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Photochemistry of 1-(2- and 3-Thienyl)diazoethanes: Spectroscopy and Tunneling Reaction of Triplet 1-(3-Thienyl)ethylidene

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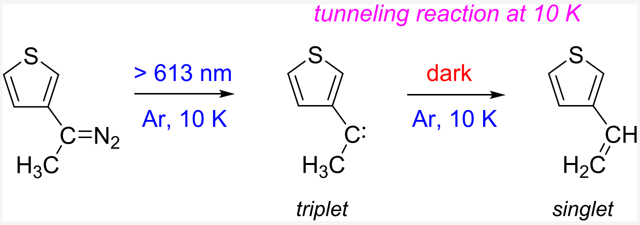
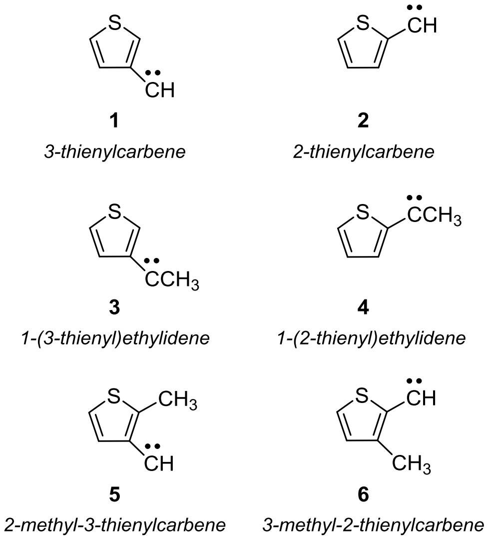


ABSTRACT: Photolysis (λ > 613 nm) of 1-(3-thienyl)diazoethane (**21**) yields the *s-E* rotamer of triplet 1-(3-thienyl)ethylidene (**3**), as characterized by UV/vis and EPR spectroscopy. The *s-Z* rotamer of **3** was not observed. EPR and UV/vis signals attributed to carbene **3** decrease by approximately 50% upon standing in the dark for 68 h at 10 K. Although formally spin-forbidden, an intramolecular [1,2]-hydrogen shift in triplet carbene **3** to afford singlet *s-E* 3-vinylthiophene (**8**) is presumed to occur via quantum mechanical tunneling. The behavior of the CD_3 analogue supports this interpretation. Photolysis (λ > 613 nm) of 1-(3-thienyl)diazoethane-d_3 (**21**-d_3) yields triplet 1-(3-thienyl)ethylidene-d_3 (**3**-d_3), as characterized by IR, UV/vis, and EPR spectroscopy. No change in the signal intensity of EPR and UV/vis signals of triplet **3**-d_3 is observed upon standing in the dark for 68 h at 10 K. In a series of 2-substituted thienyl derivatives, irradiation of 1-(2-thienyl)diazoethane (**22**), 1-(2-thienyl)diazoethane-d_3 (**22**-d_3), or (3-methyl-2-thienyl)diazomethane (**23**) does not yield triplet carbene intermediates. Positioning and labeling of the methyl group proved to have a large effect on products observed for these species. 1-(2-Thienyl)diazoethane (**22**) yields the products of [1,2]-hydrogen migration, *s-Z* and *s-E* 2-vinylthiophene (**7**), while **22**-d_3 and **23** give products derived from opening of the thiophene ring.

■ INTRODUCTION

Continuing interest in the chemistry and spectroscopy of aryl carbenes is derived from fundamental considerations of the structure and reactivity of these reactive species[1−3] as well as the general relevance of organic reactive intermediates to the chemistry of harsh reaction environments in combustion or astrochemistry.[4−7] Interest in the reactivity of aryl carbenes and nitrenes has been augmented in recent years by the diverse range of quantum mechanical tunneling reactions that they exhibit.[8−15] Previously, we reported the spectroscopic detection and characterization of triplet 3-thienylcarbene, a species that had long eluded direct spectroscopic detection.[16] Given the success of the earlier study and spurred by some unique characteristics associated with the triplet EPR spectrum of 3-thienylcarbene (**1**), we sought to broaden our investigation beyond this singular example. We embarked on the current study with the goals of generating and detecting the first example of a triplet 2-thienylcarbene derivative, detecting additional derivatives of triplet 3-thienylcarbene, and investigating intramolecular trapping reactions of these carbenes through the use of a proximal methyl substituent (Scheme 1). These studies provide an opportunity to study quantum mechanical tunneling reactions associated with the intramolecular hydrogen migrations. An extensive computational study of the C_6H_6S isomers provided insights into the potential energy surface and computed infrared spectra in support of the experimental matrix isolation studies.

