

## New mechanisms centered on reactive intermediates: Examples from diazirine and carbene chemistry\*

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**Abstract:** Laser flash photolysis (LFP) of appropriate diazirine precursors afforded the UV spectra of methylchlorocarbene, benzylchlorocarbene, cyclopropylchlorocarbene, and 1-adamantylchlorocarbene. The  $\sigma \rightarrow p$  transitions of these carbenes were used to directly monitor their reaction kinetics. The unusual and highly reactive  $N_2CO$  compound, diazirinone, was obtained from the reaction of fluoride ion with *p*-nitrophenoxychlorodiazirine. Diazirinone fragmented to CO and  $N_2$  in a reaction that was exothermic by >90 kcal/mol. Dichlorodiazirine (DCD) was generated by the reaction of chloride ion with *p*-nitrophenoxychlorodiazirine. Reactions of dichlorocarbene generated from DCD are discussed.

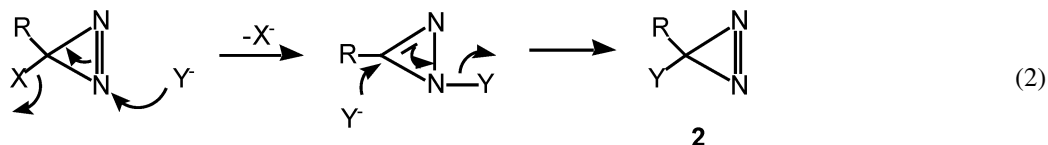
**Keywords:** diazirines; carbenes; diazirinone; dichlorodiazirine.

### INTRODUCTION

Halodiazirines **1** are ideal precursors for spectroscopic and mechanistic studies of carbenes [1]. The diazirines can be conveniently produced by Graham oxidations of amidines with NaOCl (or NaOBr); eq. 1 [2]. Here, X can be Cl or Br, while R includes alkyl, aryl, vinyl, alkoxy, and aryloxy groups.



The halodiazirine products of the Graham reaction provide access to many halocarbenes, and, given their nitrogen leaving group, they constitute spectroscopy-friendly precursors [3]. Moreover, the synthetic reach of the Graham reaction can be greatly extended by coupling it with the diazirine exchange reaction, where a nucleophile ( $Y^-$ ) displaces diazirine substituent X via a double  $S_N2'$  mechanism; eq. 2 [4,5]. In the new diazirine (**2**), Y can be alkoxide, aryloxide, fluoride, acetate, cyanide, azide, or an amine (although the last two examples are unstable) [1].



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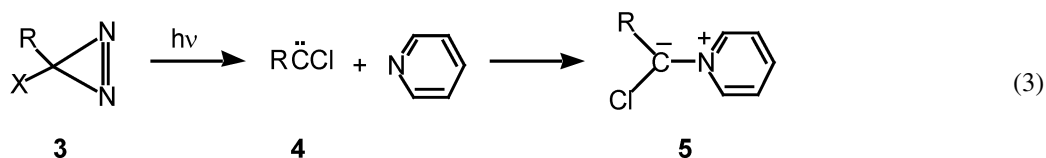
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It is beyond the scope of the present report to discuss the mechanisms of the Graham and diazirine exchange reactions; these matters have been reviewed [1,6]. It is clear, however, that the Graham/exchange reaction sequence yields a wide variety of new diazirines, thus granting access to many electrophilic, ambiphilic, and nucleophilic carbenes [7]. The properties of these species can then be studied by matrix isolation or transient spectroscopy, while absolute rate constants and activation parameters can be measured for their intramolecular and intermolecular reactions. Additionally, the fragmentations of alkoxyhalocarbenes to ion pairs and carbocations can also be studied [8].

In this report, we focus on three investigations, which are made possible by the availability of diazirines **1** and **2**, as well as diazirine exchange chemistry: the transient spectroscopy of alkylchlorocarbenes; the generation of diazirinone; and the preparation of dichlorodiazirine (DCD) and dichlorocarbene.

### SPECTROSCOPY OF ALKYLCHLOROCARBENES

Alkylchlorocarbenes do not absorb strongly above 300 nm and are generally considered “invisible” for purposes of laser flash photolysis (LFP) with UV–vis detection [9]. To circumvent this problem, these carbenes are usually generated in the presence of pyridine, which yields a strongly chromophoric ylide upon reaction with the carbene; eq. 3 [9,10]. The ylide absorbs in the 350–450 nm range and can be used to indirectly monitor the kinetics of the carbene’s reactions. Consider, for example, the simplest alkylchlorocarbene, methylchlorocarbene.



