

Communications to the Editor

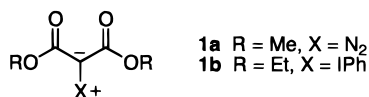
A Phenyliodonium Ylide as a Precursor for Dicarboethoxycarbene: Demonstration of a Strategy for Carbene Generation

Margaret B. Camacho, Aurora E. Clark,
Tabitha A. Liebrecht, and JoAnn P. DeLuca*

Department of Chemistry
Central Washington University
Ellensburg, Washington 98926-7539

Received January 31, 2000
Revised Manuscript Received April 4, 2000

Thermal or photochemical decomposition of carbene precursors, especially diazocompounds and diazirenes, leads in many cases to both a free carbene intermediate and products formed directly from the precursor.^{1,2} This ability of precursors to mimic carbenes often complicates mechanistic studies. For example, direct photolysis of dimethyl diazomalonate (**1a**) leads to products stemming from reactions of substrate with ¹C(CO₂Me)₂, ³C(CO₂Me)₂, and photoexcited **1a** (**1a***) as outlined in Scheme 1.³ In situations such as this, alternative modes of carbene generation have proved valuable in characterizing the reactive species.⁴ Here we describe a strategy for identifying new carbene precursors and report the facile generation of ¹C(CO₂Et)₂ by thermal decomposition of iodonium ylide **1b**, as well as a supporting computational study.



Reaction with compounds containing atoms with unshared electron pairs to produce ylides is one of the typical reactions of singlet carbenes (eq 1).⁵ If reversible, this reaction might be useful



as a source of carbenes. Inspection of eq 1 leads to the prediction that the weaker the carbene–nucleophile bond, the more likely that thermal, and possibly photochemical, decomposition of the ylide will lead to free carbenes without intervention of masquerading precursors.

Iodonium ylides have been shown to decompose under thermal, photochemical, and catalytic conditions to give products consistent

(1) (a) Frey, H. M.; Stevens, I. D. R. *J. Chem. Soc.* **1965**, 3101. (b) Mansoor, A. M.; Stevens, I. D. R. *Tetrahedron Lett.* **1966**, 1733. (c) Chang, K.-T.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 5082. (d) Chambers, G. R.; Jones, M., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 4516. (e) Modarelli, D. A.; Morgan, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 7034.

(2) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971.

(3) (a) Jones, M., Jr.; Ando, W.; Hendrick, M. E.; Kulczycki, A.; Howley, P. M.; Hummel, K. F.; Malament, D. S. *J. Am. Chem. Soc.* **1972**, *94*, 7469. (b) Wulfman, D. S.; Poling, B.; McDaniel, R. S., Jr. *Tetrahedron Lett.* **1975**, 4519. (c) Wang, J.-L.; Toscano, J. P.; Platz, M. S.; Nicolaev, V.; Popik, V. *J. Am. Chem. Soc.* **1995**, *117*, 5477.

(4) See, for example: (a) Chen, N.; Jones, M., Jr.; White, W. R.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 4981. (b) Fox, M. J.; Scacheri, J. E. G.; Jones, K. G.; Jones, M., Jr.; Shevlin, P. B.; Armstrong, B.; Szyrbicka, R. *Tetrahedron Lett.* **1992**, *33*, 5021. (c) Armstrong, B. M.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 3685. (d) Nigam, M.; Platz, M. S.; Showalter, B. M.; Toscano, J. P.; Johnson, R.; Abbot, S. C.; Kirchoff, M. M. *J. Am. Chem. Soc.* **1998**, *120*, 8055.

(5) Padwa, A.; Hornbuckle, S. F. *Chem. Rev.* **1991**, *91*, 263.

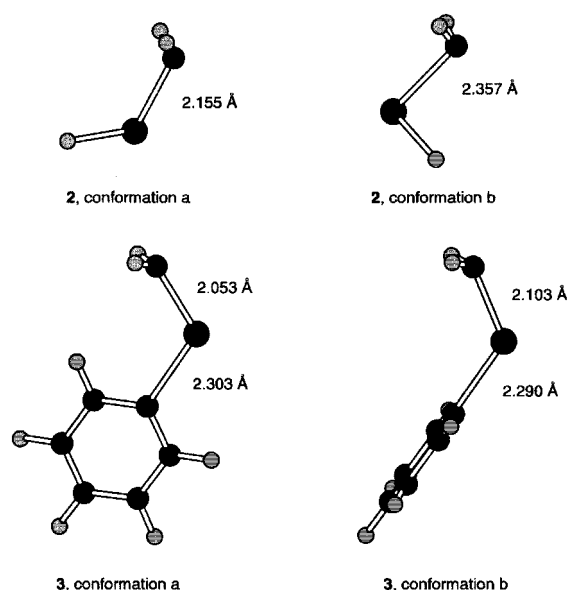
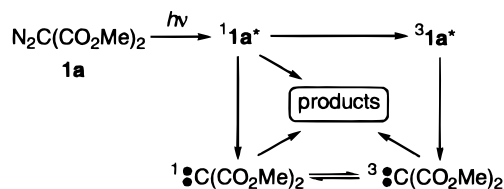


Figure 1. B3LYP/LANL2DZ optimized structures.

