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A surprising rearrangement of a carbene–ethylene sulfide ylide

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Abstract

Photolysis of 2-methoxy-2-methyl-5,5-dipropyl-Δ^3-1,3,4 oxadiazoline in methylene chloride produces 4 diazoheptane which can undergo secondary photolysis to form dipropylcarbene. Dipropylcarbene reacts with ethylene sulfide to form a ylide which rearranges to form a vinyl sulfide. Calculations indicate that this rearrangement is a concerted and asynchronous process in the gas phase.

For years chemists believed that the lifetimes of dialkylcarbene were so short (femtoseconds) as to preclude their chemical interception. Recent kinetic[1] and theoretical studies[2] demonstrate that dimethylcarbene has a lifetime of several ns indicating that it should have useful bimolecular chemistry. This has prompted recent chemical trapping studies[3] and this study of dipropylcarbene. We expected to trap this carbene with ethylene sulfide to form a ylide. The results of this study are reported below.

Warkentin et al. have demonstrated that photolysis of oxadiazolines efficiently forms dialkyldiazo compounds.[4] These compounds are sensitive and difficult to isolate and handle as pure substances despite recent improvements in methodology.[5] Nevertheless, they persist in alkane solvents and can be characterized by IR and UV–vis spectroscopy and intercepted with chemical traps.[4,5] Under suitable conditions, the dialkyldiazo compounds generated from oxadiazolines can be photolyzed to form dialkylcarbenes.

2-Methoxy-2-methyl-5,5-dipropyl-Δ^3-1,3,4 oxadiazoline **1** (0.06 M) was photolyzed in methylene chloride at 4°C (2 h, Ray-O-Net, 300 nm, quartz) containing 0.56 M ethylene sulfide. Azine **2** (derived from diazo compound **3**) was the major product (51% yield of volatiles).[6] Other volatile compounds include, *E*- and *Z*-3-heptene (15%) and 4-heptanone (11%) formed by fragmentation of **1** to form the putative methoxy diazoethane. Vinyl sulfide **4** was formed in 13% relative yield.[7]

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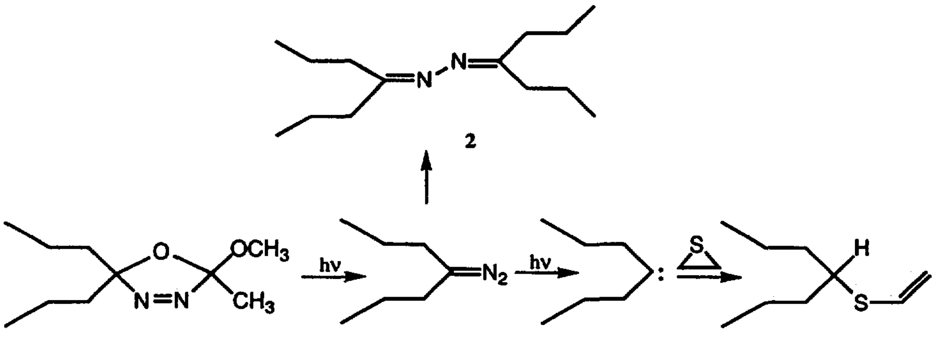
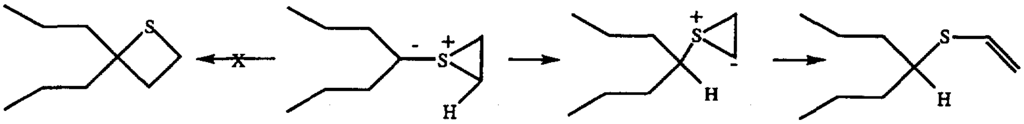


2

1 3 DPC 4

We propose that dipropylcarbene (DPC) reacts with ethylene sulfide to form ylide **5**. A 1,2-proton shift forms a type of ylide (e.g. **6**) which has been generated previously by Robson and Shechter,[8] Kondo and Ojima[9] and Wenkert et al.[10] Ylides of this type are known to rearrange to give vinyl sulfides. To our surprise, there was no trace of **7** formed in the reaction mixture, although we cannot rule out the possibility that it is unstable under our reaction conditions.



