# The Photochemistry of Sulfur Analogues of Dialkyldiazomalonates

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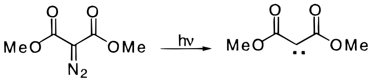
Laser flash photolysis studies (LFP) of *O,S*-diethylmonothiodiazomalonate (**1**) and *S,S*-diethyldithiodiazomalonate (**2**) in 1,1,2-trichlorotrifluoroethane (Freon-113) were consistent with the trapping of an intermediate with $\lambda_{max} = 425$ nm, attributed, in the LFP of **1**, to that of ylide **10**, formed from the reaction of singlet *O,S*-carboethoxythioethoxycarbene **(9)** with pyridine. The deduced lifetime of both singlet *O,S*-dicarboethoxycarbene (**9**) and *S,S*-dicarbothioethoxycarbene (**13)** are essentially the same in Freon-113, but compared to dicarbomethoxycarbene **14**, the lifetimes of **9** and **13** were found to be about six times shorter. The LFP studies, in addition to calculations at the B3LYP/6−31 G* level of theory, provide an explanation for the effect of sulfur perturbation that shortens the carbene lifetimes, as well as an explanation for the exclusive migration of the SEt group to ultimately form **5** upon light (300 nm) induced nitrogen extrusion and Wolff rearrangement of **1** in EtOH.

## I. Introduction

Diazomalonates have a significant role in organic synthesis, and the nature of the intermediates generated from the photolysis, thermolysis, and metal-catalyzed decomposition of these compounds has been of considerable interest to physical-organic chemists.[1] The photochemistry of dimethyldiazomalonate, for example, has been investigated by traditional chemical methods,[2] and recently in our laboratory by time-resolved laser flash photolysis (LFP) techniques.[3]



The combination of classical and contemporary techniques has shown that the photochemistry of dimethyldiazomalonate is not derived merely from singlet dicarbomethoxycarbene, as excited states of dimethyldiazomalonate may give products that formally appear to be derived from dicarbomethoxycarbene. There is considerable evidence that strongly suggests that precursor excited states are involved in many photochemical reactions.[4]

Because of our continued interest in the study of the photochemistry of α-diazo carbonyl compounds,[3,5] and because of an interest in how heteroatom perturbation affects the photochemistry of dialkyldiazomalonates,[6] we herein report the photochemistry of *O,S*-diethylmonothiodiazomalonate (**1**), and *S,S*-diethyldithiodiazomalonate (**2**) (Scheme 1).

## II. Experimental Section

**General Procedures: Synthesis.** All reactions were conducted in flame-dried glassware under an argon atmosphere. Solvents were dried prior to use by standard techniques. Reagents purchased from Aldrich were used as received. Proton NMR spectra were recorded at 300 MHz in $CDCl_3$ using the 7.26 ppm of residual $CHCl_3$ as the reference peak. FT IR spectra were recorded as $CCl_4$ solutions between NaCl plates, and GC/MS data were recorded at an ionizing voltage of 70 eV. Where mass spectral data are given, the peak abundance immediately follows in parentheses.

*O,S-Diethylmonothiomalonate (3)*: To 12.0 mL of EtSH was added 7.05 g (46.9 mmol) of ethyl malonyl chloride. The solution was stirred at 35 °C for 1 h, cooled to ambient temperature, and the excess EtSH was removed by rotary evaporation. Fractional vacuum distillation gave 7.5 g of **3** (bp = 78−80 °C, 2.5 Torr) as a clear, colorless liquid. H NMR: 1.24−1.29 (t, 3 H), 1.25−1.30 (t, 3 H); 2.89−3.00 (q, 2 H), 3.55 (s, 2 H), 4.16−4.23 (q, 2 H) ppm. GC/MS: 176 (37); 115 (100), 89 (28), 43 (39).

