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Generation and Characterization of Phenylsulfanylcarbene

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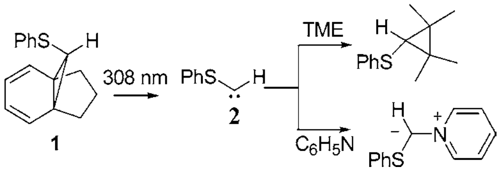
ABSTRACT



A photosensitive precursor (1) to phenylsulfanylcarbene 2 has been synthesized. Laser flash photolysis (308 nm) of 1 and chemical trapping studies of 2 are reported.

Carbenes bearing heteroatoms in the α position are of interest as a result of intriguing electronic and inductive interactions between the substituent and the carbene center.[1] These interactions are expected to dramatically influence the lifetime, reactivity, and spectroscopy of the carbene. Fluorophenylsulfanylcarbene was recently generated and characterized in our group.[2] Because halogen atoms can significantly influence the chemical properties of carbenes,[3] we decided to focus our efforts on the parent phenylsulfanylcarbene in order to isolate the influence of the sulfur substituent. In general, carbenes with a single heteroatom substituent have not been widely studied by time-resolved spectroscopic methods because of the absence of convenient light-sensitive precursors. To our knowledge, the only carbene of this class (H-C-X) studied to date is chlorocarbene.[4] Herein, we report the synthesis and photochemistry of a new precursor **1** of phenylsulfanylcarbene **2** and contrast its properties with chlorocarbene and fluorophenylsulfanylcarbene.

The synthesis of precursor **1** is described in Scheme 1. Dihydroindan **4** was prepared by Birch reduction of indan **3** as described in the literature.[5] Addition of dibromocarbene generated from bromoform and potassium *tert*-butoxide in pentane allowed us to synthesize a 30/70 mixture of **5** and **6**. Even at low temperature, it is difficult to control the addition stoichiometry of the carbene to the diene. The mixture of the two adducts was then stirred in THF with 1 molar equiv (relative to **5**) of potassium *tert*-butoxide. Under basic conditions, compound **5** decomposes rapidly, allowing ready purification of **6**. Transformation of **6** into **7** is achieved by treatment with NBS/AIBN. After reduction to the mono bromo derivative **8** with tri-*n*-butyltin hydride, bromine lithium exchange was performed with *tert*-butyllithium at low temperature, allowing us to introduce the phenylsulfanyl group on the cyclopropane ring.

Photolysis (300 nm UV lamps) of a solution of **1** in neat tetramethylethylene (TME) for 18 h yielded the corresponding adduct **9** in 80% isolated yield. This demonstrates that diene **1** is an efficient light-activated precursor of carbene **2**

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[1] See, for instance: Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39 and references therein.

[2] Buron, C.; Tippmann, E. M.; Platz, M. S. *J. Phys Chem. A* **2004**, *108*, 1033.

[3] (a) Skell, P. S.; Garner, A. Y. *J. Am. Chem. Soc.* **1958**, *78*, 5430. (b) Doering, W. v. E.; Henderson, W. A., Jr. *J. Am. Chem. Soc.* **1958**, *80*, 5274. (c) Moss, R. A. *Carbene Chemistry. From Fleeting Intermediates to Powerful Reagents*; Bertrand, G., Ed.; FontisMedia S.A.: Lausanne, 2002; p 57.

[4] Robert, M.; Toscano, J. P.; Platz, M. S.; Abbot, S. C. Kirchoff, M. M.; Johnson, R. P. *J. Phys. Chem.* **1996**, *100*, 18426.

[5] Birch, A. J.; Walkerk, A. M. *Aust. J. Chem.* **1971**, *24*, 513.