Scheme 1. 2- and 3-Thienylcarbenes and Methyl-Substituted Derivatives



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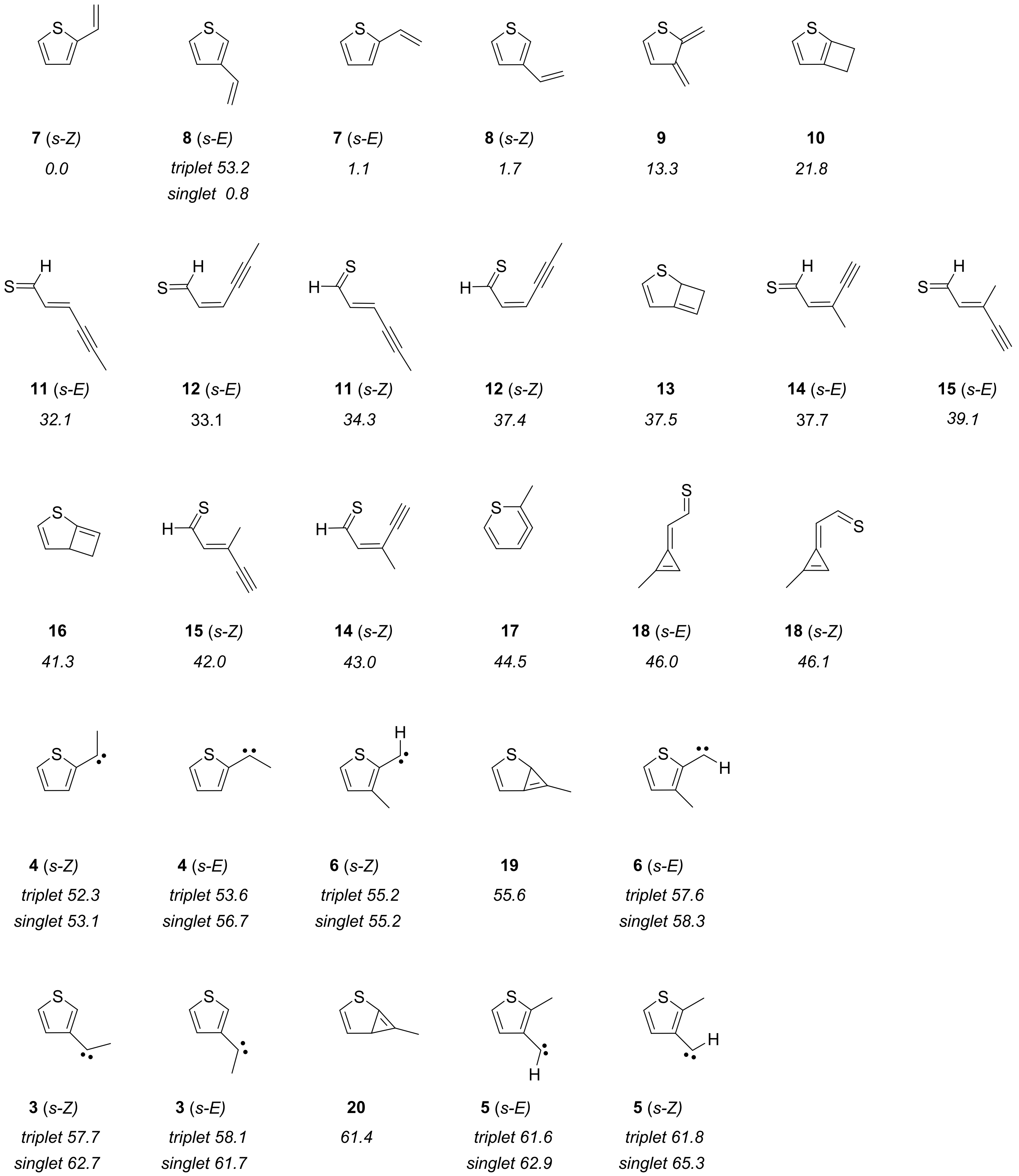
Scheme 2. C_6H_6S Isomers Listed in the Order of Increasing Computed Relative Energy[a]



