

# Formation of oxonium ylide evidenced by the laser flash photolysis of (biphenyl-4-yl)chlorodiazirine in ethers

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Laser flash photolyses of (biphenyl-4-yl)chlorodiazirine (**1**) in 2,2,4-trimethylpentane were carried out in the presence of ethers in order to study the reaction intermediates formed from singlet carbenes and ethers. The transient species generated in the absence of ether showed an absorption maximum at 360 nm with a long life time ( $\tau = 24.7 \mu\text{s}$ ), which was assigned to singlet (biphenyl-4-yl)chlorocarbene (**5**). In the presence of various kinds of ethers, additional transient absorption could not be detected but the spectrum of **5** (360 nm) shifted by about 15 nm to longer wavelength. The effect of ethers added to the reaction mixture was studied by means of typical singlet carbene reactions, *i.e.* trapping by 2,3-dimethyl-2-butene or pyridine. It was found that the rate constants of these reactions decreased by the addition of ethers and, hence, it is concluded that the reaction of **5** with ethers proceeds *via* oxonium ylide intermediate **7**. By changing the concentration of tetrahydrofuran (THF), the equilibrium constant of the reaction ( $\text{5} + \text{THF} \rightleftharpoons \text{oxonium ylide}$ ) was determined to be  $0.5 \text{ dm}^3 \text{ mol}^{-1}$  at 293 K in 2,2,4-trimethylpentane (i-Oc).

Carbenes are highly reactive intermediates undergoing various interesting reactions such as addition, insertion, hydrogen-abstraction, rearrangement, *etc.* Two non-bonding electrons of free carbenes should possess one of two electron spin structures, namely, singlet and triplet states, and the reactivity of carbenes changes drastically depending on the states. Recently, electronic structures of many typical carbenes were studied in detail by using the laser flash photolysis (LFP) technique.<sup>1</sup> Among them, chloro(phenyl)carbene, known as a singlet carbene in its ground state, was reported to have an absorption maximum at 307 nm and lifetime of *ca.* 3.6  $\mu\text{s}$  in 2,2,4-trimethylpentane (i-Oc) by using a Kr-F excimer laser apparatus.<sup>2</sup> However, there are limitations in the use of this specific carbene due to its small extinction coefficient.<sup>3</sup>

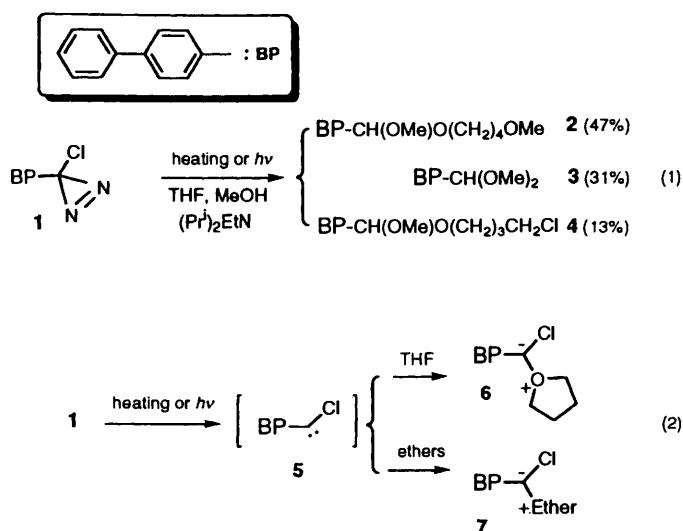
Recently, we found that the photo and thermal reactions of (biphenyl-4-yl)chlorodiazirine (**1**) in tetrahydrofuran (THF), in