Thus, photolysis of **3** (R = Me, X = Cl) in isooctane in the presence of pyridine gives MeCCl, which forms ylide **5** with  $\lambda_{\text{max}} \sim 360$  nm. A plot of  $k_{\text{obs}}$  for the formation of the ylide as a function of pyridine concentration is linear; eq. 4. Here, the slope ( $k_y$ ) is the second-order rate constant for ylide formation

$$k_{\text{obs}} = k_0 + k_y[\text{pyr}] \quad (4)$$

while  $k_0$  is the first-order rate constant for carbene decay at  $[\text{pyr}] = 0$ . Given that product studies show that MeCCl efficiently rearranges to vinyl chloride by 1,2-hydride shift in the absence of pyridine, we can equate  $k_0$  with  $k_H$ , the rate constant for the carbene rearrangement. Values of  $k_H$  determined in this manner are  $1.4 - 3.0 \times 10^6 \text{ s}^{-1}$  at room temperature [11,12].

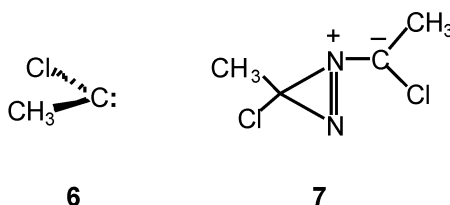
The pyridine ylide method can also be used to determine the bimolecular rate constant for the intermolecular addition of MeCCl to alkenes. In this application, the pyridine concentration is held constant while the alkene’s concentration is varied. Now, reaction of the carbene with pyridine to form the ylide competes with addition of the carbene to the olefin to give a cyclopropane. A plot of  $k_{\text{obs}}$  for ylide formation vs. the concentration of added alkene gives the linear relation of eq. 5, where  $k_0$  and  $k_y[\text{pyr}]$  are constant, and the slope of the correlation line gives  $k_{\text{add}}$ . In this way,  $k_{\text{add}}$  for the addition of MeCCl

$$k_{\text{obs}} = k_0 + k_y[\text{pyr}] + k_{\text{add}}[\text{alkene}] \quad (5)$$

to tetramethylethylene was determined as  $1.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  [13].

Now we find that the UV absorbance of MeCCl, although weak, is readily observable by LFP–UV and that the kinetics of the carbene’s intra- and intermolecular reactions can be *directly* followed without the need for pyridine ylide mediation.

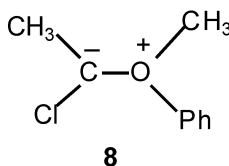
Thus, LFP of diazirine **3** ( $R = \text{Me}$ ,  $X = \text{Cl}$ ) in pentane reveals the  $\sigma \rightarrow \text{p}$  absorption of methylchlorocarbene (**6**) at 544 nm [14]. We calculate this transition at 550 nm ( $f = 0.005$ ) in simulated heptane by TD-B3LYP/6-311+G(d) excited-state calculations at the PBEPBE/6-31G(d) optimized geometry.



An absorption appearing at 272 nm can be attributed to ylide **7**, formed by attack of MeCCl on its diazirine precursor [15]. Analogous ylides have previously been observed in this spectral region [15].

We can directly follow the kinetics of MeCCl reactions by monitoring its 544-nm absorption as a function of time after generation of the carbene by LFP. The first-order decay of the absorption provides  $k_{\text{H}} = 2.0 \times 10^6 \text{ s}^{-1}$  for the formation of vinyl chloride, in good agreement with  $k_{\text{H}} = 1.4 - 3.0 \times 10^6 \text{ s}^{-1}$ , determined by the pyridine ylide method [11,12]. A correlation of  $k_{\text{obs}}$  for the decay of MeCCl at 544 nm vs. the concentration of added tetramethylethylene in pentane is linear with a slope of  $1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . This value can be taken as  $k_{\text{add}}$  for the addition of MeCCl to the alkene, and agrees well with  $k_{\text{add}} = 1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  determined by the ylide method [13].

