KINETICS AND SPECTROSCOPY OF YLIDS FROM REACTION OF p-SUBSTITUTED PHENYLCHLOROCARBENES WITH ACETONE

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Abstract: Laser flash photolysis of $p-CF_3$ and p-Cl-phenylchloro diazirines produces the corresponding carbenes which react with acetone to produce easily detected ylids. The absolute rate constants of reaction of these carbenes with acetone, and the rate constants of reaction of the ylids with diethylfumarate have been determined. No reaction was found between these carbenes and simple esters or ethylene carbonate.

In the course of a recent investigation into the reactions of arylchlorocarbenes with ester-substituted olefins, we became interested in the possibility that carbonyl ylids, formed by carbene attack on the ester functionality, could be involved in the reactions under study.¹ Fluorenylidene and the naphthyl carbenes react rapidly with acetone to produce ylids which are easily detectable by laser flash photolysis (LFP).² While phenylchlorocarbene apparently does not react at a measurable rate with acetone to produce the corresponding ylid,³ Liu *et al* have recently reported that photolysis of *p*-NO₂-phenylchlorodiazirine in acetone produces a carbene that reacts to form an ylid which in turn can be intercepted with diethylfumarate (DEF).⁴ This prompted the present LFP study of *p*-CF₃- and *p*-Cl-phenylchlorocarbene. The effects of variations in the substrate carbonyl compound were examined. In addition, we hoped to learn how the para phenyl substituents and the chlorine on the carbene affect the rate of formation of the ylid, its spectroscopy, lifetime and rates of reaction with dipolarophiles.

Figure 1: Transient O. D. Spectra of Carbonyl Ylids



Figure 1: Transient optical density spectra of ylids 3a (left) and 3b (right). These were obtained using an EG&G Princeton Applied Research Corp. Optical Multichannel Analyser (OMA). Data were collected during a 150-200 ns window, beginning 20-50 ns after the laser pulse which generated the carbene. The ca. 345 nm feature in the spectrum of 3b is probably unreacted carbene, as its relative intensity is a function of delay time. Spectres 3a was observed in 1:10 acetone:toluene, while 3b was in neat, carefully dried acetone.

LFP⁵ of diazirines 1a, b in toluene produced the known transient spectra of carbenes 2a, b. LFP of 1a, b in acetone gives rise to new transients (Figure 1), attributed to ylids 3a, b (See Scheme 1). Measurement of the rate of ylid growth at 480 nm as a function of [acetone] yielded the absolute rate constants for ylid formation, which are displayed in Table 1.6 The ylid lifetimes were reduced by the addition of DEF. Absolute rate constants for reaction of DEF with 3a, b are also shown in Table 1. For reference, Table 1 includes the corresponding rate constants found by Liu et al for p-NO₂-phenylchlorocarbene 2c in isooctane. The lifetimes of the ylids 3a, b in the absence of DEF were in the range 200-500 ns. Photolysis of 1a, b in acetone containing DEF produced 4a, b which are easily explained by dipolar cycloaddition of DEF to 3a, b followed by elimination of HCl.⁷

Scheme 1



Table	1	
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Rate Constants:	Carbenes 2 +	Acetone ->	3; and	3 + DEF	—> 4
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Carbene	p-X	$\lambda_{obs}{}^a$	^k 2,ACE ^b	Solvent ^C	$\lambda_{obs}{}^a$	k3,DEF ^b	Solvent ^C
2a	CF3	480	$1.56 \pm 0.09 \times 10^7$	Т	480	$5.53 \pm 0.41 \times 10^8$	1:10 A:T
2b	Cl	480	$4.81 \pm 0.62 \times 10^6$	Т	460	$1.46 \pm 0.37 \times 10^8$	А
2c ^d	NO_2	590	3.5 x 10 ⁷	I	590	6.4 x 10 ⁸	1:10 A:I

a. Wavelength (nm) used to observe kinetics. b. Bimolecular rate constants in units of $M^{-1}s^{-1}$.

c. Solvents: T = Toluene, I = Isooctane, A = Acetone.

d. Reference 4.

Fluorenylidene (Fl) and 1-naphthyl carbene (NC) react with actione with absolute rate constants of $k_{Fl} = 1.0 \pm 0.5 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$ and $k_{NC} = \text{ca. } 1.1 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$ to produce ylids 5 and 6 respectively.² Ylid 5 reacts with DEF with a rate constant of $k_{5,\text{DEF}} = 4.47 \pm 0.30 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$. Lifetimes for these ylides in the absence of quenchers are Fl: 3.4 µs and NC: 2.3 µs. The lifetimes of 5 and 6 are controlled by cyclization to the corresponding oxirane, and it seems likely that the same is true of ylids 3a, b, and c. However, the putative 2-chlorooxirane which would be initially expected can easily rearrange to the observed aryl isopropenyl and aryl-(2-chloroisopropyl) ketones (Scheme 1).⁸ Thus the chlorine in the arylchlorocarbenes 2a-c has no special effect on the absolute rates of acetone ylid formation or quenching of the ylid by DEF, but does appear to accelerate the intramolecular collapse to oxirane by roughly a factor of 8 (lifetimes: 3a ~430 ns; 3b ~190 ns). As expected, the ylid formation rate increases with more electron-withdrawing para phenyl substituents, and the DEF cycloaddition rate is similarly affected.