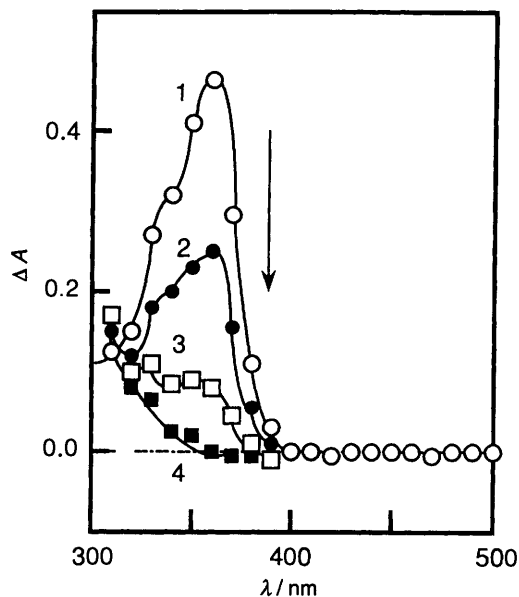
the presence of methanol and di(2-propyl)ethylamine, yielded the products **2–4** shown in eqn. (1).<sup>4</sup> Acetals **2** and **4** must be formed from the oxonium ylide intermediate **6** which was generated by the electrophilic addition of singlet carbene **5** to THF [eqn. (2)]. Kirmse<sup>5</sup> and Barcus *et al.*<sup>6</sup> also predicted the intervention of a similar ylide but they did not present any experimental evidence for it. In this regard, we studied the LFP of **1** in the presence of ethers to obtain unambiguous experimental evidence for this transient species.

## Results and discussion

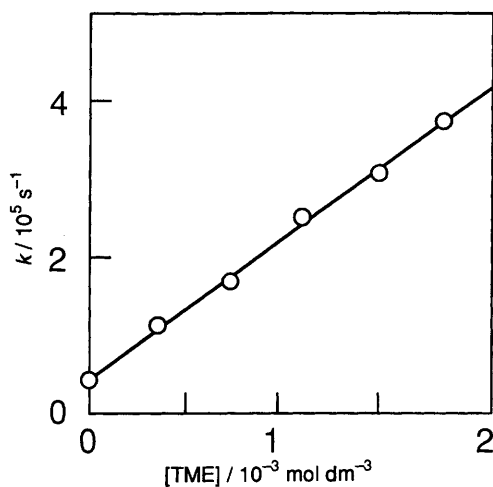
### Laser flash photolysis of (biphenyl-4-yl)chlorodiazirine

Laser flash photolyses (LFPs) of (biphenyl-4-yl)chlorodiazirine (**1**,  $\lambda_{\text{max}} = 360 \text{ nm}$ ) were carried out at room temperature in 2,2,4-trimethylpentane (i-Oc) by using a YAG laser (355 nm)





**Fig. 1** Time-resolved transient absorption spectra measured at 0.08  $\mu\text{s}$  (1), 4.9  $\mu\text{s}$  (2), 14.3  $\mu\text{s}$  (3) and 39.6  $\mu\text{s}$  (4) after the flash in the LFP of **1** in *i*-Oc.  $[\mathbf{1}] = 6 \times 10^{-4} \text{ mol dm}^{-3}$



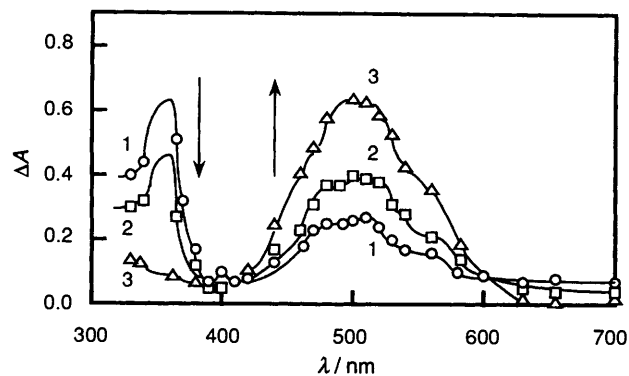
**Fig. 2** Plots of the decay rate of **5** vs. TME concentration in *i*-Oc

and Xe-Cl excimer laser apparatus (308 nm). Fig. 1 shows time-resolved absorption spectra measured in the 355 nm laser flash photolysis of **1**. The spectrum measured at 80 ns after the flash has the absorption maximum at 360 nm. The decay profile of the transient absorption obeys first order kinetics ( $4.03 \times 10^4 \text{ s}^{-1}$ ). The decay rate was independent of the monitored wavelengths, indicating that only one transient species was detected. Because the absorption maximum and decay rate of the transient species measured in the 308 nm LFP agreed well with those in the 355 nm LFP, the following studies were carried out by using a YAG laser.