*O,S-Diethylmonothiodiazomalonate (1)*: To a solution of 1.8 g (10.4 mmol) of **3** and 2.5 g (10.4 mmol) of *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) in 75.0 mL of $CH_3CN$ was added 1.5 mL (11.0 mmol) of $Et_3N$ in one portion. After 1 h the reaction was complete as determined by the disappearance of **3** (TLC-9:1 pentane:$Et_2O$). The resulting white precipitate was removed by vacuum filtration and washed with 20 mL of $CH_3CN$. The total filtrate was concentrated by rotary evaporation (no heat) to give a yellow residue that was chromatographed on silica gel using 9:1 pentane:$Et_2O$ as the eluent ($R_f = 0.27$) to give 1.7 g of **1** as a yellow oil. IR: 2129, 1724, 1621 $cm^{-1}$. H NMR: 1.25−1.33 (t, 3 H), 1.26−1.35 (t, 3 H); 2.93−3.02 (q, 2 H), 4.27−4.35 (q, 2 H) ppm.

*S,S-Dithioethoxymalonate (4)*: To 12.0 mL of EtSH was carefully added 8.69 g (61.7 mmol) of malonyl chloride dropwise (VIGOROUS HCl EVOLUTION). Once addition was complete, the solution was stirred at 35 °C for 1 h, cooled to ambient temperature, and the excess EtSH was removed by rotary evaporation. Fractional vacuum distillation gave 9.3 g of **4** (bp = 93−95 °C, 1.5 Torr) as a clear, colorless liquid. H NMR: 1.24−1.29 (t, 6 H), 2.89−2.94 (q, 4 H), 3.75 (s, 2 H) ppm. GC/MS: 192 (4), 164 (4), 131 (74), 89 (100), 69 (19).

*S,S-Diethyl Diazomalonate (2)*: To a solution of 2.0 g (10.4 mmol) of **4** and 2.5 g (10.4 mmol) of *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) in 75.0 mL of $CH_3CN$ was added 1.5 mL (11.0 mmol) of $Et_3N$ in one portion. After 2 h the reaction was complete as determined by the disappearance of **4** (TLC 9:1 pentane:$Et_2O$), and the white precipitate which was removed by vacuum filtration was washed with 20 mL of $CH_3CN$. The total filtrate was concentrated by rotary evaporation (no heat) to give a yellow residue that was chromatographed on silica gel using 9:1 pentane:$Et_2O$ as the eluent ($R_f = 0.36$) to give 1.9 g of **2** as a yellow oil. IR: 2117, 1663, 1626 $cm^{-1}$. H NMR: 1.28−1.37 (t, 6 H), 2.98−3.06 (q, 4 H).

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*2-Thioethyl Ethyl Acetate (**6**):* To a solution of 3.0 g (26.3 mmol) of ethyl diazoacetate in 30 mL of absolute EtSH cooled to 0 °C was cautiously added 2.6 g (26.5 mmol) of concentrated $H_2SO_4$ dissolved in 10 mL of absolute EtSH over 30 min. Following the addition, the solution was stirred at ambient temperature for 3 h. The solution was then poured into 200 mL of water and extracted with four 50 mL portions of $Et_2O$. The total $Et_2O$ solution was washed with 50 mL of saturated $NaHCO_3$, dried over $Na_2SO_4$, and concentrated by rotary evaporation to give an oil that was distilled under vacuum to afford 1.7 g (bp = 50−51 °C, 0.9 Torr) of **6** as a clear, colorless liquid. IR: 1732, 1632 $cm^{-1}$. GC/MS: 148 (73), 88 (71), 75 (100), 61 (29), 47 (37).