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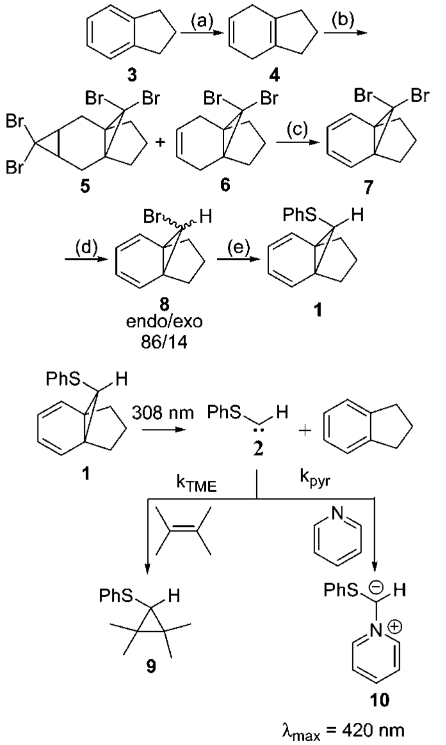
Scheme 1[a]



[a] (a) 90% (i) $Na_{(s)}/NH_{3(l)}$, −50 °C, (ii) MeOH; (b) $HCBr_3$, *t*-BuOK, pentane, −78 °C, 41%; (c) NBS, AIBN cat., cyclohexane, reflux, 3 h, 73%; (d) Bu_3SnH, Et_3B cat., O_2, C_6H_6, rt, 24 h, 73%; (e) 70% (i) *t*-BuLi 3 equiv, Et_2O, −100 °C, 20 min, (ii) PhSSPh.

in solution. This result is consistent with the work of Schöllkopf[6] and Saquet,[7] who generated **2** by treatment of $PhSCH_2Cl$ with butyllithium or sodium hydride, respectively. These groups reported that phenylsulfanylcarbene is efficiently intercepted by simple electron-rich alkenes.

Precursor **1** was studied by laser flash photolysis (LFP) techniques in several solvents, and the transient UV absorption was recorded just after (<10 ns) the laser pulse. No transient absorption was observed in the absence of pyridine between 350 and 550 nm. This result is consistent with time dependent density functional theoretical calculations (B3LYP/6-31 g(d)) that predict only weak vertical absorptions at 317 and 302 nm for carbene **2**.[8]

The transient UV spectra obtained in several solvents containing 7 mM pyridine are presented in Figure 1. We observed a broad absorption centered at 420 nm that is attributed to the pyridine ylide **10** by analogy to numerous other systems.[9]

Ylide **10** is formed in an exponential process after the laser pulse, which can be analyzed to yield the observed rate constant of ylide formation, k_{obs}. A plot (Figure 2) of the observed rate constant of ylide growth versus the concentration of pyridine is linear with a slope (k_{pyr}) of 2.5×10^8 M^{-1} s^{-1} and an intercept of $k_0 = 5.0 \times 10^5$ s^{-1} (Table 1) in $CF_2ClCFCl_2$ (Freon-113). This corresponds to a lifetime (τ) of phenylsulfanylcarbene **2** of 2 μs in deoxygenated Freon-113. Analogous LFP experiments were performed in deoxygenated heptane and showed a small decrease in the carbene lifetime and no change in the carbene reactivity toward pyridine, relative to Freon-113.

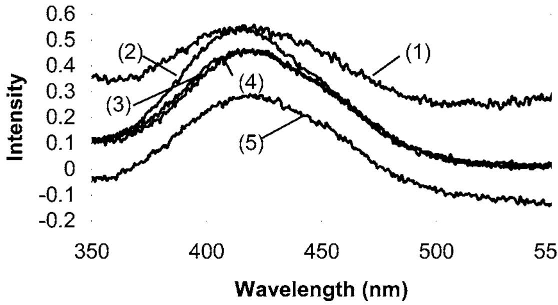


Figure 1. Transient UV spectra produced by LFP (308 nm) of **1** in deoxygenated solvents with 7 mM pyridine. The spectra were recorded immediately after the laser pulse over a window of 20 ns: (1) Freon-113; (2) cyclohexane; (3) tetrahydrofuran; (4) benzene; (5) acetonitrile.