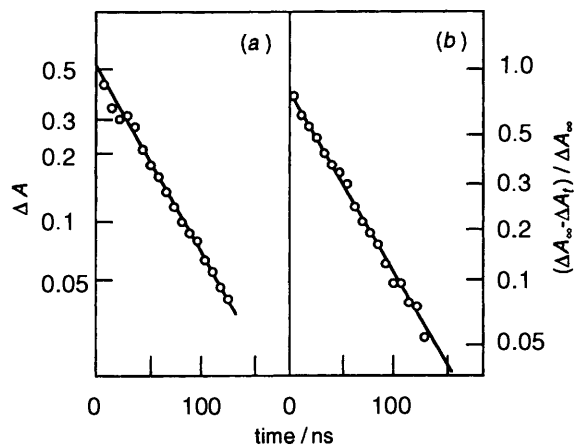
2,3-Dimethylbut-2-ene (TME) is known as a typical singlet carbene scavenger to yield cyclopropane compounds [eqn. (3)].



When the LFP of **1** was carried out in the presence of TME, the decay rate of the transient species increased with increasing TME concentration. Fig. 2 shows the plots of the decay rate



**Fig. 3** Time-resolved absorption spectra measured at 20 ns (1), 55 ns (2) and 396 ns (3) after the flash in the LFP of **1** ( $6 \times 10^{-4} \text{ mol dm}^{-3}$ ) in the presence of pyridine ( $2.47 \times 10^{-2} \text{ mol dm}^{-3}$ ) in *i*-Oc

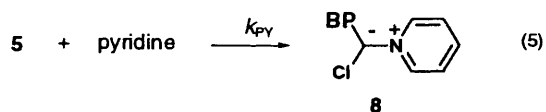
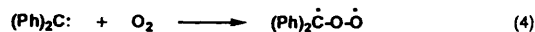


**Fig. 4** First order plots of the decay of the transient absorption measured at 365 nm (a) and the formation of absorption at 500 nm in the LFP of **1** ( $6 \times 10^{-4} \text{ mol dm}^{-3}$ ) in the presence of pyridine ( $2.47 \times 10^{-2} \text{ mol dm}^{-3}$ ) in *i*-Oc

against TME concentration. The decay rate constant  $k$  of the transient species with TME was determined to be  $1.83 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  from the slope of the linear relation in Fig. 2. This value is roughly in agreement with those reported for the reaction with TME of singlet fluoro(phenyl)carbene ( $1.6 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ),<sup>7</sup> chloro(phenyl)carbene ( $1.3 \times 10^8$  and  $3.3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ),<sup>8,2</sup> but not with the  $k$  value for triplet diphenylcarbene ( $2.1 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  in cyclohexane).<sup>9</sup>

Scaiano and co-workers<sup>10,11</sup> reported that a triplet carbene reacts with an oxygen molecule to yield a carbonyl oxide biradical, as shown in eqn. (4), and the absorption maximum of the biradical (benzophenone oxide) appears around 410 nm. However, when we carried out the LFP of **1** in oxygen-saturated *i*-Oc, no additional absorption other than at 360 nm was detected. This result strongly indicates that the transient species measured is a singlet carbene.

Platz and co-workers<sup>8</sup> reported that the reactions of singlet carbenes with pyridine form pyridinium ylides **8** [eqn. (5)], which show an absorption maximum around 500 nm [480 nm



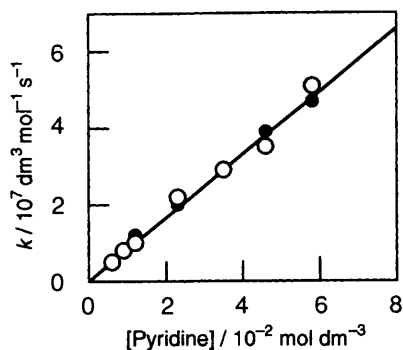


Fig. 5 Plots of the decay rates of **5** (○) and the formation rates of **8** (●) vs. pyridine concentration. Rates were measured by means of oscilloscope traces monitored at 365 and 500 nm, respectively.