*2-(Thioethyl)diethylmalonate (**5**)*: To a solution of 0.50 g (3.4 mmol) of **6** in 15 mL of THF cooled to −78 °C was added dropwise 3.5 mL of a 1.0 M solution of LHMDS in THF (3.5 mmol) over 5 min. After stirring for 45 min at −78 °C, 0.54 g (5.0 mmol) of ethyl chloroformate in 5 mL of THF was added dropwise over 5 min at −78 °C. After stirring for 12 h at ambient temperature, the mixture was poured into 100 mL of water, and extracted with four 30 mL portions of $Et_2O$. The total $Et_2O$ solution was washed with 30 mL of saturated brine, dried over $Na_2SO_4$, and concentrated by rotary evaporation to give an oil that was chromatographed on silica gel using 9:1 pentane:$Et_2O$ as the eluent to afford 0.352 g of 5 as a clear, colorless liquid ($R_f = 0.43$). IR: 1736, 1691 $cm^{-1}$. H NMR: 1.22−1.29 (t, 3 H), 1.25−1.30 (t, 6 H), 2.69−2.78 (q, 2 H), 4.15 (s, 1 H), 4.19−4.27 (q, 4 H) ppm. C NMR: 13.9, 25.8, 50.8, 62.1, 166.9 ppm. GC/MS: 220 $M^+$, parent (**1**), 160 (100), 147 (40), 133 (39), 102 (21) 91 (32), 75 (34), 45 (19).

*2-Ethoxy Ethyl Acetate (**8**)*: To a solution of 3.0 g (26.3 mmol) of ethyl diazoacetate in 50 mL of absolute EtOH cooled to 0 °C was cautiously added 2.6 g (26.5 mmol) of concentrated $H_2SO_4$ dissolved in 10 mL of absolute EtOH over 30 min. Following the addition, the solution was stirred at ambient temperature for 3 h. The solution was then poured into 200 mL of water and extracted with four 50 mL portions of $Et_2O$. The total $Et_2O$ solution was washed with 50 mL of saturated $NaHCO_3$, dried over $Na_2SO_4$, and concentrated by rotary evaporation to give an oil that was distilled under vacuum to afford 1.0 g (bp = 55−57 °C, 1.9 Torr) of **8** as a clear, colorless liquid. IR: 1755, 1638 $cm^{-1}$. GC/MS: 103 (8), 88 (65), 59 (100), 45 (13).

*2-(Ethoxy)-O,S-diethylmonothiomalonate (**7**)*: To a solution of 0.1 g (0.8 mmol) of **8** in 3 mL of THF cooled to −78 °C was added dropwise 1.0 mL of a 1.0 M solution of LHMDS in THF (1.0 mmol) over 5 min. After stirring for 45 min at −78 °C, 0.15 g (1.2 mmol) of ethyl chlorothioformate in 1 mL of THF was added dropwise over 5 min at −78 °C. After stirring for 12 h at ambient temperature, the mixture was poured into 40 mL of water, and extracted with four 20 mL portions of $Et_2O$. The total $Et_2O$ solution was washed with 20 mL of saturated brine, dried over $Na_2SO_4$, and concentrated by rotary evaporation to give an oil that was chromatographed on silica gel using 9:1 pentane:$Et_2O$ as the eluent to afford 0.027 g of **7** as a clear, colorless liquid ($R_f = 0.31$). GC/MS: 192 (4), 176 (20), 160 (29), 119 (42), 103 (74), 75 (100), 47 (11).

*Steady-State Photolysis of **1***: In a quartz vessel was placed 0.305 g of **1** in 75 mL of absolute EtOH. The solution was degassed by purging with dry, oxygen-free argon for 15 min, then the solution was irradiated at 0 °C using 300 nm light (Rayonet reactor). After 1.5 h of photolysis, the IR spectrum of the reaction mixture showed that a significant amount of **1** remained, and photolysis was continued for a total of 17 h. The IR spectrum after 17 h of photolysis showed that **1** had been totally consumed, as evident by the absence of the $C{=}N_2$ band of **1**. Analysis of the photolyzed mixture showed that **5** and **3** were produced in a 3:1 ratio, respectively. It was possible to separate the mixture of **3** and **5** by chromatography on silica gel using 9:1 pentane:$Et_2O$ as the eluent.