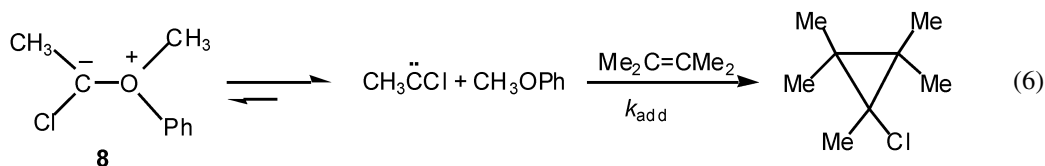
Computational studies suggest the formation of weak  $\pi$  and ylidic complexes between MeCCl and anisole [16]. The LFP-UV spectrum of MeCCl in anisole manifests several changes relative to its spectrum in pentane: (a) the (uncomplexed) carbene band, which appears at 544 nm in pentane, shifts to 520 nm in anisole, and is calculated (see above for methodology) at 532 nm; (b) a new band appears at 368 nm; and (c) the carbene-diazirine ylide (**7**) band at 272 nm in pentane is absent in anisole. We attribute changes (b) and (c) to the formation of MeCCl-anisole ylide complex **8**, for which absorptions are calculated at 487 and 359 nm [TD-B3LYP/6-311+G(d)]. The 487-nm absorption is assigned to the  $\sigma \rightarrow \text{p}$  absorption of complex **8**, but this feature is not distinctly expressed in the observed spectrum. The calculated absorption at 359 nm is a charge-transfer excitation from the anisole  $\pi$ -system to the carbene's p-orbital, in good agreement with the observed absorbance at 368 nm.



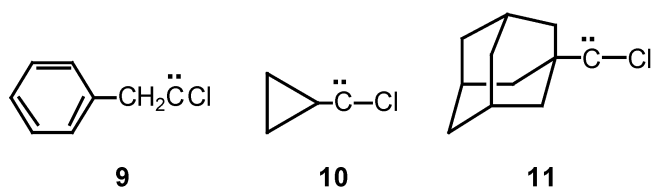
The UV-spectrum of MeCCl in anisole is the same whether it is obtained under air or nitrogen, excluding the contribution of a carbene-oxygen ylide. Additionally, the spectrum is anisole-specific: there is no change in the MeCCl spectrum in pentane (544 nm) upon substitution of benzene, tetrahydrofuran (THF), or 1,4-dioxane as solvent.

At present, we do not understand why the spectrum of the MeCCl-anisole ylide (**8**) is so readily observed, whereas that of a putative MeCCl-THF ylide is not. Computationally [PBEPBE/6-31g(d)], the latter species with  $\Delta E = -9.95 \text{ kcal/mol}$  should be more stable than **8** (with computed  $\Delta E = -4.5 \text{ kcal/mol}$ ). Absorptions for the MeCCl-THF ylide are predicted at 295 ( $f = 0.045$ ) and 248 ( $f = 0.08$ ) nm, but these are not observed—only MeCCl itself is visible at 544 nm in THF. Additional experimental and theoretical work on MeCCl-solvent interactions is under way in our laboratories.

Although ylide **8** is a very weak “complex”, with a computed binding energy of 4.5 kcal/mol and a long (2.45 Å) C–O bond, it appears to have consequences for the kinetics of MeCCl in anisole. Thus, we can follow the addition of MeCCl to tetramethylethylene in anisole “indirectly”, using ylide **8** and an equation analogous to eq. 5, much as one might use pyridine ylide **5**. A correlation of  $k_{\text{obs}}$  for the formation of **8** in anisole, followed at 368 nm, vs. the concentration of added alkene is linear, with a slope of  $5.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , which we take as  $k_{\text{add}}$  for MeCCl. This is  $\sim 3.5$  times *slower* than the MeCCl–tetramethylethylene (TME) addition in pentane. At 520 nm in anisole, the absorption is still dominated by MeCCl, rather than by ylide **8**. The absorbance is quenched by added alkene, and the concentration dependence affords  $k_{\text{add}} = 4.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , similar to the value determined by monitoring ylide **8**. One could attribute the decrease in  $k_{\text{add}}$  for MeCCl in anisole, relative to pentane, to ylide formation; cf., eq. 6. However, it is unclear that the formation of a small equilibrium concentration of **8** can account for the 3.5-fold retardation of the MeCCl–TME addition in anisole. It may be that the rate difference reports the kinetic advantage of a “free” carbene relative to a solvated carbene. Related considerations have been discussed for the addition reactions of halocarbene amides to TME in dioxane and THF as opposed to Freon-113 [17].