Table 1 Effect of ethers on the reaction of singlet carbene **5** with 2,3-dimethylbut-2-ene (TME)

Additive	$c/\text{mol dm}^{-3}$	$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$k/k_0^a$	Solvent
None	0.00	$1.83 \times 10^8$	1.00	i-Oc
THF	0.49	$1.43 \times 10^8$	0.78	i-Oc
Dioxane	0.50	$1.56 \times 10^8$	0.85	i-Oc
Et <sub>2</sub> O	0.50	$1.59 \times 10^8$	0.87	i-Oc
MeOBu <sup>t</sup>	0.50	$1.35 \times 10^8$	0.74	i-Oc
MeO[CH <sub>2</sub> ] <sub>2</sub> OMe	0.50	$1.56 \times 10^8$	0.85	i-Oc
PhOMe	0.50	$1.59 \times 10^8$	0.87	i-Oc
1,3-Dioxazoline	0.50	$1.39 \times 10^8$	0.76	i-Oc
THF	—	$6.70 \times 10^7$	0.37	THF

<sup>a</sup> Relative rate on the basis of  $k_{\text{none}} = k_0$  ( $1.83 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ).

for the pyridinium ylide of chloro(phenyl)carbene]. Fig. 3 shows time-resolved absorption spectra measured in the LFP of **1** in the presence of pyridine ( $2.47 \times 10^{-2} \text{ mol dm}^{-3}$ ). A new absorption maximum at 500 nm, which was assigned to pyridinium ylide **8**, increased with the decrease in the transient absorption at 365 nm. Fig. 4 shows first order plots of oscilloscope traces monitored around 365 nm (for the decay of the transient species) and 500 nm (for the formation of **8**). Ylide **8** seems to be considerably more stable compared with singlet carbene. The decay rate ( $2.2 \times 10^7 \text{ s}^{-1}$ ) completely agrees with the formation rate of **8** ( $2.1 \times 10^7 \text{ s}^{-1}$ ) and hence it is concluded that the transient species, which reacts with pyridine to yield **8** quantitatively, is assigned to singlet carbene **5**. The rate constant for ylide formation ( $k_{\text{PY}}$ ) was determined to be  $8.24 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  by means of the linear plots of formation rates vs. pyridine concentration as shown in Fig. 5. The same rate constant was obtained from the slope of linear plots of the decay rate of **5** vs. pyridine concentration. The determined  $k_{\text{PY}}$  value agrees roughly with that reported for singlet chloro(phenyl)carbene [ $k_{\text{PY}} = (3.35 \pm 0.29) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ]<sup>8</sup> but it is larger than the one for triplet 1-phenylethylidene [ $2.0 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ].<sup>12</sup> These results clearly indicate that the transient species measured in the LFP of **1** is singlet carbene **5**. Because **5** has an absorption maximum at 365 nm in i-Oc and also lives for 24.7 μs, it is a useful reaction intermediate for spectroscopic studies on the reaction behaviour of singlet carbene with ethers.

#### Reaction of singlet carbene **5** with ether

To verify the intermediacy of oxonium ylide **6**, LFP of **1** was carried out in THF. The observed spectrum seems to be the same as that of **5** in i-Oc (360 nm), although the absorption maximum shifted to 375 nm, and the decay rate for the transient species was determined to be  $5.08 \times 10^4 \text{ s}^{-1}$ . Although several LFPs of **1** were carried out in the presence of various types of ethers (THF, 1,4-dioxane, diethyl ether, dibenzofuran, methyl 2,2-dimethylethyl ether, 1,2-dimethoxyethane, methoxybenzene, diphenyl ether, cyclohexene oxide, trimethylene oxide,

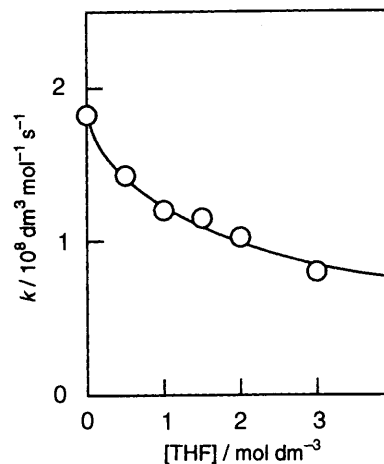


Fig. 6 Plots of the reaction rate constant  $k$  of **5** with TME vs. THF concentration

1,3-dioxolane), the transient spectra were similar to those taken in i-Oc but new absorption maxima were not observed. Thus, spectrometric direct observation of oxonium ylide **6** seemed difficult. Therefore, the presence of **6** was investigated indirectly by means of kinetic studies.

