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Sulfur ylides generated from the reaction of adamantylidene and phenylcarbene with sulfur substrates

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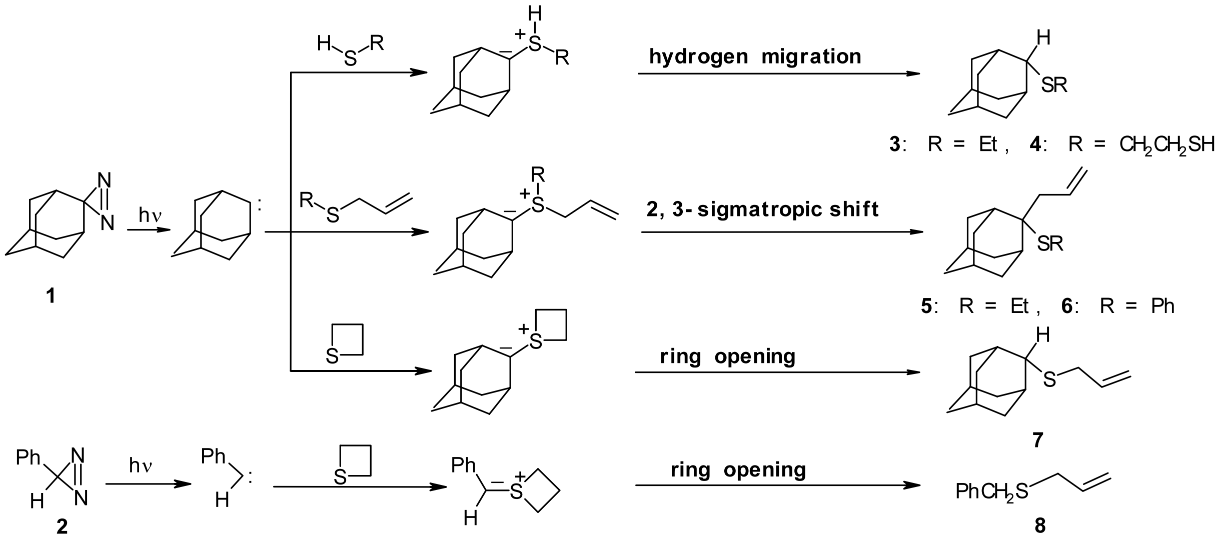
Abstract—Reaction of adamantylidene and phenylcarbene with ethylthiol, ethylene dithiol, allylethylsulfide, allylphenylsulfide, and trimethylenesulfide involves the formation of a sulfur ylide intermediate, followed by H-migration, 2,3-sigmatropic shift, or ring opening to give sulfides. The sulfur ylide formed in the reaction of phenylcarbene with trimethylenesulfide is directly observed by laser flash photolytic techniques.

Sulfur ylides are increasingly useful intermediates in synthetic organic chemistry. Their chemistry has been thoroughly reviewed in a number of monographs and reviews.[1] The generation of sulfur ylides from carbenes and sulfur containing organic compounds is a useful alternative to widely employed base-promoted methodology.[1] Recently we reported the reaction of arylchlorocarbene with trimethylenesulfide (TMSF) which gives a mixture of two thioacetals via a sulfur ylide intermediate.[2] Herein we report the photochemistry of 2-adamantane-2,3′-[3*H*]-diazirine **1** and 3-phenyldiazirine **2** and the reactions of the photogenerated carbenes with a number of sulfur containing organic compounds. In addition, the intervention of a sulfur ylide in the reaction of phenylcarbene with TMSF is demonstrated by laser flash photolytic (LFP) techniques.



Scheme 1.

Keywords: diazirine; carbene; adamantylidene; sulfur ylide; trimethylenesulfide; kinetics; laser flash photolysis.

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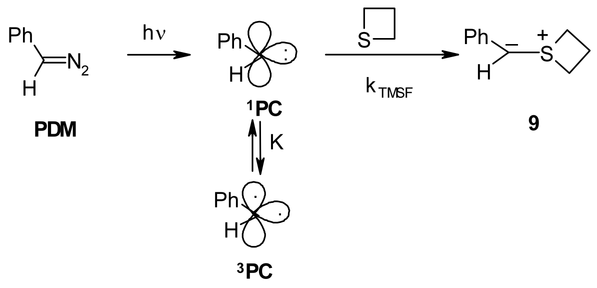

Scheme 2.

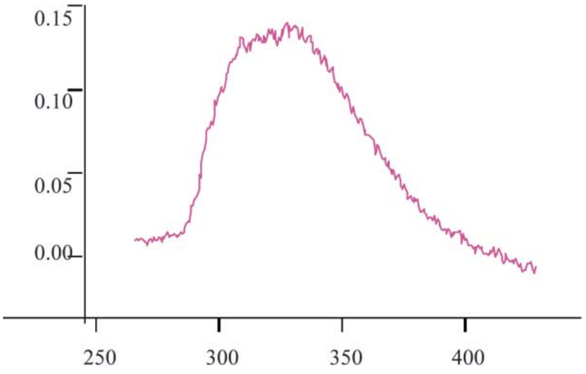

Figure 1. The transient absorption spectrum of the ylide **9** formed upon reaction of ^{1}PC with TMSF.