Scheme 1



with carbene, or at least carbenoid, intermediates,⁶ yet they have not previously been exploited as sources of true carbenes. Although they are known to be less stable than the analogous diazonium ylides, no information is available concerning the strength of the carbene–nucleophile bond in iodonium ylides. Paying particular attention to these ylides vs diazo compounds as sources of free carbenes, we have started to carefully characterize the photochemical and thermal decompositions of selected iodonium ylides through both computational and laboratory studies.

As the first step in the computational study, structures were calculated for N₂–CH₂, HI–CH₂ (**2**) and PhI–CH₂ (**3**), using the B3LYP density functional method⁷ and LANL2DZ basis set,⁸ and the Gaussian 94 software package.⁹ Two stable conformations were found for both HI–CH₂ and PhI–CH₂ and were confirmed as minima through calculation of vibrational frequencies. The calculated structures and selected bond distances are shown in Figure 1. The C–I bond distance in the more stable conformation of HI–CH₂ is shorter than the C–I bond distance calculated for

(6) Stang, P. J.; Zhdankin, V. V. *Chem. Rev.* **1996**, *96*, 1123.

(7) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(8) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.

(9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94* (Revision E.2); Gaussian, Inc.: Pittsburgh, PA, 1995.

Table 1. Relative Energies (kcal/mol) Calculated at the B3LYP/LANL2DZ Level of Theory

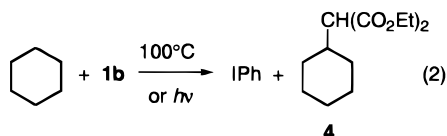
	E_{rel}^a	H_{rel}°		E_{rel}^a	H_{rel}°
HI-CH ₂ (2 , conf a)	0.0	0.0	HI + CH ₂ -N ₂	0.0	0.0
HI-CH ₂ (2 , conf b)	6.0	6.2	2 , conf a + N ₂	44.1	44.2
PhI-CH ₂ (3 , conf a)	0.0	0.0	PhI + CH ₂ -N ₂	0.0	0.0
PhI-CH ₂ (3 , conf b)	0.3	0.3	3 , conf a + N ₂	37.6	38.5

^a Total electronic energies were corrected for zero-point energies scaled by a factor of 0.9806. See: Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

CH₃I (2.19 Å) at the B3LYP/LANL2DZ level. The distance between the carbon atom of the CH₂ fragment and the iodine atom in PhI-CH₂ is also shorter than the C-I distance in CH₃I. These shorter C-I bond distances are consistent with some double bond character in the ylide C-I bonds. The phenyl C-I bond distance in PhI-CH₂ is longer than the C-I distance calculated for iodobenzene, possibly indicating less interaction between the phenyl π -system and the iodine substituent.

To compare the strength of the carbene-nucleophile bonds, the energy changes associated with transfer of the CH₂ fragment from HI or PhI to N₂ were calculated (Table 1).¹⁰ Both reactions were calculated to be exothermic with over 35 kcal/mol released. The bond dissociation energy for the C-N bond in CH₂N₂, calculated using experimental heats of formation, is 50 kcal/mol.^{10b} The thermal decomposition of the iodonium ylides to give carbenes should be facile, requiring an enthalpy change of no more than 15 kcal/mol. Properties of the excited states have not been calculated, but it is plausible that decomposition of photoexcited iodonium ylides might be very rapid. Our prediction and the computational results point to iodonium ylides as potential carbene precursors.

In the laboratory, ylide **1b** was prepared by the reaction of iodobenzene diacetate, diethyl malonate, and base, followed by recrystallization from benzene/hexane, and stored in the freezer.¹¹ Ylide **1b**, rather than the dimethyl ester, was chosen because of its greater solubility in hydrocarbon solvents. Ylide **1b** was still only sparingly soluble in alkane solvents at room temperature, yet dissolved readily at 100 °C to give a pale yellow solution that became colorless as **1b** decomposed. Heating a stirred mixture of **1b** and cyclohexane in a sealed tube at 100 °C for 45 min produced iodobenzene and C-H insertion product **4** as the major products (eq 2), consistent with the formation of either ¹C(CO₂-



