ddagger = -96 \text{ J K}^{-1} \text{ mol}^{-1}$ in i-Oc; $\Delta\Delta G^\ddagger = 10.9 \text{ kJ mol}^{-1}$, $\Delta\Delta H^\ddagger = -14.2 \text{ kJ mol}^{-1}$, and $\Delta\Delta S^\ddagger = -84 \text{ J K}^{-1} \text{ mol}^{-1}$ in toluene, $\Delta\Delta G^\ddagger = 11.7 \text{ kJ mol}^{-1}$, $\Delta\Delta H^\ddagger = -6.7 \text{ kJ mol}^{-1}$, and $\Delta\Delta S^\ddagger = -63 \text{ J K}^{-1} \text{ mol}^{-1}$ in MeCN; temperature range: 240–300 K).⁸

Turro *et al.* also pointed out that the parameters in MeCN were rather different from the values in i-Oc and in toluene.⁸ If PCC forms NY in MeCN, the same treatments cannot be applied to the reaction in MeCN. Indeed, the plots of $\log(k_{-1}/k_2)$ vs. T^{-1} measured in EtCN were curved. This curving is ascribed to the NY formation. Because the dissociation of the complex and product formation are unimolecular reactions, a linear relationship can be expected to exist for the plots determined in the nitrile solvent with the slope being the same as that in i-Oc. Substituting eqn. (10) into eqn. (8) gives eqn. (11).

$$k' = f k_1 k_2 / (k_{-1} + k_2) \quad (11)$$

When $k_{-1} \gg k_2$, the logarithmic ratio of the rate constants, $\log(k_{-1}/k_2)$, is the sum of $\log(k_1/k')$ and $\log f$. Thus, the vertical

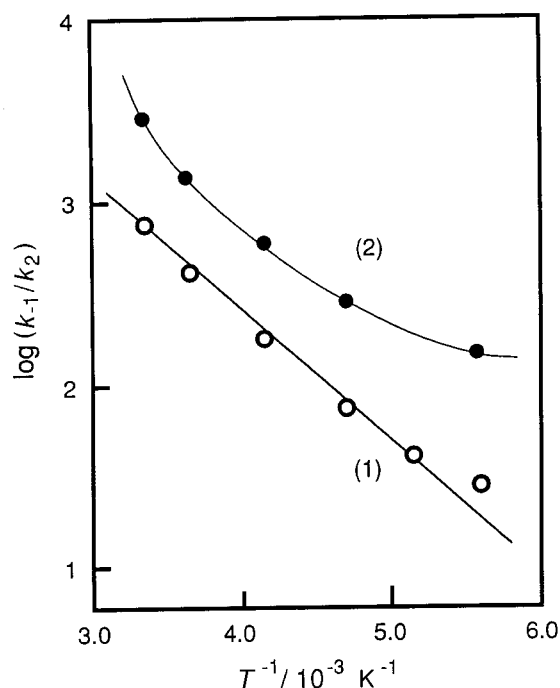


Fig. 7 Plots of $\log(k_{-1}/k_2)$ vs. T^{-1} in i-Oc (1) and in EtCN (2).

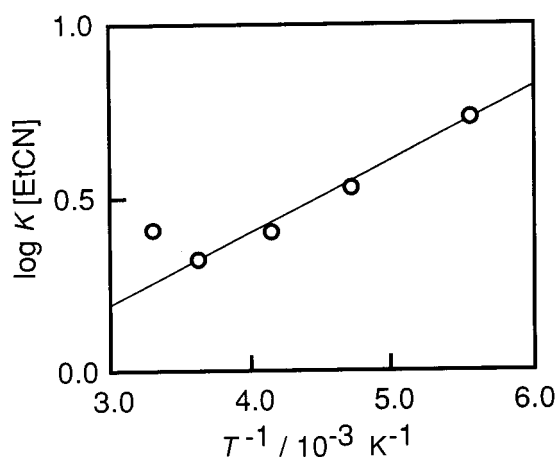


Fig. 8 Plot of $\log K[\text{EtCN}]$ vs. T^{-1} .

axis in Fig. 8 must be the term of $[\log(k_{-1}/k_2) - \log f]$ and the difference in the two relationships is $\log f$. The fraction of BCC, f , changes with temperature. Because LFP in EtCN was carried out at different temperatures from those in i-Oc, the $\log f$ value was obtained by means of the difference between the ratio of the rate constants k_{-1}/k_2 in EtCN and the ratio determined by means of the relation in i-Oc. The molar ratio, $[\text{NY}]/[\text{BCC}] (=K[\text{EtCN}])$, was calculated from $\log f$ value at each temperature. When the term, $\log(K[\text{EtCN}])$, was plotted against T^{-1} , a good linear dependence was obtained as shown in Fig. 8. Because the EtCN concentration was constant in the present study, the K value must increase with decreasing temperature. The ΔH value derived from the K value was estimated to be *ca.* $-1.0 \text{ kcal mol}^{-1}$ from the slope of the linear relation in Fig. 8. Although the thermodynamic parameter seems to be changed by the solvent properties, the determined energy depends chiefly on the free energy of the equilibrium constant.

Experimental

Materials

(Biphenyl-4-yl)chlorodiazirine (BCD) was prepared from 4-cyanobiphenyl *via* the corresponding 4-phenylbenzamide

salt (*vide infra*).¹⁰ White crystals: UV-VIS-data, $\lambda_{\text{max}} = 358 \text{ nm}$ ($\epsilon = 4.2 \times 10^3 \text{ dm}^2 \text{ mol}^{-1}$), 376 nm ($\epsilon = 6.2 \times 10^3 \text{ dm}^2 \text{ mol}^{-1}$) and 395 nm ($\epsilon = 5.2 \times 10^3 \text{ dm}^2 \text{ mol}^{-1}$) in 2,2,4-trimethylpentane (i-Oc).

Spectroscopic grade i-Oc, acetonitrile (MeCN) and pyridine were used without further purifications. Propionitrile (EtCN), 2-methylpropionitrile (i-PrCN), 2,2-dimethylpropionitrile (t-BuCN) and chloroacetonitrile (ClMeCN) were purified by refluxing five times for 10 hours over diphosphorus pentoxide. After purification, the solvents were distilled twice under N_2 stream. Benzonitrile (PhCN) was purified by distillation under reduced pressure over diphosphorus pentoxide three times. 2,3-Dimethylbut-2-ene (TME) was distilled twice over calcium hydride. Dimethyl fumarate (MF) was purified by recrystallization twice from ethanol. The viscosities of MeCN, EtCN, i-PrCN, t-BuCN, PhCN and ClMeCN were measured at 293.1 K.

Laser flash photolysis

The laser flash photolysis (LFP) of BCD was carried out using a Quanta-Ray GCR-11 (355 nm, 15 ns pulse, *ca.* 60 mJ). The concentration of BCD was *ca.* $6 \times 10^{-4} \text{ mol dm}^{-3}$.

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