**1. Effect of ether addition on the reaction of **5** with olefin.** 2,3-Dimethyl-2-butene (TME) is one of the typical carbene scavengers to yield a cyclopropane compound. The rate constant  $k$  for the reaction of singlet carbene **5** with TME is expected to decrease by the formation of oxonium ylide **7** in the presence of ether [eqn. (2)]. In this expectation, rate constants  $k$  for the reaction of **5** with TME in the presence of ethers ( $0.5 \text{ mol dm}^{-3}$ ) were measured in the LFP of diazirine **1** (Table 1). The  $k$  values were not measured in the presence of cyclohexene oxide,<sup>13</sup> trimethylene oxide, or furan, because the lifetimes of **5** were shorter than 500 ns. In the presence of other ethers,  $k$  decreased in the order of none > methoxybenzene ≈ diethyl ether > dioxane ≈ 1,2-dimethoxyethane > THF > *tert*-butyl methyl ether. In the presence of *tert*-butyl methyl ether  $k$  is only 70% of the one without ethers.

To investigate the effect of ethers, the rate constants  $k$  were measured at various THF concentrations (Fig. 6). The  $k$  decreased with the increase of THF concentration, e.g.,  $k = 8.0 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at  $[\text{THF}] = 3.0 \text{ mol dm}^{-3}$ , and  $6.7 \times 10^7$  in pure THF. Because the difference in diffusion constants of carbene **5** in i-Oc and THF is assumed to be small based on the solvent viscosity [ $\eta \approx 5.04 \times 10^{-4} \text{ Pas}$  (cyclohexane) and  $5.75 \times 10^{-4} \text{ Pas}$  (THF), respectively, at 297 K],<sup>14</sup>  $k$  in THF can be roughly estimated to be only one-third of that in i-Oc. The reason for causing such a decrease in the rate constant is most reasonably ascribed to the intermediacy of oxonium ylide **6**, which is in equilibrium with **5**.

Because carbene **5** is reported to be a strong electrophile,<sup>15</sup> rate constants for the reaction with various olefins must decrease with the increase in ionization potential ( $E_i$ ) of olefins, a parameter of electron density of double bonds. In this regard, rate constants  $k$  for the reactions of **5** with various olefins were measured in the absence or presence of THF ( $2.0 \text{ mol dm}^{-3}$ ) ( $E_i$  of olefins: dimethyl fumarate 11.00 eV,<sup>16</sup> acrylonitrile 10.91 eV,<sup>17</sup> methyl methacrylate 10.53 eV,<sup>16</sup> methacrylonitrile 10.37 eV<sup>17</sup>). Results are listed in Table 2. Although the measured  $k$  may partly consist of a fraction of other reactions such as with carbonyl and cyano groups of olefins [eqn. (6), where  $k_{\text{olefin}}$  and  $k_{\text{substituent}}$  are

$$k = k_{\text{olefin}} + \sum k_{\text{substituent}} \quad (6)$$

the rate constant for the reaction of **5** with olefin and substituent, respectively], they mainly consist of that with olefin. In the absence of ether,  $k$  decreased as the  $E_i$  increased, showing

**Table 2** Rate constants for the reaction of **5** with olefins<sup>a</sup>

Olefin	$E_i/eV^b$	Rate constant/dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>		
		$k_0$	$k$	$k/k_0$
Dimethyl fumarate	11.00 <sup>16</sup>	$1.50 \times 10^7$	$4.6 \times 10^6$	0.31
Acrylonitrile	10.91 <sup>17</sup>	$2.06 \times 10^7$	$6.0 \times 10^6$	0.29
Methyl methacrylate	10.57 <sup>16</sup>	$3.3 \times 10^7$	$2.7 \times 10^7$	0.82
Methacrylonitrile	10.37 <sup>17</sup>	$4.4 \times 10^7$	$2.6 \times 10^7$	0.65
2,3-Dimethylbut-2-ene	8.30 <sup>18</sup>	$1.83 \times 10^8$	$1.03 \times 10^8$	0.56

<sup>a</sup> Values  $k$  and  $k_0$  are the rate constants in the presence of THF (2.0 mol dm<sup>-3</sup>) and in its absence, respectively. <sup>b</sup> Numerical superscripts are reference numbers.