*Steady-State Photolysis of Authentic **3**, **5**, and **7**.* To quartz cuvettes were each added 5 mg of the respective samples and 2 mL of absolute EtOH. The solutions were degassed by purging with dry, oxygen-free argon for 15 min, then the solutions were irradiated at 0 °C using 300 nm light (Rayonet reactor) for 17 h. Analysis of the photolyzed samples by GC/MS showed that none of these compounds had decomposed.

**Calculations.** Ab initio molecular orbital calculations were performed using the GAUSSIAN 94 suite of programs.[13]

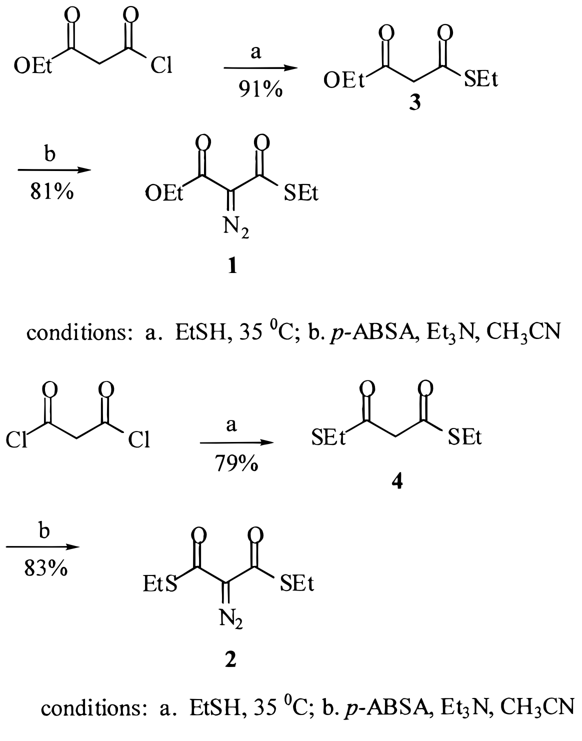
**LFP Studies: General Procedures.** The LFP apparatus in use at Ohio State University has been previously described.[14] Pyridine was distilled and stored over 4 Å molecular sieves. Freon-113 (Aldrich, HPLC grade) was passed through a column of alumina prior to use.

**LFP Studies: Kinetics.** Stock solutions of **1** and **2** in Freon-113 were prepared to an optical density of ~ 0.6 at 308 nm, and 1.0 mL of the stock solution was added to a quartz cuvette. To the cuvette was then added a specific amount of pyridine, followed by addition of an appropriate amount of Freon-113 such that the total volume in the cuvette was 2.0 mL. The cuvette was capped with a rubber septum, wrapped in foil, and degassed by purging with dry, oxygen-free argon for 5 min immediately prior to LFP at 308 nm. Three transient spectra were recorded using the Δ O. D. at 425 nm, and the averaged $A_{425}$ values were used in the data analysis. The [pyridine] typically ranged from 0.1 to 3.0 M for a series of 8−10 cuvettes.

## III. Synthesis and Photochemistry

The diazo malonates **1** and **2** were readily prepared in high yield, and were quite stable, and both could be purified by silica gel column chromatography (Scheme 1).

**SCHEME 1**



conditions: a. EtSH, 35 ºC; b. *p*-ABSA, $Et_3N$, $CH_3CN$

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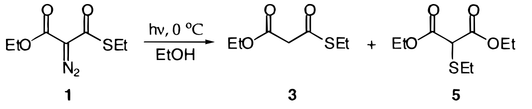
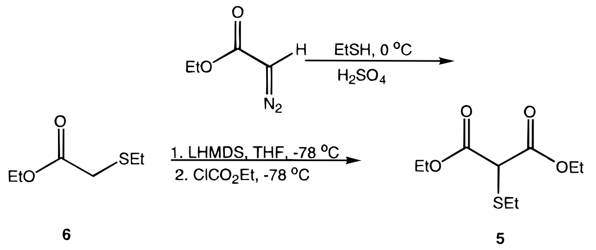
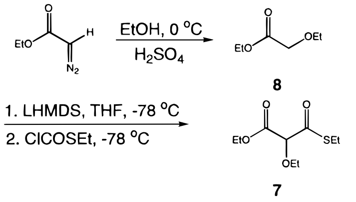
Photolysis of a degassed EtOH solution of **1** (300 nm, Ray-o-Net) gave **5** and **3** in a 3:1 ratio, respectively. The product ratio was determined by GC/MS by comparison with the retention time and EI fragmentation pattern of authentic samples.