In light of their observed reactivity with acetone, we found it somewhat surprising that carbenes 2a, b show no reactivity with ester substrates. The carbonyl oxygen of a simple ester is typically 0.5-1.5 pK_A units more basic than that of acetone.⁹ Since carbenes are strongly electrophilic, one might reasonably expect them to react more rapidly with esters than with ketones. However, a concerted search for ester-carbonyl ylids turned up no new transients. In fact, we found ethyl acetate to be a useful solvent in which to study carbene-olefin reactions. Even such likely substrates as ethyl formate, dimethyl oxalate, γ -butyrolactone and ethylene carbonate showed neither new ylid absorptions nor quenching of the carbene signal. Thus, we must improve on the simple Lewis acid-base picture in which a voracious electrophile--the carbene--attacks a carbonyl oxygen at a rate reflecting the lone pair's basicity. Theoretical and experimental efforts toward such an understanding are currently underway.

REFERENCES AND NOTES:

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- N. Soundararajan, J. E. Jackson, M. S. Platz, unpublished observations. We estimate an upper bound for the carbene-acetone rate constant of ~2 x 10⁴ M⁻¹s⁻¹, limited by dimerization and reaction with diazirine precursor.
- 4. M. T. H. Liu, N. Soundararajan, S. M. Anand, I. Ibata, Tetrahedron Lett. 28, 1011 (1987).
- 5. Samples of diazirines were dissolved in spectral grade solvents to give absorbances of ca. 0.1 at 351 nm, placed in 1 cm² suprasil cells, degassed by N₂ bubbling, and irradiated with the pulses of a Lumonics TE-861-4 Excimer laser (Xe, F₂, He gas mix, 351 nm, 10 ns, ca. 80 mj) perpendicular to the monitoring beam which consisted of the light from a 1000W Xe arc lamp, focussed through the sample and then through an Oriel monochromator onto an IP 28 photomultiplier tube. Signals were digitized with a Tektronix 7912 A/D converter and passed to the controlling Apple IIe for processing. For more details see reference 1.

- Kinetic studies were performed on 7-10 static samples containing varying concentrations of the quenching reagent (Acetone or DEF) to be studied. Three k_{obs} measurements were made at each quencher concentration.
 Preparation of 4a, b: A solution of acetone (25 ml) containing 5.0 x 10⁻⁴ M diazirine 1a or 1b and 5.5 x 10⁻⁴
- Preparation of 4a, b: A solution of acetone (25 ml) containing 5.0 x 10⁻⁴ M diazirine 1a or 1b and 5.5 x 10⁻⁴ M diethylfumarate was degassed by three freeze-pump-thaw cycles and sealed in pyrex tubing (10 mm OD) at 77 K. The solution was photolysed at 20° C for 3 hours in a Rayonet photoreactor using a battery of 3500 Å UV lamps. It was then concentrated and the products isolated by preparative thin-layer chromatography (TLC) using 0.5 mm silicagel precoated plates (Sigma Corp.). The actual yields are probably 10-15% higher than the isolated yields reported here, due to inefficient recovery from TLC.
 4a: Yield 56% colorless heavy oil. IR (neat) 2890, 2860, 2850, 1735, 1720, 1610, 1580, 1510, 1460, 1410, 1370, 1325, 1300, 1250, 1170, 1060 cm⁻¹. ⁻¹H NMR (CDCl₃, 250 MHz): δ 1.18 (t, J = 7 Hz, 3H, ester CH₃), δ 1.29 (t, J = 7 Hz, 3H, ester CH₂), δ 1.47 (s, 3H, CH₃), δ 1.60 (s, 3H, CH₃), δ 3.91 (s, 1H, dihydrofuran ring H), δ 4.09-4.30 (m, 4H, ester CH₂), δ 7.66 (d, J = 8 Hz, 2H, aromatic H), δ 7.95 (d, J = 8 Hz, 2H, aromatic H). MS: m/e 386 (M⁺), 341, 313, 267, 240, 1730, 1700, 1620, 1580, 1480, 1460, 1390, 1360, 1325, 1280, 1250, 1150, 1080 cm⁻¹. ⁻¹H NMR (CDCl₃, 250 MHz): δ 1.18 (t, J = 7 Hz, 3H, ester CH₃), δ 1.28 (t, J = 7 Hz, 3H, ester CH₃), δ 1.45 (s, 3H, CH₃), δ 1.57 (s, 3H, CH₃), δ 3.87 (s, 1H, dihydrofuran ring H), δ 4.09-4.26 (m, 4H, ester CH₂), δ 7.35 (d, J = 8 Hz, 2H, aromatic H), δ 7.80 (d, J = 8 Hz, 2H, aromatic H). MS: m/e 386 (M⁺), 341, 313, 267, 240, 1730, 1700, 1620, 1580, 1480, 1460, 1390, 1360, 1325, 1280, 1250, 1150, 1080 cm⁻¹. ⁻¹H NMR (CDCl₃, 250 MHz): δ 1.18 (t, J = 7 Hz, 3H, ester CH₃), δ 1.28 (t, J = 7 Hz, 3H, ester CH₂), δ 7.35 (d, J = 8 Hz, 2H, aromatic H), δ 7.80 (d, J = 8 Hz, 2H, aromatic H). MS: m/e 352 (M⁺), 279, 233, 206, 239, and 111. Exact Mass: Calc. for C₁₈H₂₁ClO₅: 352.1077; Found: 352.1069
- 8. I. Ibata, personal communication about phenylchlorocarbene to M.T.H. Liu. We observe the analogous products by GC-MS from photolysis of 1a, b in acetone, along with substantial amounts of azine and an unidentified product with the m/e of (3 + acetone 22).
- 9. See for example: A. Streitwieser, Jr., C. H. Heathcock, "Introduction to Organic Chemistry," Second Edition, Macmillan Publishing Co., New York, 1981, p. 536.

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