7 5 6 4

To better appreciate this reaction, the rearrangement of $\mathbf{5} \rightarrow \mathbf{6} \rightarrow \mathbf{4}$ was studied by ab initio molecular orbital calculations of the reaction of parent methylene with ethylene sulfide using the Gaussian 94 software package.[11] All stationary points were checked by a Hessian calculation. Geometries were optimized using the B3LYP[12] and MP2 methods with the 6-31G* basis set.[13]

Methylene compound **8** is a minimum at the HF/6-31G*, MP2/6-31G*, B3LYP/6-31G* and CASSCF (4,4)/6-31G* levels of theory. However, at the MP2 and B3LYP levels of theory, the C–S bond lengthens and the C–S bond between sulfur and the acyclic methylene shortens to form a structure which resembles a complex of $CH_2{=}S$ and $CH_2{=}CH_2$ (type A). The CASSCF (4,4) method[15] predicts a ylide structure for the related methylene–water ylide[14] and CASSCF (4,4) calculations of **8** using the two highest occupied and two lowest unoccupied orbitals predicts the type B ylide like structure of **8** shown in Figs. 1 and 2. The energies computed at the MP2 and B3LYP levels at the CASSCF geometry are given in Fig. 2. Any error in this approach will, of course, have no influence on the computed differential activation energy for the competitive formation of **4** versus **7** from ylide **8**.

As shown in Fig. 2, ylide **8** has a slight preference ($\Delta\Delta Ea=4.1$ kcal/mol at MP2/6-31G* and 2.1 kcal/mol at B3LYP/6-31G* including zero point vibrational energy correction) for isomerization to vinyl sulfide **9** rather than for ring expansion to thietane **10** in the gas phase. Isomerization of ylide **8** to ylide **11** is rate determining in the gas phase. In fact, the barrier to isomerization of ylide **11** to vinyl sulfide **9** is so close to zero that the predicted overall reaction of **8** to **9** may be considered concerted and asynchronous. However, solvation should stabilize **8** and **11** substantially more than the transition states and may change the timing of the rearrangement steps in solution.

In conclusion, photolysis of oxadiazoline **1** generates 4-diazoheptane in situ which itself is photolyzed to form dipropylcarbene. The carbene can be trapped with ethylene sulfide to form a ylide which isomerizes to form a vinylsulfide. Calculations predict that this is a concerted process in the gas phase.

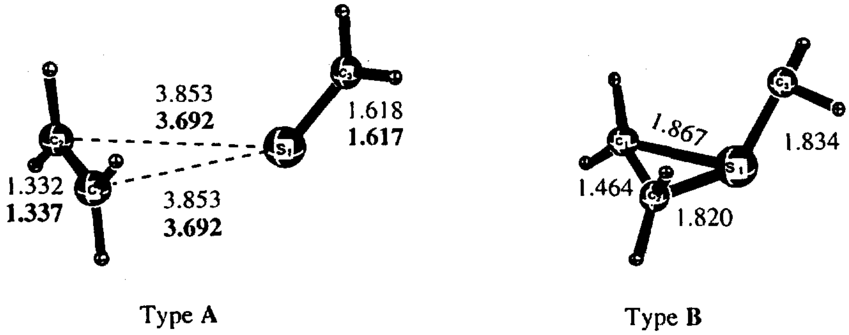


Figure 1. Calculated minimum energy structures of compound 8. The type A structure is optimized at B3LYP/6-31G* and MP2/6-31G* levels and the bold number is from the MP2/6-31G* calculation. The type B structure is found using CASSCF (4,4)/6-31G*. Bond distances are listed in Å