We prepared diazirine **1** from 2-adamantanone[3] and diazirine **2** from benzaldehyde.[4] We photolyzed (350 nm) solutions of diazirine **1** (1 mmol) in the presence of either ethylthiol or ethylene dithiol (10 mmol) in 10 mL of *i*-octane at 25°C for 24 h. After the work-up, we isolated sulfides **3** (85% yield) and **4** (65% yield) by column chromatography on silica gel with eluent hexane/ether = 10:1. We suggest that the reaction of adamantylidene (Ad:) with thiols involves formation of the sulfur ylide followed by H-migration to give sulfides **3** or **4** (Scheme 1).

Similarly, photolysis of diazirine **1** in *i*-octane in the presence of ethyl- and phenylallylsulfides yielded sulfides **5** (57% yield) and **6** (52% yield). The sulfide **6** could not be separated from allylphenylsulfide by column chromatography, and the NMR spectrum of the mixture was recorded. In this case, the formation of sulfur ylide is followed by 2,3-sigmatropic shift to yield the final product. Photolysis of diazirine **1** in the presence of TMSF leads to the formation of a sulfur ylide followed by ring opening to yield sulfide **7** (46% yield). Finally, irradiation of a solution of diazirine **2** and TMSF in *i*-octane leads to allylbenzylsulfide **8** (10% yield), similar to the product isolated from the reaction of chlorocarbenes with TMSF[2] (eluent hexane/ether = 95:5 was used). Selected physical data of sulfides **3**–**8** are provided.[5]

LFP (308 nm, 17 ns) of phenyldiazomethane (PDM) in Freon-113 produces singlet phenylcarbene (^{1}PC) in rapid equilibrium with the ground triplet state (^{3}PC)[6] (Scheme 2), which has no significant absorption above 300 nm.[6,7] LFP in the presence of TMSF produces a new transient signal with $\lambda_{max} = 340$ nm (Fig. 1). The transient is assigned to ylide **9**, which has a lifetime longer than 10 µs.

Ylide **9** is formed after the laser pulse in an exponential process (Fig. 2) which was analyzed to yield observed rate constant k$_{OBS}$. The value of k$_{OBS}$ is linearly dependent on the concentration of TMSF. The slope of this plot (Fig. 3) is 4.2×10^7 M^{-1} s^{-1} which in the context of Scheme 2 is equal to k_{TMSF} K. Chlorophenylcarbene (^{1}CPC) has a singlet ground state which reacts with TMSF with rate constant 8.9×10^9 M^{-1} s^{-1}.[2] Assuming

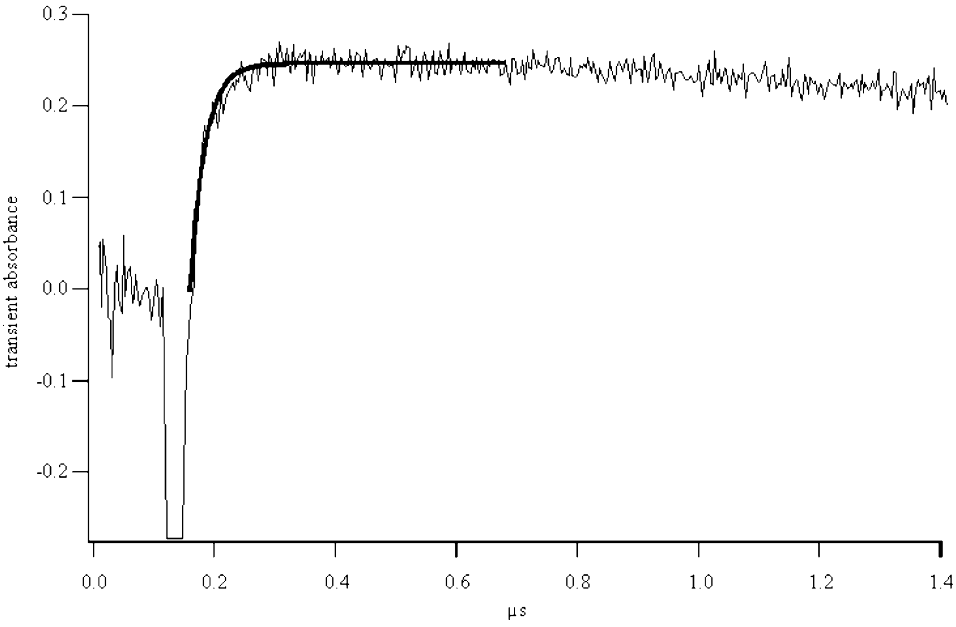

Figure 2. The formation of PhCH–TMSF ylide **9** (349 nm) following LFP of PDM in Freon-113 containing trimethylenesulfide.