Authentic adduct **5** was synthesized as shown below.

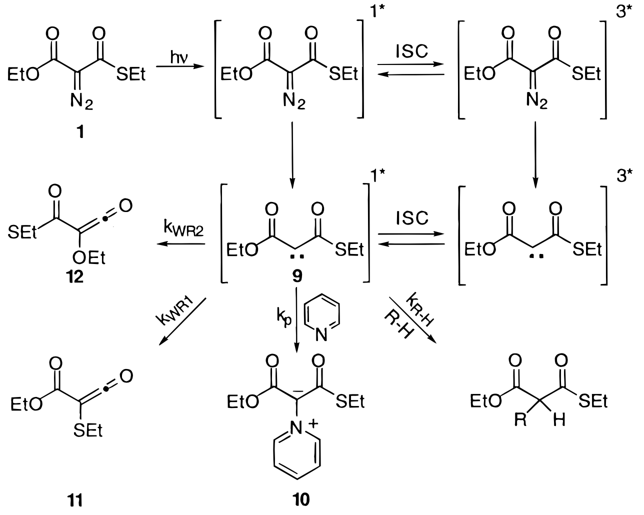


We believe that **3** is produced from a formal reduction of the triplet excited state of **1**[7] and that **5** is produced from migration of the SEt group. Thus, the Wolff rearrangement of **1** appears to be highly selective, as the Wolff rearrangement could have also proceeded with migration of the OEt group to give **7**. To test the possibility that **7** could have been formed, an authentic sample of **7** was prepared and was found to be stable under the conditions used for photolysis of **1** and the GC/MS conditions used for product analysis.



Authentic samples of **3** and **5** were stable under the conditions used for photolysis of **1** and the GC/MS conditions used for product analysis. Given these results, we believe that **3** and **5** are primary photoproducts generated from the photolysis of **1** in oxygenated ethanol.

