Pergamon

Tetrahedron Letters 43 (2002) 7–9

TETRAHEDRON
LETTERS

Pyridine trapping of chlorocyanocarbene

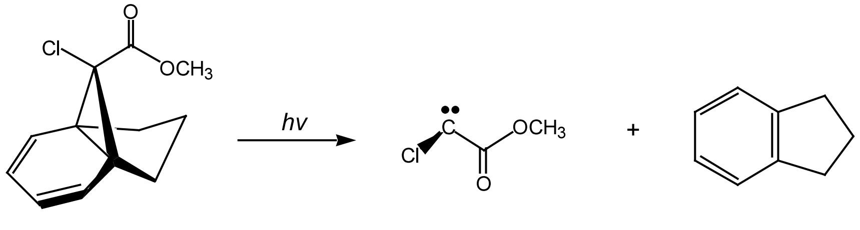
Ying Sun, Igor Likhotvorik and Matthew S. Platz*

Department of Chemistry, The Ohio State University, 100 W. 18th Avenue, Columbus, OH 43210, USA

Received 23 August 2001; accepted 16 October 2001

Abstract—Laser flash photolysis (308 nm) of precursor **3** releases chlorocyanocarbene which can be trapped with pyridine. © 2001 Elsevier Science Ltd. All rights reserved.

Recently, we have demonstrated that photolysis of chloroester **1** efficiently produces carbene **2** and indane.[1] Diazirine precursors of **2** are not known,[2] which prompted the use of a Jones[3] type of precursor in this system.



1

2

This encouraged us to synthesize **3**[4] to study chlorocyanocarbene. Once again a diazirine precursor of **4** is not known.[2] Aryl cyano diazirines are known[5] but they are unstable at room temperature and are therefore not convenient for laser flash photolysis studies. Chlorocyanocarbene has been observed in a cryogenic matrix and its IR spectrum is consistent with a ground singlet state.[6] To our knowledge, ClCCN has not been previously generated in solution.

Precursor **3**[6] was photolyzed (Ray-o-Net, 300 nm 10–14°C, 12 h) in an NMR tube in cyclohexane-d12 containing methylbenzoate as internal standard. The yield of indane measured by NMR was 12%, which is also the maximum yield of carbene **4** from this precursor.

Continuous photolysis (Ray-o-Net, 300 nm bulbs, pyrex cells, 10–14°C, 16 h) of **3** (50 mM) in cyclohexane, benzene and tetramethylethylene led to the complete consumption of the precursor (determined by gas chromatography[7]) and indane as the only significant volatile product. Only trace (<1%) quantities of products with mass spectra consistent with adducts of ClCCN and solvent trap were detected by GC–MS. A few products were formed in ≈3% yield, but did not have mass spectra that could be interpreted. As a result of the inefficiency of the precursor and the low yield of adducts formed, these products were not isolated and characterized.

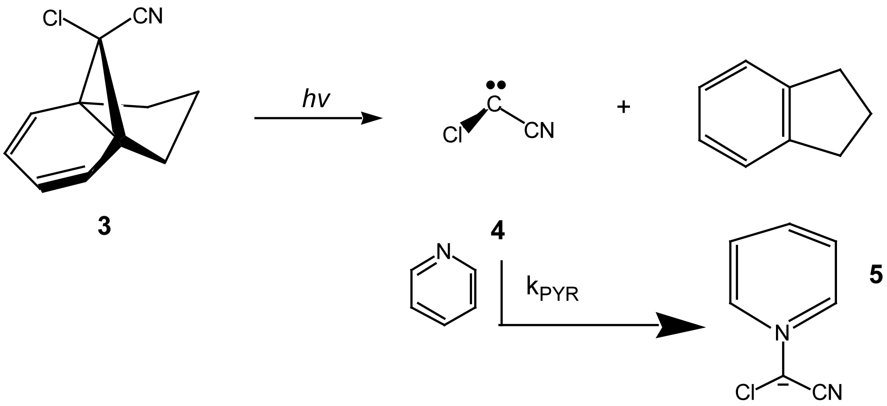
LFP (308 nm) of **3** ($\lambda_{max} = 276$ nm, $\varepsilon_{276} = 1944$ cm^{-1} M^{-1}, $\varepsilon_{308} = 237$ nm^{-1} M^{-1} in cyclohexane) in deoxygenated hexafluorobenzene, acetonitrile, cyclohexane and $CF_2ClCFCl_2$ produced only weak transient signals. The presence of oxygen in $CF_2ClCFCl_2$ had no effect on the signal. If carbene **4** had a triplet ground state it would surely react with oxygen to form a UV–vis active oxide, but a transient spectrum consistent with this species was not observed.