**Table 3** Rate constants for the formation of pyridinium ylide (**8**) in the presence of ethers

Additive <sup>a</sup>	$k_{PY}/dm^3$ mol <sup>-1</sup> s <sup>-1</sup>	$k_{PY}/k_{PY_0}$ <sup>b</sup>	Solvent
None	$8.24 \times 10^8$	1.00	i-Oc
THF	$5.80 \times 10^8$	0.70	i-Oc
Dioxane	$5.58 \times 10^8$	0.68	i-Oc
Et <sub>2</sub> O	$6.68 \times 10^8$	0.81	i-Oc
MeO'Bu	$6.92 \times 10^8$	0.84	i-Oc
MeOCH <sub>2</sub> CH <sub>2</sub> OMe	$6.92 \times 10^8$	0.84	i-Oc
THF	$4.06 \times 10^7$	0.49	THF

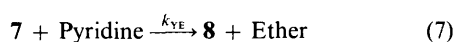
<sup>a</sup> Concentration of additive (ethers) in i-Oc was 2.0 mol dm<sup>-3</sup> unless the ether was used as solvent. <sup>b</sup>  $k_{PY}$  and  $k_{PY_0}$  ( $8.24 \times 10^8$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) are the rate constants in the presence or absence of ether, respectively.

that the addition of **5** to olefin is electrophilic. In the presence of THF, its effect on  $k$  became larger as the  $E_i$  of the olefin increases. The change in the values of  $k/k_0$  (Table 2) can be rationally explained, again, in terms of the formation of oxonium ylide **7**.

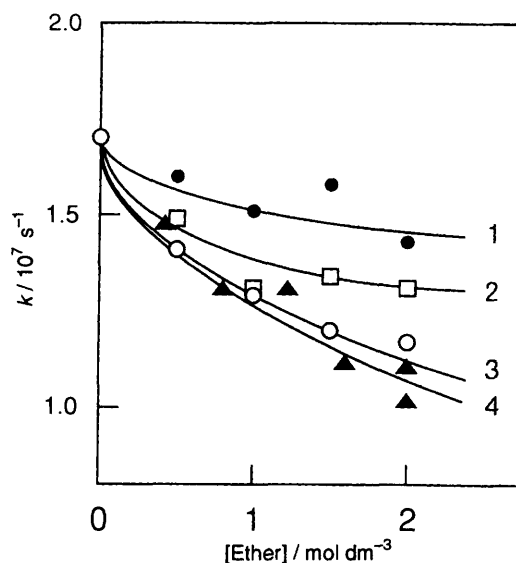
**2. Effect of ethers on pyridinium ylide formation.** Formation of pyridinium ylides in the reaction of singlet carbenes with pyridine has been well elucidated.<sup>8</sup> If the singlet carbene **5** forms oxonium ylide **7** in the mixture of pyridine and an ether, the rate constant  $k_{PY}$  for the formation of pyridinium ylide **8** is expected to decrease in a similar manner to that observed in the reaction of **5** with TME. In this expectation, the rate constants  $k_{PY}$  were measured in the presence of various types of ethers (concentrations of ether 2.00 mol dm<sup>-3</sup>) (Table 3). In fact, the constants decreased in the following order: none > 1,2-dimethoxyethane  $\approx$  *tert*-butyl methyl ether > diethyl ether > THF > dioxane, and this order is almost the same to that observed in the reaction with TME.

The effect of ether was studied further by measuring the rates of pyridinium ylide formation (not the rate constant) at a constant pyridine concentration ( $2.03 \times 10^{-2}$  mol dm<sup>-3</sup>). The rates decreased with the increase in ether concentration (Fig. 7) and, again, it can be concluded that the  $k_{PY}$  is decreased by the formation of oxonium ylide.

The ratios of rate constants  $k_{PY}/k_{PY_0}$  ( $k_{PY_0}$ : rate constant in the absence of ether,  $8.24 \times 10^8$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) are somewhat smaller, on average, than those for the reaction with TME (Table 1). The ratio  $k/k_0$  is, however, as small as 0.56 at [THF] = 2.0 mol dm<sup>-3</sup>. The difference in  $k_{PY}/k_{PY_0}$  (Table 3) can be explained in terms of ylide exchange reaction between **7** and pyridine, as shown in eqn. (7), and the rate constant for the

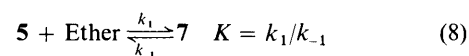


exchange reactions ( $k_{YE}$ ) can be estimated roughly to be  $(2-3) \times 10^8$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> based on the difference in  $k/k_0$  ratio obtained in the presence of THF. Every oxonium ylide **6** or **7** must react with pyridine to yield **8** via a ylide exchange reaction.