Et)₂ or ³C(CO₂Et)₂ as reaction intermediate(s).² Iodobenzene was produced in 80% of the theoretical yield and **4** was produced in 46% of the theoretical yield, as determined from a ¹H NMR spectrum of a crude product mixture to which diethyl fumarate had been added as a standard. Photolysis (450W Hanovia Hg lamp, Pyrex, 45 min) of a stirred suspension of **1b** in cyclohexane led to formation of iodobenzene in 77% yield.¹² Product **4** was produced in very low yield (<2% of theory). The low yield of **4** may result from the low solubility of **1b** in cyclohexane at room temperature. Analysis by GC/MS indicates substantial amounts of carbene dimer, possibly produced by attack of a carbene

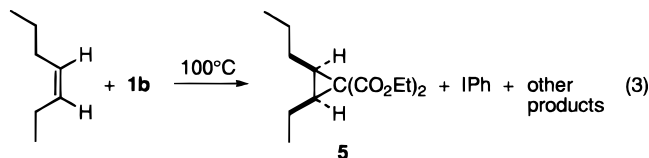
(10) (a) Heats of reaction (kcal/mol) calculated at the B3LYP/LANL2DZ level compare reasonably well with those calculated using experimental heats of formation. CH₂N₂ + CH₃I → CH₃CH₂I + N₂, -51 (calcd) vs -55 (exptl). CH₂N₂ + CH₄ → CH₃CH₃ + N₂, -48 (calcd) vs -52 (exptl). (b) Experimental heats of formation from Mallard, W. G., Ed. *NIST Chemistry WebBook*; <http://www.nist.gov/chemistry/>.

(11) (a) Neiland, O.; Karele, B. *J. Org. Chem. USSR (Engl. Transl.)* **1965**, *1*, 1854. (b) Schank, K.; Lick, C. *Synthesis* **1983**, 392.

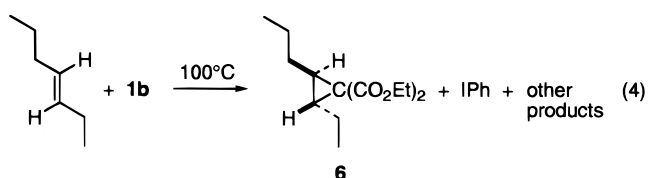
(12) Ylide **1b**, λ_{max} = 280 nm in benzene solution.

intermediate on **1b**. Iodocyclohexane is also formed, possibly by radical reactions stemming from a triplet carbene or cleavage of C-I bonds.

The reaction with 3-heptene was used to examine the spin state of the intermediates. Heating a mixture of **1b** and *cis*-3-heptene led to formation of iodobenzene and cyclopropane **5** as well as several minor products (eq 3). Heating a mixture of **1b** and *trans*-



3-heptene led to formation of iodobenzene, cyclopropane **6**, and several minor products (eq 4). For both reaction mixtures GC/



MS analysis of the minor products was consistent with the structures of the anticipated products of C-H insertion. GC analysis showed that compound **5** accounted for less than 1% of the cyclopropanated products when **1b** was heated with *trans*-3-heptene, and **6** accounted for only 2% of the cyclopropanes when **1b** was heated with *cis*-3-heptene. The very high degree of stereospecificity indicates cyclopropanation of the double bond by a singlet carbene, with cyclopropanation faster than intersystem crossing to the more stable carbene triplet state.²

Photolysis of a mixture of **1b** and *cis*-3-heptene produced low yields of cyclopropanes **5** and **6** in the ratio 34:66. Photolysis of **1b** and *trans*-3-heptene led to cyclopropanes **5** and **6** in the ratio 22:78. Since results of thermal decomposition indicate that reaction of singlet carbene with the alkene is faster than intersystem crossing under these conditions, photoexcited **1b** is the intermediate that likely undergoes intersystem crossing and leads to triplet carbene (see Scheme 1). In comparison, Jones et al. found that about 10% of the "wrong" isomer was formed when **1a** was irradiated in alkene solution.^{3a} The greater extent of nonstereospecific reaction seen in direct photolysis of **1b** is probably a result of more efficient intersystem crossing due to the presence of the iodine atom (heavy atom effect).¹³

As predicted on the basis of our hypothesis and calculation of bond dissociation energies for model ylides, thermal decomposition of **1b** under mild conditions appears to be an efficient source of ¹C(CO₂Et)₂, uncontaminated by ¹b* or ³b*. Further explorations of the reactivity of ¹C(CO₂Et)₂, produced from **1b**, vs the intermediates produced from **1a** are in progress. We are also applying this strategy to the identification of other carbene precursors.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Camille and Henry Dreyfus Foundation, the M. J. Murdock Trust, and Central Washington University for financial support.

JA0003340

(13) Bartrop, J. A.; Coyle, J. D. *Excited States in Organic Chemistry*; John Wiley & Sons: New York, 1975.