In deoxygenated Freon-113 containing 7 mM of pyridine it is possible to resolve the growth of the ylide absorption at several concentrations of alkene trap (2,3-dimethyl-2-butene or tetramethylethylene TME). A plot of the observed rate constant of ylide formation versus the concentration of TME (constant pyridine concentration) is linear, allowing us to extract $k_{TME} = 8.9 \times 10^7$ M^{-1} s^{-1} in Freon-113 (Table 1).

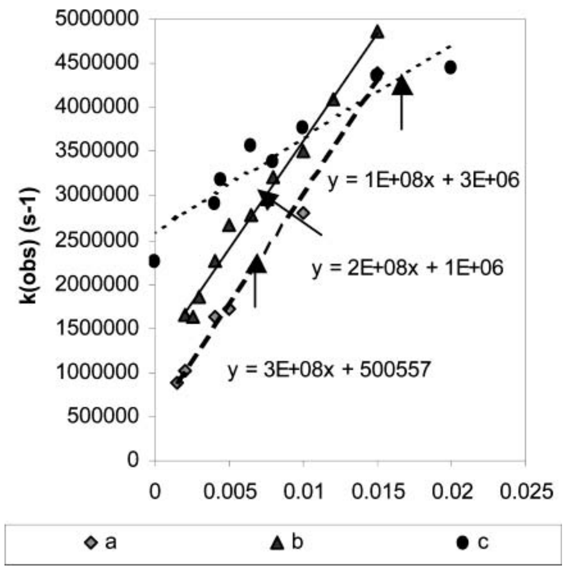


Figure 2. Plots of the observed rate constant of transient growth at 420 nm versus concentration of trapping agent produced by LFP (308 nm) of **1**: (a) trapping with pyridine in deoxygenated Freon-113; (b) trapping with pyridine in nondeoxygenated Freon-113; (c) trapping with 2,3-dimethyl-2-butene in deoxygenated Freon-113 containing 7 mM pyridine.

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[6] Schöllkopf, U.; Lehmann, G. J.; Paust, J.; Härtl, H.-D. *Chem. Ber.* **1964**, *97*, 7.

[7] Saquet, M. *C. R. Acad. Sci. Paris: C* **1972**, 283.

Table 1. Lifetime and Rate Constants of Carbene **2** with 2,3-Dimethyl-2-butene (TME) and Pyridine in Deoxygenated Freon-113 Containing 7 mM Pyridine

	PhSCH[b]	PhSCF[2]	ClCH[4]
τ ($CF_2ClCFCl_2$, Ar) ns	2000	2000	<20
τ ($CF_2ClCFCl_2$, air) ns	800		<20
k_{PYR}, M^{-1} s^{-1}	2.5×10^8	2.0×10^7	[a]
k_{TME}, M^{-1} s^{-1}	8.9×10^7	5.0×10^6 [b]	[a]
k_{AC}, M^{-1} s^{-1}	3.0×10^7	2.0×10^6	[a]
E(HOMO) eV[8,c]	−10.14	−10.74	−10.97
E(LUMO) eV[8,c]	2.26	2.09	0.97

[a] Lifetime too short to measure, but the bimolecular rate constant is likely ~10^9 M^{-1} s^{-1}; see text. [b] This work. [c] Orbital energies were calculated (HF 4-31G) as described by Rondan, N. G.; Houk, K. N.; Moss R.A, *J. Am. Chem. Soc.* **1980**, *102*, 1770 to maintain consistency with earlier studies. The carbene lone-pair is the HOMO of ClCH but is not the HOMO of PhSCH and PhSCF. To retain consistency with earlier work, we will use the energy of the carbene lone pair.