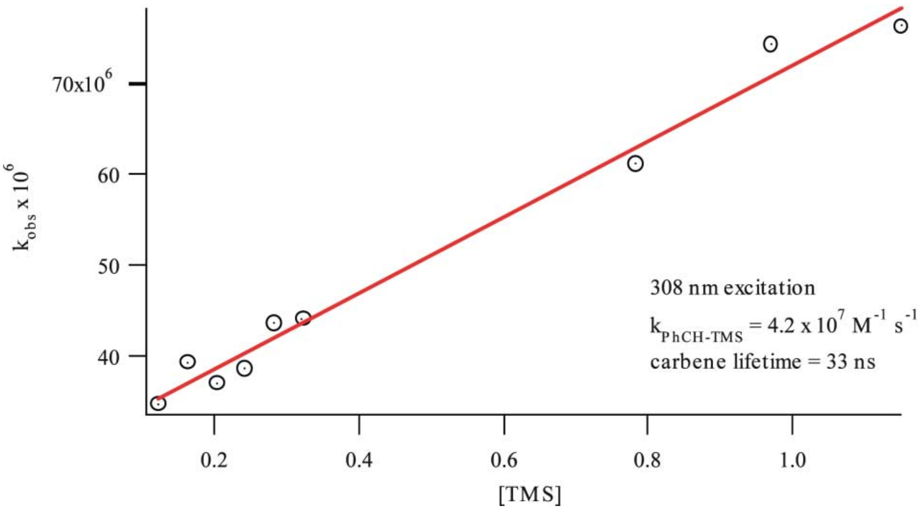

Figure 3. The observed rate constant of formation of PhCH–TMSF ylide **9**, as a function of TMSF concentration, monitored at 349 nm in Freon-113.

that singlet ^{1}PC and ^{1}CPC react with TMSF with comparable rate constants leads to the deduction that $K = 0.0048$ and $\Delta G_{298°K} = 3.2$ kcal/mol in favor of the triplet state. This is consistent with previous estimates.[6,7]

In summary, the photolysis of adamantylidene and phenylcarbene in the presence of ethylthiol, ethylene dithiol, allylethylsulfide, allylphenylsulfide, and TMSF proceeds via the formation of a sulfur ylide as an intermediate, followed by H-migration, 2,3-sigmatropic shift, or ring opening to give sulfides. The existence of the sulfur ylide in the reaction of phenylcarbene with TMSF has also been demonstrated by laser flash photolytic techniques.

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5. For **3**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.27 (3H, t, $J = 7$ Hz), 1.50–1.61 (2H, m), 1.71–2.01 (10H, m), 2.10–2.20 (2H, m), 2.55 (2H, t, $J = 7$ Hz), 3.07 (1H, s). ^{13}C NMR (300 MHz, CDCl$_3$): 15.496, 26.026, 27.842, 28.095, 32.401, 33.655, 38.157, 39.146, 53.084.
   For **4**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.37 (1H, t, $J = 8$ Hz), 1.5–1.6 (2H, m), 1.7–2.0 (10H, m), 2.1–2.2 (2H, m), 2.63 (2H, t, $J = 7$ Hz), 2.64 (2H, t, $J = 7$ Hz), 3.035 (1H, s). ^{13}C NMR (300 MHz, CDCl$_3$): 23.985, 27.804, 28.068, 30.462, 32.356, 33.671, 34.185, 38.114, 39.119, 53.582.
   For **5**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.22 (3H, t, $J = 7$ Hz), 1.50–1.60 (2H, m), 1.61–1.91 (10H, m), 2.01–2.12 (2H, m), 2.38 (2H, t, $J = 7$ Hz), 2.51–2.63 (2H, m), 5.06–5.16 (2H, m), 5.97–6.13 (1H, m). ^{13}C NMR (300 MHz, CDCl$_3$): 14.488, 20.477, 27.906, 28.129, 33.291, 33.799, 34.730, 39.198, 39.830, 56.392, 116.673, 135.400.
   For **6**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.64–2.11 (12H, m), 2.40–2.46 (2H, m), 2.80–2.91 (2H, m), 5.08–5.22 (2H, m), 6.23–6.41 (1H, m), 7.19–7.54 (5H, m).
   For **7**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.50–1.60 (2H, m), 1.70–1.98 (10H, m), 2.09–2.19 (2H, m), 3.02 (1H, s), 3.15 (2H, d, $J = 7$ Hz), 5.01–5.14 (2H, m), 5.72–5.89 (1H, m). ^{13}C NMR (300 MHz, CDCl$_3$): 27.802, 27.807, 28.088, 32.595, 33.448, 34.864, 38.170, 39.061, 51.908, 116.698, 135.526; m/z 208, 166, 135.
   For **8**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.05 (2H, d, $J = 7$ Hz), 3.68 (2H, s), 5.05–5.15 (2H, m), 5.7–5.9 (1H, m), 7.1–7.3 (5H, m).
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