## SCHEME 2



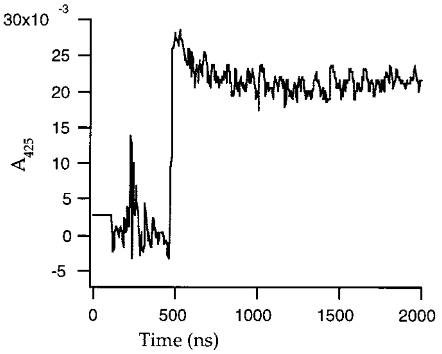


**Figure 1.** Rate of formation of **8** in Freon-113 at [pyridine] = 2.48 M.

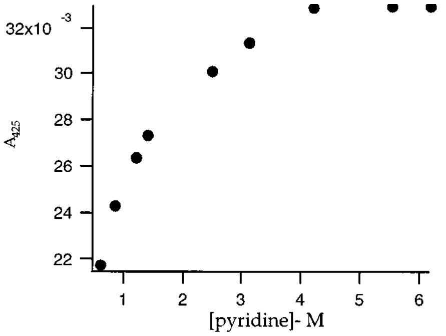


**Figure 2.** Absorbance at $\lambda$ = 425 nm as a function of pyridine concentration.

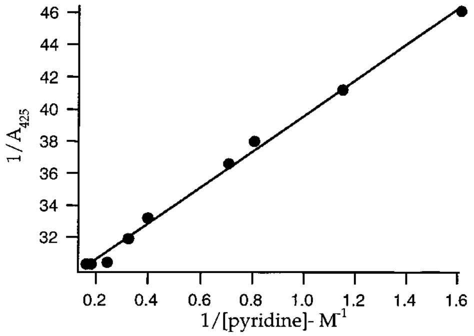


**Figure 3.** Double reciprocal treatment of the data in Figure 2.

**Laser Flash Photolysis.** LFP (308 nm, XeCl) of **1** in 1,1,2-trichlorotrifluoroethane (Freon-113) fails to produce a UV–visible transient absorption. In the presence of 3.12 M pyridine; however, a transient absorption with $\lambda_{max}$ = 425 nm was detected. This absorption is attributed to that of ylide **10**, formed by reaction of singlet **9** with pyridine (Scheme 2).

Ylide **10** is formed faster than the time resolution of the spectrometer (~ 20 ns, Figure 1). Thus, the lifetime of singlet **9** was deduced by measuring the absorption at 425 nm as a function of pyridine concentration (Figure 2), which shows that the absorbance increases until [pyridine]~ 4.0 M, at which point the yield of ylide **10** does not increase further with increasing [pyridine]. Thus, at [pyridine] > 4.0 M, every singlet carbene **9** generated by the laser pulse is captured by pyridine prior to its decay by other pathways (Scheme 1), and the optical yield of **10** is saturated.

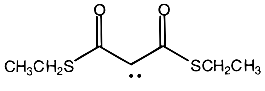
Double reciprocal treatment of the data in Figure 2 as we have previously described is predicted and found to be linear (Figure 3).[8] Division of the intercept by the slope gives $k_p$, assuming that ISC of singlet **9** to triplet **9** is slow relative to all other processes which lead to decay of singlet **9**. It has been

**TABLE 1: Values of $k_p$ and Deduced Values of $\tau$ for Singlet 9, 13, and 14 in Freon-113**

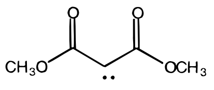
| carbene | $k_p\tau$ | $t$ |
|---|---|---|
| **9** | 2.6 | 0.5−2.6 |
| **13** | 2.3 | 0.5−2.3 |
| **14** | 13.2 | 3−13 |

determined that typical values of $k_p$ are $1-5 \times 10^9$ $M^{-1}$ $s^{-1}$,[9] thus, the deduced lifetime of singlet carbene **9** is given in Table 1, along with that of singlet carbene **13**, which was deduced in the same manner as done for **9**.

The data of Table 1 suggest that the lifetime of **9** and **13** are essentially the same in Freon-113, at ambient temperature, yet compared to dicarbomethoxycarbene, **14**,[3] the lifetimes of **9** and **13** are about six times shorter.



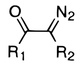
**13**



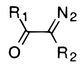
**14**

## IV. Computational Chemistry and Discussion

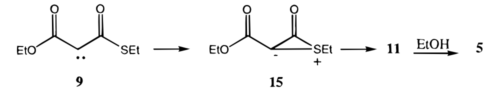
Kaplan, Meloy, and Mitchell first proposed that the photochemistry of α-diazoketones could be influenced by conformational factors, and that the photochemical Wolff rearrangement takes place preferentially from the *s*-cis conformer, in which displacement of nitrogen concurrent with migration of R is possible.[10] Indeed, it has been shown that α-diazoketones locked into an *s*-cis conformation undergo Wolff rearrangement more efficiently than their corresponding acyclic analogues.[2a,3] Due to the fact that in the photochemical Wolff rearrangement of **1** only the S-Et group migrates, it was of interest to examine four possible arrangements of the carbonyl ester groups in **1** with respect to the diazo group at the B3LYP/6−31 G* level of theory.[11] To simplify the calculations, methyl esters rather than the ethyl esters were examined since the relative energies and geometrical parameters about the carbonyl and diazo groups should not be greatly affected by the change from ethyl to methyl substitution. The relative energies and structural data for the four conformers is given in Figure 4. It is interesting to note that the lowest energy conformers (Figure 4) are the two in which the carbonyl bonded to the *S*-Me group is cis to the diazo group. This requires that the *S*-Me group bonded to the cis carbonyl occupy a trans position relative to the diazo group. Therefore, in both of these conformations the migrating *S*-Me group is ideally located to migrate with displacement of nitrogen. Assuming that there is good Franck−Condon overlap[12] between the calculated relative energies of ground-state conformers **1A**−**1D**, and their corresponding excited states **1A***−**1D***, explains the result of steady-state photolysis of **1** in EtOH, in which only the product of SEt migration, **5**, was produced. The product studies and LFP studies indicate that the lifetime of singlet carbene **9** is limited by $k_{WR1}$, such that $\tau \sim 1/k_{WR1}$. Furthermore, the lifetimes of both singlet carbenes **9** and **13** are approximately six times shorter than that of the all oxygen analogue **14** in Freon-113. This may be attributed to the possible involvement of ylide **15** on the reaction coordinate leading to ketene **11** and ultimately to **5**.