Our ability to directly follow the reactions of RCCl in solution by LFP at ambient temperature is not limited to MeCCl. Benzylchlorocarbene (**9**), cyclopropylchlorocarbene (**10**), and adamantylchlorocarbene (**11**) can also be studied. For example, carbene **9** exhibits LFP–UV absorptions in pentane at 575 nm ( $\sigma \rightarrow p$ ) and  $\sim 290$  nm. The 290-nm absorption is complex, and probably includes contributions from both carbene **9** [18] and a carbene-diazirine ylide [15], as well as the product  $\beta$ -chlorostyrene (formed directly from the excited diazirine carbene precursor). It is possible to derive  $k_{\text{H}}$  for rearrangement of **9** to  $\beta$ -chlorostyrene from the 290-nm absorbance [18], but clearly the  $\sigma \rightarrow p$  absorbance at 575 nm, which belongs exclusively to **9**, provides a “cleaner” monitor. Following the decay of **9** at 575 nm leads to  $k_{\text{H}} = 3.0 \times 10^7 \text{ s}^{-1}$ , in good agreement with  $k_{\text{H}} = 6 \times 10^7 \text{ s}^{-1}$ , determined by the pyridine ylide method [11,18].



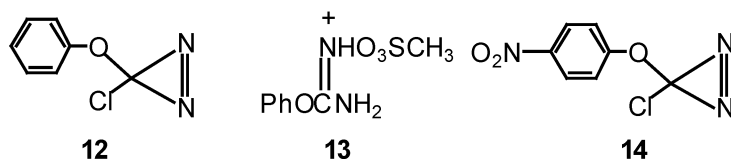
The weak  $\sigma \rightarrow p$  absorbance of carbene **10** at 460 nm has been observed in a nitrogen matrix at 14 K, together with a  $\sigma \rightarrow \sigma^*_{\text{C-Cl}}$  transition at 240 nm [19]. We observe these absorptions in pentane solution by LFP–UV at 490 and 250 nm. From the decay of the 490-nm signal, we derive  $k_{\text{c}} = 1.4 \times 10^6 \text{ s}^{-1}$  for the 1,2-C migration that converts **10** to 1-chlorocyclobutene. This value is in good agreement with  $k_{\text{c}} = 9 \times 10^5 \text{ s}^{-1}$ , derived from decay of the 250-nm signal [19], and  $6 \times 10^5 \text{ s}^{-1}$  [11] or  $1.5 \times 10^6 \text{ s}^{-1}$  [19] obtained by the pyridine ylide method.

Finally, we observe the  $\sigma \rightarrow p$  absorbance of 1-adamantylchlorocarbene (**11**) at 540 nm in pentane solution at 25 °C. This band was previously assigned to **11** in an argon matrix at 10 K [20]. Following the disappearance of the 540-nm band, we obtain  $k_{\text{c}} = 4.0 \times 10^5 \text{ s}^{-1}$ , which, from product studies, appears to represent azine formation by attack of **11** on its diazirine precursor.

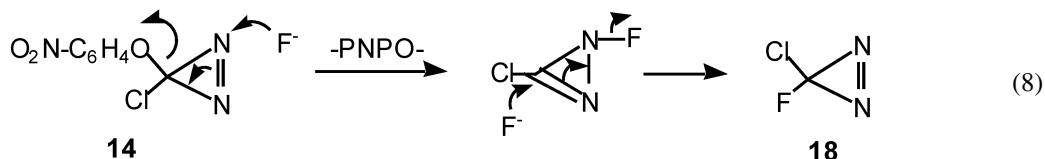
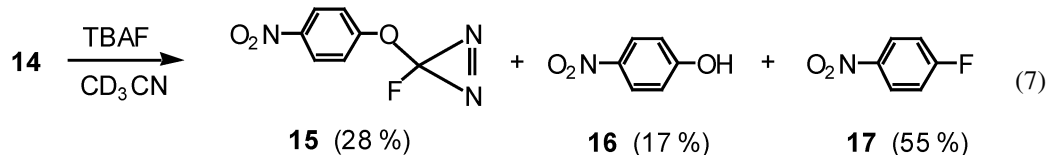
## DIAZIRINONE

We have seen that a combination of the Graham and diazirine exchange reactions, eqs. 1 and 2, provides access to many diazirines **1** and **2**. However, *dihalodiazirines* are not immediately available by this methodology. We need to convert the “R” group of **1** (X = halogen) to a leaving group so that a second halogen can be introduced by diazirine exchange.