A broadly absorbing transient was observed (Fig. 1) upon LFP (308 nm) of **3** in neat pyridine, which was attributed to carbene–pyridine ylide **5**. The transient was observed in other solvents containing pyridine but the rate of formation of the transient in all solvents was faster than the time resolution (20 ns) of the spectrometer even at the lowest concentrations of pyridine at which the transient could be detected.

---

* Corresponding author.

PII: S0040-4039(01)02086-X



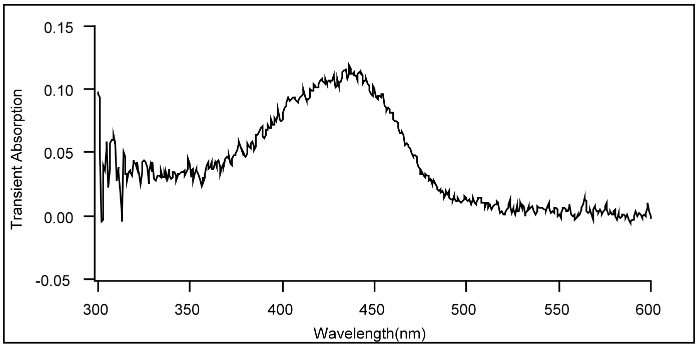


Figure 1. Transient spectrum obtained upon LFP of **3** in pyridine at ambient temperature.

As predicted plots of $1/\Delta A_{450}$ of ylide **5** versus 1/[pyridine] are linear (inset Fig. 2) and division of the intercept by the slope of such plots yields the ratio $k_{PYR}/k_{SH}[SH]$ ($=k_{PYR}\ \tau$), where k_{PYR} and k_{SH} are the absolute rate constants of reaction of carbene **4** with pyridine and solvent (SH), respectively, and τ is the carbene lifetime in the solvent of interest in the absence of pyridine.[8] It is possible to estimate τ values assuming that $k_{PYR} = 5\times10^9$ M^{-1} s^{-1}. The value of k_{PYR} for related carbene **2** is 2.0×10^9 M^{-1} s^{-1} in $CF_2ClCFCl_2$.[1] These values are listed in Table 1.

It seems clear that carbene **4** has greater bimolecular reactivity then analog **2**, which has a lifetime of 114 ns in $CF_2ClCFCl_2$.[1] Singlet carbene ester **2** is non-planar. This allows the filled hybrid orbital of the carbene to interact with the π* system of the carbonyl group. Lone pairs of electrons on the carbonyl oxygen of **2** are now

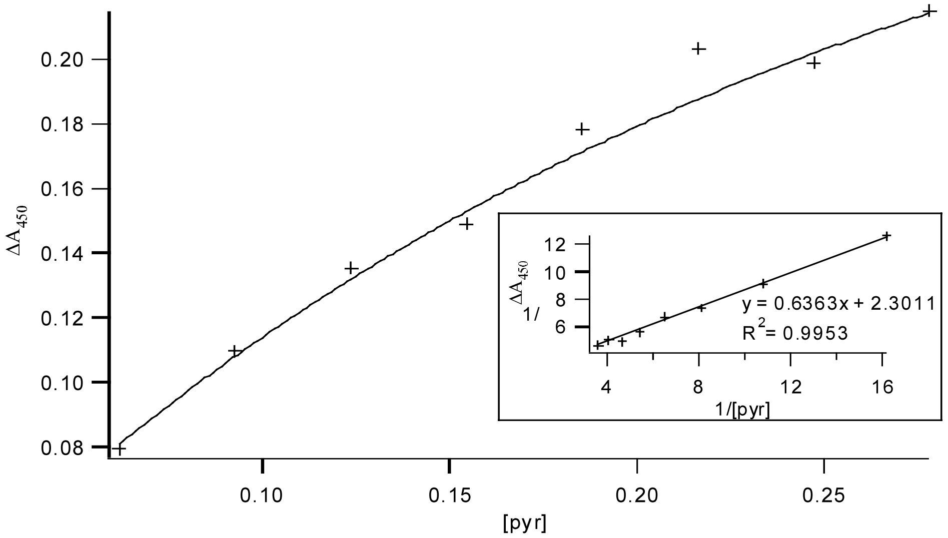
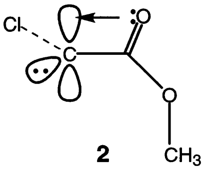


Figure 2. Transient absorption at 450 nm produced by LFP (308 nm) of **3** in cyclohexane as a function of pyridine concentration at ambient temperature. Inset: a double reciprocal treatment of the data.