s-cis



s-trans



Ylides related to **15** have been posited[13] and such an intermediate would be expected to rearrange very rapidly to ketene **11**. The involvement of ylide **15** may also be the reason for the shorter deduced lifetimes of the sulfur analogues.

Although our data are consistent with the trapping of singlet **9** with pyridine, our data does not rule out the possibility that we are actually trapping **15**.

The shorter lifetime for **9** and **13** as compared to **14** may reflect a large effect on $k_p$. If **15** is the trappable intermediate, then the lone-pair of electrons on the nitrogen of pyridine would have to attack a carbon with a formal negative charge to give adduct **10**, thus, the actual $k_p$ value may be considerably smaller than the value of $1-5 \times 10^9$ $M^{-1}$ $s^{-1}$ that is typically used in our laboratory to deduce the lifetime of singlet carbenes by double reciprocal treatment of LFP data. Hence, a smaller $k_p$ value would lead to a longer carbene lifetime, $\tau$, than we have deduced.

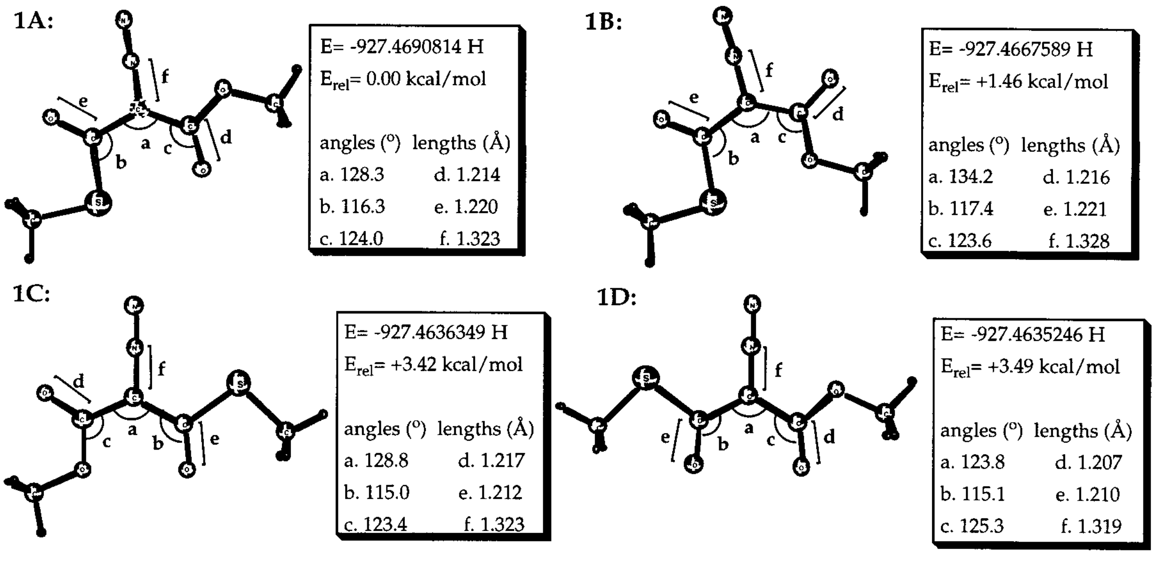
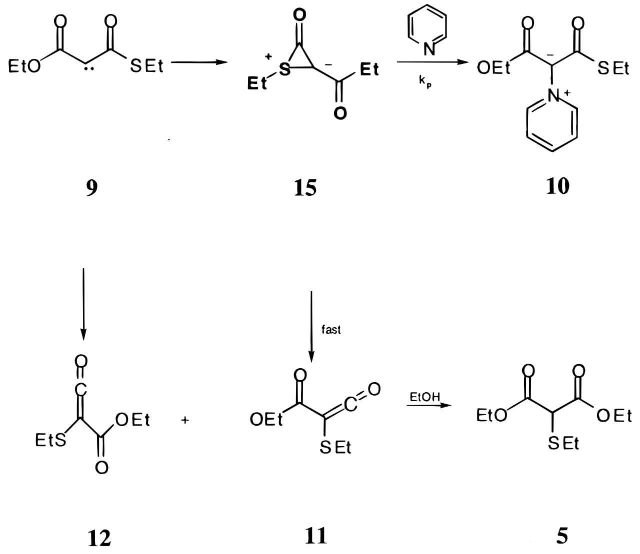