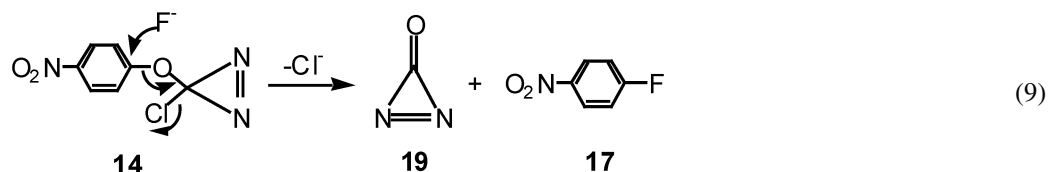
We accomplished this by nitrating phenoxychlorodiazirine (**12**), which is readily available from isouronium salt **13**, itself preparable from phenol [21]. Thus, nitration of **12** with  $\text{NO}_2^+\text{BF}_4^-$  at 0 °C in nitromethane gave the *p*-nitroderivative **14** in 40 % yield [22].



Treatment of **14** with tetrabutylammonium fluoride (TBAF) gives three high-boiling products, **15–17**; eq. 7 [22]. *p*-Nitrophenoxyfluordiazirine (**15**) is the F/Cl diazirine exchange product derived from **14**. *p*-Nitrophenol (**16**) represents a diazirine exchange of **14** in which fluoride replaces *p*-nitrophenoxide (PNPO). The product of this exchange should be fluorochlorodiazirine (**18**); cf., eq. 8. Indeed, diazirine **18** could be isolated by a continuous nitrogen sweep of the TBAF/**14** reaction [22]. The diazirine was characterized by  $^{19}\text{F}$  NMR, IR, and UV. Also, photolysis of **18** in isobutene afforded the known 1-chloro-1-fluoro-2,2-dimethylcyclopropane adduct of chlorofluorocarbene [22].

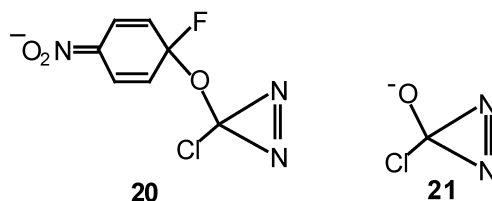


The third product in eq. 7, *p*-nitrofluorobenzene (**17**), represents the most unusual of the three reaction channels; cf., eq. 9. Here, *ipso* attack of fluoride on the *p*-nitrophenyl moiety of **14** leads to the formation of diazirinone (**19**). Indeed, mixing **14** with TBAF in an IR cell at –10 to –15 °C immediately affords **19**, as signaled by a strong IR absorption at 2150  $\text{cm}^{-1}$  (computed at 2064  $\text{cm}^{-1}$  by B3LYP or 2079  $\text{cm}^{-1}$  by MP2 methods). The diazirinone band decays over 5–9 min with the formation of  $\text{N}_2$  and CO, the latter indicated by IR bands growing in at 2117 and 2168  $\text{cm}^{-1}$  [23].



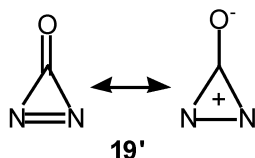
Computationally, we tried to locate a stationary state for the putative Meisenheimer complex (**20**) expected as the initial product of the *ipso* attack of fluoride on **14**. However, after many optimization

cycles at the B3LYP/6-31G(d) level, **20** evolved to *p*-nitrofluorobenzene, chloride ion, and diazirinone **19** [22]. We also found that **21**, the carbonyl-chloride adduct of diazirinone and a likely fragment from **20**, is not a bound species. Thus, the direct formation of **19** from **14** and  $F^-$ , as depicted in eq. 9, appears apposite.