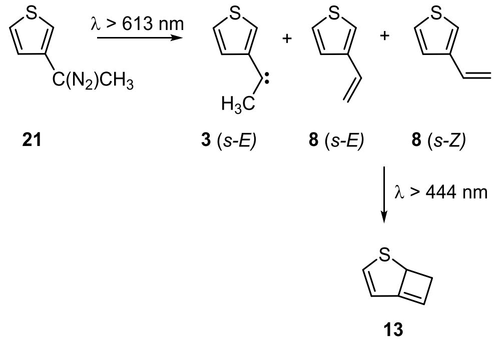
[a] Energy (kcal/mol; ZPVE included). B3LYP/6−31G(d) level of theory.

■ RESULTS

Computational Studies of C_6H_6S Isomers. The current study draws heavily on computational data. Predicted infrared vibrational frequencies and intensities enable the interpretation and assignment of the experimental infrared spectra. Computed relative energies provide important context for understanding reaction pathways and assessing whether tunneling processes are viable. Given the rather large number of isomers considered, density functional methods were employed in order to treat the variety of different structural types equivalently. The calculations proved to be sufficient for the purposes of the current study.

Structures of C_6H_6S isomers and their computed relative energies (B3LYP/6−31G(d) + ZPVE) are presented in Scheme 2. Thienylcarbenes **3**−**6** are calculated to have triplet ground states. Computed singlet−triplet energy gaps for the 2-thienylcarbenes are small (0−3 kcal/mol) and perhaps smaller than the expected accuracy of the calculation. The computed singlet−triplet energy gaps for the 3-thienylcarbenes are slightly larger (1.5−4.0 kcal/mol). Singlet−triplet energy gaps are discussed in more detail in the Discussion section. Although the 2-thienylcarbenes are calculated to be slightly lower in energy than the corresponding 3-thienylcarbenes, none of the 2-thienylcarbenes were experimentally observed during the study of these molecules.

Scheme 3. Photochemistry of 1-(3-Thienyl)diazoethane (21) (Ar or N_2, 10 K)



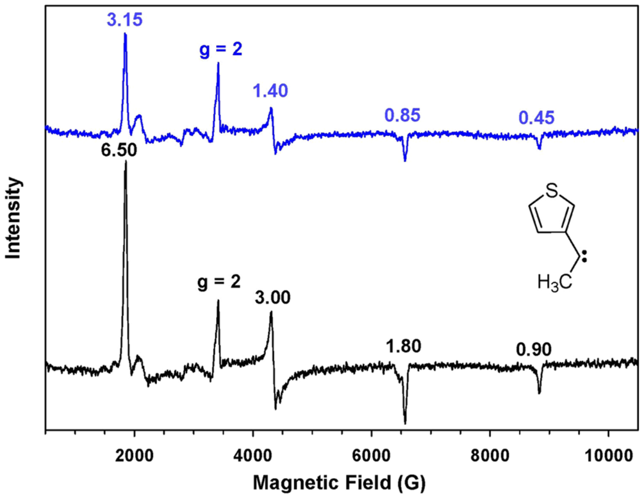


Figure 1. (bottom, black) EPR spectrum of triplet 1-(3-thienyl)ethylidene (**3**) upon generation (*λ* > 497 nm, 89 h) from 1-(3-thienyl)diazoethane (**21**). (top, blue) EPR spectrum after standing in the dark for 68 h (Ar, 15 K). Spectra are on the same scale; numerical values represent the relative peak height (arbitrary units).