The carbene lifetime in aerated samples is shortened from 2.0 to 0.8 μs. This result is somewhat surprising, as singlet carbenes typically do not react rapidly with oxygen. This observation is not unprecedented, however, as Liu et al. have previously reported such behavior with *p*-nitrophenylchlorocarbene.[10] At the B3LYP/6-31G(d) level of theory singlet **2** is predicted to be 17.7 kcal/mol more stable than the corresponding triplet state of the carbene. Thus, it seems very unlikely that a small equilibrium quantity of triplet **2** is responsible for the observed reaction of phenylsulfanylcarbene with oxygen.

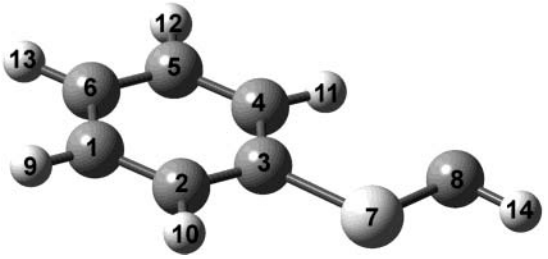

Figure 3. Optimized structure (B3LYP/6-31g(d)) of phenylsulfanyl carbene **2**. Calculated selected bond lengths: $d(C_8S_7) = 1.66$ Å; $d(C_8H_{14}) = 1.10$ Å; angle at the carbene carbon $S_7C_8H_{14} = 103.8°$.

Phenylsulfanylcarbene **2** is found to be a much longer-lived species than chlorocarbene, which has a lifetime of less than 20 ns in Freon-113 at ambient temperature.[4] This very short lifetime prevented measurement of its absolute rate constant of reaction with pyridine. It was possible to determine that $k_{TME}/k_{PYR} = 1.01$ in cyclohexane at ambient temperature. The absolute value of k_{PYR} was assumed to be 8.0×10^9 M^{-1} s^{-1} (average of the k_{PYR} values of chloromethyl-, chlorobenzyl-, and dichlorocarbene).[11] Therefore phenylsulfanylcarbene is also much less reactive toward pyridine and TME than chlorocarbene (Table 1).

These observations can be understood with the aid of DFT calculations.[8] The optimized structure of phenylsulfanylcarbene **2** is shown in Figure 3. A natural population analysis (NPA)[12] of carbene **2** and of chlorocarbene calculated at the same level of theory is shown in Table 2. This analysis clearly shows that there is substantial π back-bonding from sulfur to the carbene center. The C_8-S_7 bond length of 1.66 Å is much closer to that of a typical carbon−sulfur double bond (1.60 Å) than to that of a single bond (1.82 Å).[13] This leads to greater charge separation in the case of phenylsulfanylcarbene relative to chlorocarbene. The charge on the carbenic center is −0.54 (versus −0.15 for chlorocarbene). This explains in a simple way why PhSCH reacts more rapidly with methyl acrylate than does fluorophenylsulfa-

Table 2. Natural Population Analysis (B3LYP/6-31g(d)) for Phenylsulfanylcarbene, Fluorophenylsulfanylcarbene, and Chlorocarbene[a]

PhS-CH		PhS-CF		HCCl	
atom no.	natural charge	atom no.	natural charge	atom no.	natural charge
C1	−0.23	C1*	0.11	C1*	−0.15
C2	−0.23	F2	−0.33	Cl2	0.024
C3	−0.22	S3	0.33	H3	0.13
C4	−0.22	C4	−0.21		
C5	−0.22	C5	−0.23		
C6	−0.23	C6	−0.22		
S7	0.47	C7	−0.22		
C8*	−0.54	C8	−0.23		
H14	0.18	C9	−0.23		

[a] Asterisk denotes carbenic carbon.

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(8) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1998**, *37*, 785. (c) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, J. V.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998. (d) Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R. *J. Chem. Phys.* **1998**, *108*, 4439.

(9) Platz, M. S. In *Carbene Chemistry. From Fleeting Intermediates to Powerful Reagents*; Bertrand, G., Ed.; FontisMedia S.A.: Lausanne, 2002; p 27.