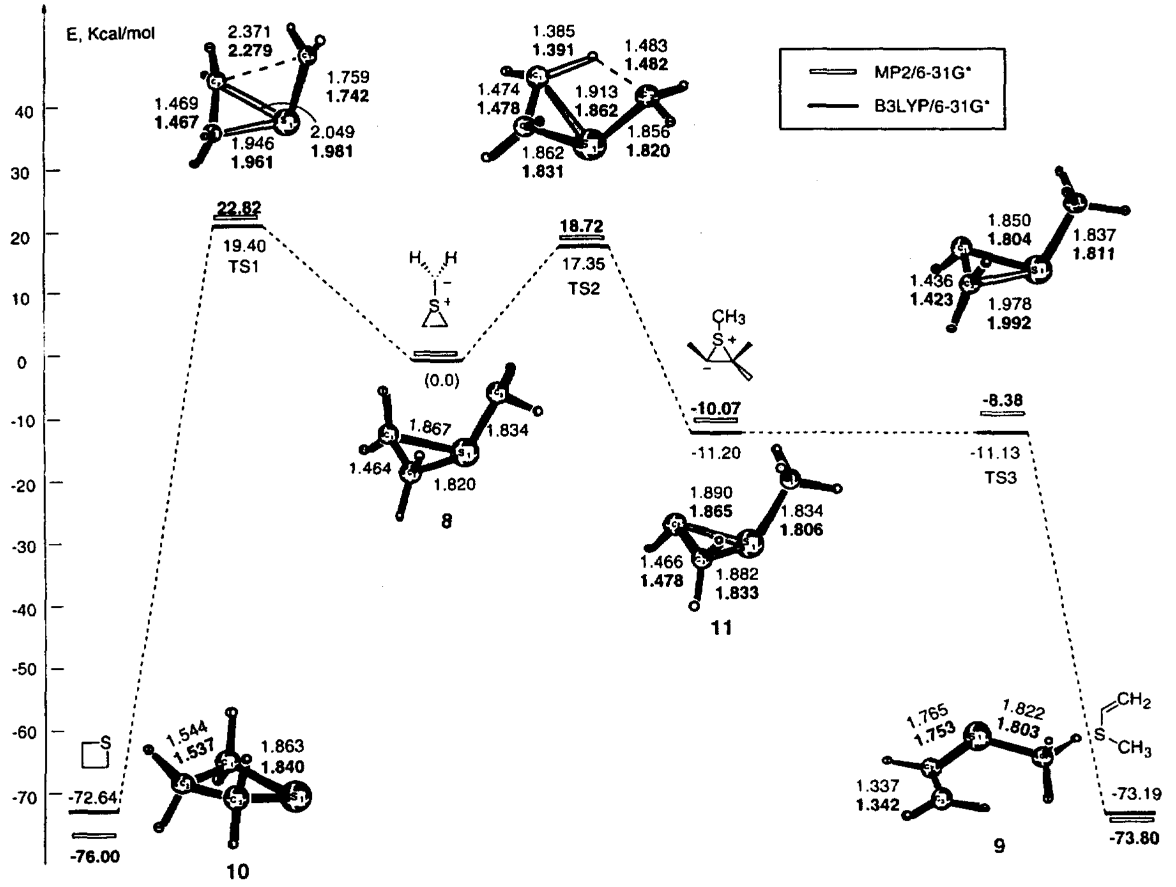


Figure 2. The structures and relative energies of the rearrangement reaction are calculated at the B3LYP/6-31G* and MP2/6-31G* levels of theory. The ZPVE correction is included. Bold numbers are from MP2/6-31G*. The black bar is from B3LYP/6-31G*. The geometry of ylide 8 was optimized at the CASSCF(4,4)/6-31G* level. This geometry was used in a single point energy calculation using the B3LYP/6-31G* and MP2/6-31G* methods

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6. Photolysis experiment: 0.06 M of oxadiazoline **1** in dichloromethane at 4°C was photolyzed with 0.56 M of ethylene sulfide. The sample was degassed by purging with oxygen-free argon for 3 min then irradiated with sixteen 300 nm bulbs in a Ray-O-Net reactor for 2 h. Product analyses were performed using an HP-6890 Series GC System with an HP-methyl siloxane capillary column (40.0 m×100 μm×0.20 μm). The initial column temperature was 100°C and was raised 25°C/min to 250°C. The gas chromatograph was linked to an HP 5973 Mass Selective Detector. The retention times of *E,Z*-3-heptene, 4-heptanone, vinyl sulfide and azine were 5.17, 5.23, 6.82, 8.13 and 11.50 min. The relative yield of volatile products obtained upon decomposition of oxadiazoline **1** was measured by integration of peaks in the gas chromatograms.
7. 4-Heptylvinylsulfide **4**: oxadiazoline **1** (0.019 g, 0.095 mmol) and ethylene sulfide (0.04 g, 0.67 mmol) in cyclohexane (1.45 mL) were added to a cuvette. It was photolyzed with 300 nm light for 2 h. The mixture was chromatographed (silica, hexane). ^{1}H NMR (200 MHz, $CDCl_3$, ppm) 6.47 (dd, 1H, J=280, 160 Hz) 5.25 (dd, 2H, J=260, 140 Hz), 2.83 (q, 1H, J=100 Hz), 1.55 (m, 4H), 1.32 (m, 4H), 0.87 (m, 6H); ^{13}C NMR (63 MHz, $CDCl_3$, ppm) 132.0, 111.8, 46.7, 37.2, 20.0, 14.1; MS (EI) *m/z* (rel. intensity) 158 (M, 38), 98 (22), 69 (19), 57 (100), 41 (34).
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