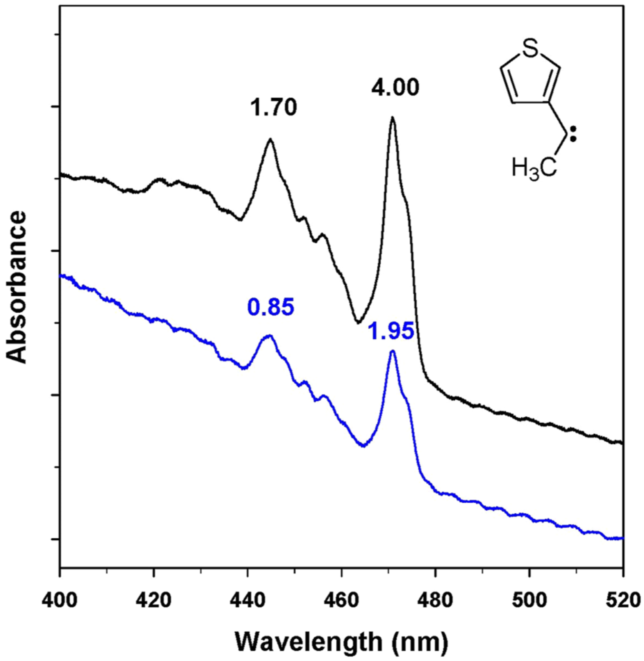


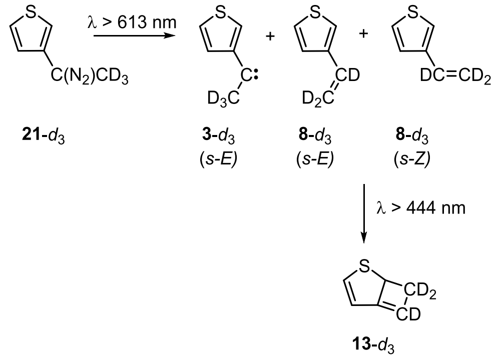
Figure 2. (top, black) UV/vis spectrum of triplet 1-(3-thienyl)ethylidene (**3**) upon generation (*λ* > 497 nm, 16 h) from 1-(3-thienyl)diazoethane (**21**). (bottom, blue) Spectrum after standing in the dark for 68 h (Ar, 10 K). Spectra are on the same scale with *y*-axis values offset to facilitate viewing; numerical values represent the relative peak height (arbitrary units).

Photochemistry of 1-(3-Thienyl)diazoethane (21). Irradiation of 1-(3-thienyl)diazoethane (**21**) (*λ* > 613 nm; Ar or N_2, 10 K) gives a mixture of triplet 1-(3-thienyl)ethylidene (**3**) and 3-vinylthiophene (**8**) (Scheme 3). The *s-Z* and *s-E* conformers of 3-vinylthiophene (**8**) are the major species present in the matrix, as observed by IR spectroscopy (Figure S1). Triplet 1-(3-thienyl)ethylidene (**3**) is observed by EPR and UV/vis spectroscopy (Figures 1 and 2), but triplet **3** cannot be observed in the IR spectrum because the most intense vibration predicted by B3LYP calculations overlaps with an intense vibration of the diazo compound that is disappearing and the concentration of the carbene does not build up to an appreciable extent. Interestingly, only one geometric isomer of 1-(3-thienyl)ethylidene (**3**) is observed in the EPR spectrum (Figures 1). The EPR and UV/vis signals of triplet 1-(3-thienyl)ethylidene (**3**) persist upon shorter wavelength irradiation to *λ* > 497 nm. Irradiation at *λ* > 444 nm results in the disappearance of triplet **3**, as observed by EPR and UV/vis spectroscopy, as well as the decrease in the amount of 3-vinylthiophene (**8**) and the appearance of 2-thiabicyclo[3.2.0]hepta-3,5-diene (**13**), as seen by IR spectroscopy (Figure S2).