Table 1. A summary of data obtained from plots of $1/A_{450}$ versus 1/[pyridine] assuming that $k_{\text{PYR}} = 5\times10^9$ $\text{M}^{-1}\ \text{s}^{-1}$

Solvent	$k_{\text{PYR}}\ \tau$	$\tau_{\text{(ns)}}$
$CF_2ClCFCl_2$	285	57
c-C_6H_{12}	3.6	1
c-C_6D_{12}	4.3	1
C_6H_6	1.1	0.2
CH_3CN	0.14	0.03

disposed to coordinate with the empty *p* orbital of the carbene.[9]



2

This stabilizing interaction is absent in **4**, hence its greater reactivity. The cyano group is more electron withdrawing than carbomethoxy and this factor may also increase its reactivity.

References

1. Likhotvorik, I.; Zhu, Z.; Tae, E. L.; Tippmann, E.; Hill, B. T.; Platz, M. S. *J. Am. Chem. Soc.* **2001**, *123*, 6061.
2. Moss, R. A. In *Chemistry of Diazirines*; Liu, M. T. H., Ed.; CRC Press: Boca Raton, FL, 1987; Vol. I, p. 99.
3. (a) Hartwig, J. F.; Jones, M. Jr.; Moss, R. A.; Lawrynowicz, W. *Tetrahedron Lett.* **1986**, *27*, 5907; (b) Banwell, M. G.; Halton, B.; Hambley, T. W.; Ireland, N. K.; Papamihail, C.; Russell, S. G. G.; Snow, M. R. *J. Chem. Soc., Perkin Trans. 1* **1992**, *6*, 715–724.
4. **Synthesis of 8-chloro-8-cyano-3a,7a-methanoindan (3)**. A solution of *n*-butyllithium in hexanes (1.6 M, 1.5 ml) was added under argon dropwise at −78°C to a solution of 10,10′-dichloro-tricyclo$[4,3,1,0^{1,6}]^3$decadiene-2,4 (0.42 g, 2 mmol) in dry THF (1.8 mL) and dry ether (1.8 mL), which were freshly distilled from benzophenone ketyl. The mixture was stirred for 0.5 h at −78°C, then transferred through a cooled (−78°C) needle into a solution of tosyl cyanide (0.446 g, 2.3 mmol) in dry ether with stirring at −78°C. The mixture was stirred with cooling by a dry ice–acetone bath for 45 min, then poured into water (25 mL) and extracted with ether (2×10 mL). The combined organic extracts were washed with water (4×10 mL), dried over sodium sulfate, decolorized with charcoal and evaporated. The product was crystallized from isopropyl alcohol, yield 0.21 g (52.5%), colorless solid, mp 104–106°C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.78 (m, 2H), 2.17 (m, 2H), 2.47 (m, 2H), 5.91 (dd, $J=7.2$, 2.6 Hz, 2H), 6.22 (dd, $J=7.2$, 2.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.50, 28.64, 34.27, 50.17, 117.42, 122.74, 126.22; λ_{max} 276 nm; IR, cm^{-1} (microcrystalline film) 2983, 2951, 2934, 2229, 1444, 1307, 741; EI MS *m*/*z* (rel. intensity) 191 (M^+, 16), 181 (5), 165 (21), 163 (56), 156 (100), 140 (9), 128 (45), 117 (20); HRMS calcd for $C_{11}H_{10}N^{35}Cl$ 191.0502, found 191.0499. The structure of **3** was confirmed by X-ray crystallography.
5. (a) Moss, R. A.; Zdrojewski, T.; Krogh-Jespersen, K.; Wlostowski, M.; Matro, A. *Tetrahedron Lett.* **1991**, *32*, 1925; (b) Moss, R. A.; Kmiecik-Lawrynowicz, G.; Cox, D. P. *Synth. Commun.* **1984**, *14*, 21.
6. Maier, G.; Bothur, A.; Eckwert, J.; Reisenauer, H. P. *Chem. Eur. J.* **1998**, *4*, 1964.
7. GC–MS analyses were performed with a Hewlett–Packard 5973 GC equipped with a mass-selective detector. The injector temperature was 100°C, the oven temperature was 50°C. Precursor **3** has a retention time of 18 min under these conditions with a 5 MS crosslinked 5% PH ME siloxane capillary column. At higher injector and oven temperatures, precursor **3** decomposes.
8. Platz, M. S.; Modarelli, D. A.; Morgan, S.; White, W. R.; Mullins, M.; Celebi, S.; Toscano, J. P. *Prog. React. Kinetics* **1994**, *19*, 93.
9. Scott, A. P.; Platz, M. S.; Radom, L. *J. Am. Chem. Soc.* **2001**, *123*, 6069.