(10) Liu, M. T. H.; Bonneau, R.; Jefford, C. W. *Chem. Commun.* **1990**, *21*, 1482.

(11) (a) Liu, M. T. H.; Bonneau, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 6873. (b) Jackson, J. E.; Soundarajan, N.; Platz, M. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1988**, *110*, 5595. (c) Liu, M. T. H.; Bonneau, R. J. *J. Phys. Chem.* **1989**, *93*, 7298. (d) Liu, M. T. H.; Bonneau, R. J.; Rayez, M. T. *J. Am. Chem. Soc.* **1989**, *111*, 5973. (e) Jackson, J. E.; Soundarajan, N.; White, W.; Liu, M. T. H.; Bonneau, R. J.; Platz, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 6874. (f) Chateauneuf, J. E.; Johnson, R. P.; Kirehoff, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 3217.

(12) Reed, A. E.; Weinhold, F. A.; Curtiss, C. A. *Chem. Rev.* **1988**, *88*, 899.

(13) *CRC Handbook of Chemistry and Physics*; Lide, D. A.; CRC Press: Boca Raton, FL, 2003.

Table 3. HOMO−LUMO Separations of Three Carbenes with Tetramethylethylene and Methylacrylate in eV

	ClCH		PhSCH		PhSCF	
	p/π	π*/σ	p/π	π*/σ	p/π	π*/σ
TME	9.24	13.24	10.53	12.41	10.36	13.01
acrylate	11.69	11.77	12.98	10.44	12.81	11.54

nylcarbene, which has a charge of +0.11 on the carbene carbon according to an NPA analysis.

Although the NPA analysis explains why PhSCH is more nucleophilic than PhSCF, it does not explain why it is also more electrophilic than the fluoro analogue. Moss[14] has demonstrated that singlet carbene reactivities are best understood on the basis of frontier molecular orbital (FMO) interactions. Thus, the HOMO−LUMO orbital energies of chloro-, fluorophenylsulfanyl-, and phenylsulfanylcarbene were calculated (HF/6-31G). As stated by Moss,[14b] "What determines the carbene expressed philicity is whether, in the transition state, it is the $\mathrm{LUMO_{carbene}-HOMO_{alkene}}$ (p/π) electrophilic (E) orbital interaction or the $\mathrm{HOMO_{carbene}-LUMO_{alkene}}$ (σ/π^*) nucleophilic (N) interaction that is dominant." The relevant data can be found in Table 3.

The data predict that chlorocarbene is electrophilic because the p/π energy separation $\mathrm{LUMO_{carbene}-HOMO_{alkene}}$ (E) term is smaller and more favorable than the $\mathrm{HOMO_{carbene}-LUMO_{alkene}}$ (N) term with both TME and acrylate. However, both sulfur-substituted carbenes are expected to be ambiphilic because the electrophilic term is more favorable with TME, but the nucleophilic term is more favorable with acrylate.

In summary, we have synthesized a new light-sensitive precursor of phenylsulfanylcarbene **2**. Continuous photolysis of **1** in the presence of tetramethylethylene (TME) releases indan and carbene **2** as evidenced by the formation of the anticipated carbene−TME cyclopropane adduct. Laser flash photolysis (LFP) of precursor **1** fails to produce an observable transient spectrum of **2**, but LFP in the presence of pyridine produces an easily detected spectrum of the ylide. The lifetime and reactivity of carbene **2** was determined by the pyridine ylide technique. Phenylsulfanylcarbene is less reactive than chlorocarbene and is found to be ambiphilic. This is in agreement with a frontier orbital analysis as previously formulated by Moss.[14]

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Supporting Information Available: Optimized geometry, energy, zero-point correction, natural population analysis, IR frequencies, and TD-DFT of **2** and experimental details for synthesis of compounds **1** and **3**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] (a) Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58. (b) Moss, R. A. *Acc. Chem. Res.* **1989**, *22*, 15.