**Figure 4.** Conformations of *O,S*-dimethylmonothiodiazomalonate and theirrelative energies calculated at the B3LYP/6-31G* level of theory.

**SCHEME 3**



## V. Conclusions

The photochemistry of **1** and **2** was studied. The steady-state photolysis of **1** in EtOH demonstrates that the primary photoproducts **5** and **3** are produced in a 3:1 ratio, respectively. Furthermore, none of the product **7** that would result from the Wolff rearrangement of **1** in EtOH is produced. Thus, the Wolff rearrangement of **1** gives exclusive migration of SEt over OEt. LFP studies are consistent with the trapping of an intermediate with $\lambda_{max} = 425$ nm, attributed to that of ylide **10**, likely formed from the reaction of singlet **9** with pyridine. The deduced lifetime of both **9** and **13** are essentially the same in Freon-113, yet compared to dicarbomethoxycarbene **14**, at ambient temperature[3] the lifetime of **9** and **13** was found to be about six times shorter. Calculations at the B3LYP/6−31 G* level of theory indicate that the two lowest energy conformers **1A** and **1B**, are those in which the carbonyl moiety bonded to the S-Et group is cis to the diazo group. This forces the S-Et group bonded to the cis carbonyl to occupy a trans position relative to the diazo group. Therefore, in both of these conformations the migrating SEt group is ideally located to migrate with displacement of nitrogen. These findings are in agreement with Kaplan, Meloy, and Mitchell[10] who proposed that the photochemistry of α-diazo ketones could be influenced by conformational factors, and that the photochemical Wolff rearrangement takes place preferentially from the *s*-cis conformer, in which displacement of nitrogen concurrent with migration of R is possible. Possibly contributing to the exclusive migration of SEt is the involvement of ylide **15** on the reaction coordinate leading to **5**. Although our data are consistent with the trapping of singlet **9** with pyridine, our results do not rule out the possibility that we are trapping **15**. Thus, the shorter lifetime for **9** and **13** as compared to **14** may also be a result of a large effect on $k_p$. If **15** were the trappable intermediate, then the lone-pair of electrons on the nitrogen of pyridine would have to attack a carbon with a formal negative charge to give adduct **10**, thus, the actual $k_p$ value may be considerably smaller than the value of $1-5 \times 10^9$ $M^{-1}$ $s^{-1}$ that is typically used in our laboratory to deduce the lifetime of singlet carbenes.

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