**Fig. 7** Rates of pyridinium ylide formation vs. concentration of several different ethers [*tert*-butyl methyl ether (1), diethyl ether (2), THF (3), 1,2-dimethoxyethane (4)] under a constant pyridine concentration ( $2.03 \times 10^{-2}$  mol dm<sup>-3</sup>) in i-Oc

**3. Formation of oxonium ylide.** In the preceding sections, transient formation of oxonium ylides in the reaction of carbene **5** with ethers was proven clearly by examining the effect of ethers on the  $k$  values for the reaction with TME or pyridine. The reaction seems to be reversible as shown in eqn. (8) where  $k_1$



and  $k_{-1}$  are the rate constants for oxonium ylide formation and its dissociation, respectively. If the reaction establishes a fast equilibrium, a steady state treatment can be applied. Since the difference between lifetime of **5** in i-Oc and that of **6** in THF is small, the concentration of **5** can be calculated according to eqn. (9), where  $K$  is the equilibrium constant ( $K = k_1/k_{-1}$ ) and  $[5]_0$

$$[5] = [5]_0 / (K[\text{Ether}] + 1) \quad (9)$$

and  $[5]$  are the concentrations of carbene **5** obtained from the normal flash photolysis in the absence and presence of ether, respectively.

There was no appreciable difference in the transient optical density between **5** in i-Oc and oxonium ylide **6** in THF. Because oxonium ylides are assumed not to react with TME, the measured rate constants  $k$  in the presence of an ether can be expressed in the formula eqn. (10), where  $k_0$  is the rate constant

$$k = k_0 / (K[\text{Ether}] + 1) \quad (10)$$

for the reaction of **5** with TME ( $= 1.83 \times 10^8$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) in the absence of ether. Thus, the constant  $K$  for THF was calculated to be  $(0.5 \pm 0.1)$  dm<sup>3</sup> mol<sup>-1</sup> based on the plotting in Fig. 6.

## Experimental

### Materials

(Biphenyl-4-yl)chlorodiazirine **1** was prepared from 4-cyanobiphenyl via the corresponding amidine hydrochloride salt (*vide infra*).<sup>19</sup> White crystals;  $\lambda_{max} = 358$  nm ( $\epsilon = 4.2 \times 10^3$  dm<sup>2</sup> mol<sup>-1</sup>), 376 nm ( $6.2 \times 10^3$  dm<sup>2</sup> mol<sup>-1</sup>) and 395 nm ( $5.2 \times 10^3$  dm<sup>2</sup> mol<sup>-1</sup>) in 2,2,4-trimethylpentane (i-Oc). Spectroscopic grade i-Oc, diethyl ether, tetrahydrofuran, 1,4-dioxane and pyridine were used without further purification. Other ethers

were dried over calcium hydride and distilled twice before use.

#### Laser flash photolysis

The laser flash photolyses (LFPs) of **1** were carried out in *i*-Oc using a Quanta-Ray GCR-11 (355 nm, 15 ns pulse) or a Lumonics Excimer 500 (308 nm, *ca.* 20 ns pulse). The concentrations of **1** in *i*-Oc were  $6 \times 10^{-4}$  mol dm<sup>-3</sup> for the irradiation at 355 nm and  $1 \times 10^{-3}$  mol dm<sup>-3</sup> at 308 nm.

#### Product analysis

Photolysis products **2**, **3** and **4**, formed in the reaction of **1** in THF in the presence of MeOH under irradiation with a high-pressure Hg lamp, were separated from the reaction mixture and their structures were confirmed by <sup>1</sup>H NMR spectral analysis. Spectral data will be reported shortly in a separate report.

The irradiated reaction of **1** with 2,3-dimethylbut-2-ene (TME) in *i*-Oc produced an addition product 1-(biphenyl-4-yl)-1-chloro-2,2,3,3-tetramethylcyclopropane (isolated yield: 86%),  $\delta$  0.98 (6 H, s), 1.28 (6 H, s) and 7.2–7.7 (9 H, m, BP).

#### References

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