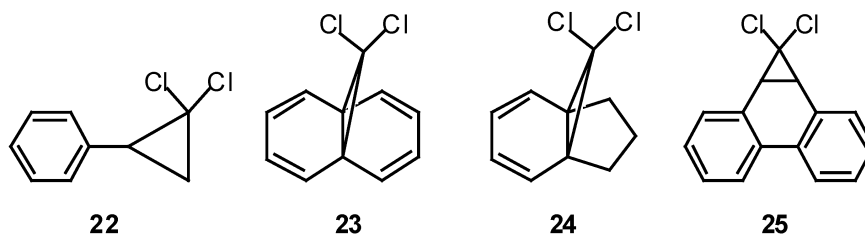
Diazirinone has been the subject of computational interest [24,25]. Its decomposition to  $N_2$  and CO is computed to be exothermic by >90 kcal/mol, but requires an activation energy of ~24–27 kcal/mol, which is why it persists long enough to be detected. Diazirinone is also computed to be the most stable of the various  $N_2CO$  isomers; for example, it is ~11 kcal/mol more stable than nitrosyl cyanide,  $O=N-CN$ , its known linear isomer [24]. We prepared nitrosyl cyanide by the reaction of NOCl and AgCN [26]. Nitrosyl cyanide was immediately unstable to TBAF at  $-20^\circ C$  [22], in contrast to diazirinone, which persists for 5–9 min under comparable conditions [22].

Now that diazirinone can be prepared, its chemistry can be studied. Can it be trapped by reactive dienes in cycloaddition reactions? Will it add nucleophiles at its carbonyl group? Although, as the diaza analog of cyclopropanone, diazirinone is formally aromatic (**19'**), its computed stabilization energy is only 7–9 kcal/mol [24,25], so that it could exhibit a rich chemistry.

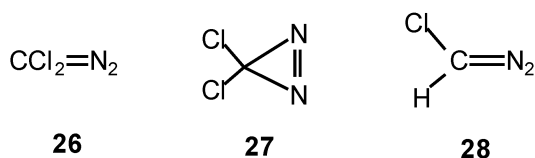


## DICHLORODIAZIRINE AND DICHLOROCARBENE

Given our successful preparation of fluorochlorodiazirine, **18**, from diazirine **14** [22], we wondered whether DCD could be similarly generated. DCD should be a spectroscopy-friendly precursor for dichlorocarbene, the archetypal dihalocarbene [27]. There are already several photochemical precursors for  $CCl_2$ . These are adducts of  $CCl_2$  and arylalkenes from which the carbene can be regenerated by photoextrusion; cf., **22** [28], **23** [29], **24** [30], and **25** [31]. However, these precursors necessarily produce aromatic byproducts that might obscure the UV spectrum of  $CCl_2$ . For example, upon LFP generation of  $CCl_2$  from its phenanthrene adduct (**25**), any spectral signature of the carbene is “overwhelmed” by absorptions due to triplet phenanthrene [31].



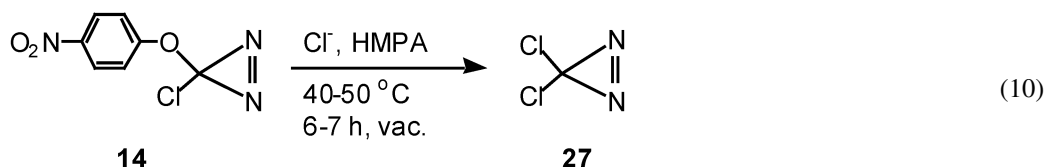
It is reported that photolysis of cyanogen azide in a chlorine-doped argon matrix at 14 K generates  $\text{CCl}_2$  which absorbs at  $\sim 500$  nm [32]. However, photolysis of dichlorodiazomethane (**26**) or DCD (**27**) would provide  $\text{CCl}_2$  in a much more straightforward process. In 1965, Closs and Coyle prepared monochlorodiazomethane (**28**), a precursor for  $\text{CHCl}$ , by the chlorination of diazomethane with *t*-butyl hypochlorite in pentane at  $-100$  °C [33]. However, further chlorination of **28** in an attempt to prepare **26** led to rapid nitrogen evolution, even at  $-100$  °C [33]. Some dichlorodiazomethane might have been generated in this process, but it is obviously not a practical preparation.



What about DCD (**27**)? Treatment of *p*-nitrophenoxychlorodiazirine (**14**) with tetrabutylammonium chloride (TBACl) in  $\text{CD}_3\text{CN}$  for 1 week at 25 °C gave 30 % of *p*-nitrophenol and 70 % of *p*-nitrochlorobenzene [34]. This process parallels the reaction of **14** with TBAF, eq. 7, and suggests that DCD is produced as a “partner” to the *p*-nitrophenol, just as fluorochlorodiazirine **18** is generated in eq. 8. The mechanism for DCD formation would be analogous to that shown in eq. 8, with Cl replacing F.

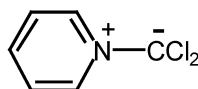
Indeed, treatment of **14** with TBACl in the presence of cyclopentene, cyclohexene, or tetramethylethylene gave the appropriate  $\text{CCl}_2$  cyclopropane adducts, an indication that DCD was produced in the reaction and thermally decomposed to  $\text{CCl}_2$  under the reaction conditions [34].

In an effort to enhance the nucleophilicity of the chloride reagent, and thus to accelerate the reaction of TBACl with **14**, we treated this diazirine with a 1.1:1.0:1.6 mixture of TBACl, CsCl, and butylmethylimidazolium chloride (an ionic liquid under our reaction conditions) in a little dry hexamethylphosphoramide (HMPA); cf., eq. 10. DCD was removed under vacuum as it formed, and trapped in pentane at  $-70$  °C [34].



It exhibited UV absorptions between 327 and 359 nm, a diazirine IR band at  $1560\text{ cm}^{-1}$ , and it was moderately stable in the dark, undergoing  $\sim 10$  % of decomposition after 13 h at 25 °C. Indeed, B3LYP/6-311+G(2d,p) computations gave  $\Delta H^\ddagger = 28.2$  kcal/mol for the fragmentation of **27** to  $\text{CCl}_2 + \text{N}_2$ , whereas linear isomer **26** required only 11.2 kcal/mol for the analogous fragmentation at the same computational level. DCD is therefore both experimentally and computationally more stable than dichlorodiazomethane [33,34].

LFP of DCD in pentane containing pyridine affords the dichlorocarbene-pyridinium ylide **29**,  $\lambda_{\text{max}} = 387$  nm, which has been previously made using  $\text{CCl}_2$  generated from precursor **25** [31]. But what of  $\text{CCl}_2$  itself? LFP of DCD in pentane at 25 °C affords a UV spectrum with  $\lambda_{\text{max}} = 465$  nm, in reasonable agreement with  $\lambda_{\text{max}} = 498$  nm ( $f = 0.0036$ ) computed for the  $\sigma \rightarrow \text{p}$  transition of  $\text{CCl}_2$  in simulated heptane by TD-B3LYP/6-311+G(d) methodology. The transient has a lifetime of 4–5  $\mu\text{sec}$ , and it is tempting to assign it to  $\text{CCl}_2$  [34]. Unfortunately, it is not quenched by alkenes and is not observed when the LFP of DCD is carried out under nitrogen! It therefore seems unreasonable to assign this species to dichlorocarbene. Perhaps the absorption of  $\text{CCl}_2$  is simply too weak to be detected under our current conditions. The identity of the 465-nm transient, an improved synthesis of DCD, and additional reactions of dichlorocarbene are the subjects of a full paper now in preparation [35].

**29**

## SUMMARY

LFP–UV of alkylchlorodiazirines affords the UV spectra of several alkylchlorocarbenes,  $\text{RCCl}$ . Thus,  $\sigma \rightarrow \text{p}$  transitions are located for methylchlorocarbene, benzylchlorocarbene, cyclopropylchlorocarbene, and 1-adamantylchlorocarbene. The kinetics of these carbenes' intra- and intermolecular reactions can be directly followed by monitoring their UV absorptions; the use of pyridine-carbene ylides for this purpose is not necessary.

The reaction of fluoride ion with *p*-nitrophenoxychlorodiazirine (**14**) produces fluorochlorodiazirine as well as the unusual and highly reactive  $\text{N}_2\text{CO}$  compound diazirinone (**19**). Diazirinone can be visualized by IR spectroscopy. It decomposes to  $\text{N}_2$  and CO over 5–9 min at temperatures between  $-15$  and  $25^\circ\text{C}$  in a reaction that is estimated to be exothermic by  $>90$  kcal/mol.

DCD (**27**) is prepared by reaction of chloride ion with *p*-nitrophenoxychlorodiazirine. Photolysis of DCD produces dichlorocarbene, which adds to alkenes and forms an ylide with pyridine.

## ACKNOWLEDGMENTS

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