In contrast to their rapid disappearance under photochemical conditions, the EPR and UV/vis signals of triplet 1-(3-thienyl)ethylidene (**3**) decrease slowly upon standing in the dark in an argon matrix at 10−15 K (Figures 1 and 2). Over the course of 68 h, signals from **3** decreased by over fifty percent in both EPR and UV/vis experiments, which were carried out under comparable conditions.

Photochemistry of 1-(3-Thienyl)diazoethane-d_3 (21-d_3). Irradiation of 1-(3-thienyl)diazoethane-d_3 (**21**-d_3) (*λ* > 613 nm; Ar, 10 K) gives a mixture of triplet 1-(3-thienyl)ethylidene-d_3 (**3**-d_3) and 3-vinylthiophene-d_3 (**8**-d_3) (Scheme 4). In contrast to the protio case, both 1-(3-thienyl)ethylidene-d_3 (**3**-d_3) and 3-vinylthiophene-d_3 (**8**-d_3) are observed by IR spectroscopy as a result of a shift in the diagnostic IR absorptions of carbene **3**-d_3 and diazo compound **21**-d_3 such that they are no longer overlapping (Figure S3). Triplet 1-(3-thienyl)ethylidene-d_3 (**3**-d_3) is also observed by EPR spectroscopy (Figure 3). As in the case of protio carbene **3**, only one geometric isomer of 1-(3-thienyl)ethylidene-d_3 (**3**-

Scheme 4. Photochemistry of 1-(3-Thienyl)diazoethane-d_3 (21-d_3) (Ar, 10 K)



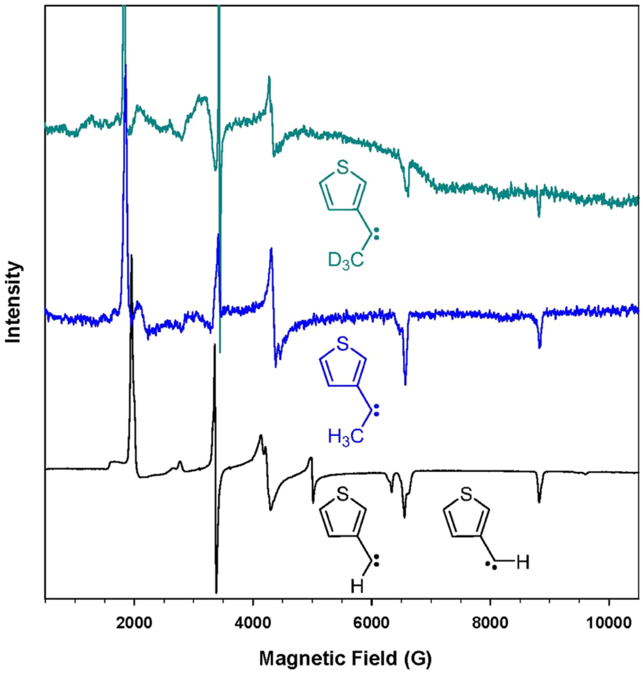


Figure 3. EPR spectra of triplet 3-thienylcarbene derivatives (Ar, 15 K). (top, cyan) 1-(3-Thienyl)ethylidene-d_3 (**3**-d_3). (middle, blue) 1-(3-Thienyl)ethylidene (**3**). (bottom, black) 3-Thienylcarbene (**1**).

d_3) is observed in the EPR spectrum. Upon irradiation at $\lambda >$ 444 nm, the IR and EPR signals of triplet **3**-d_3 disappear from the matrix and 3-vinylthiophene (**8**-d_3) continues to grow (Figure 4). The observed IR spectrum most closely aligns with the calculated IR spectrum of the *s-E* conformer of 1-(3-thienyl)ethylidene-d_3 (**3**-d_3): a major peak expected for the *s-Z* conformer of 1-(3-thienyl)ethylidene-d_3 (**3**-d_3) is absent from the experimental IR spectrum. Notably and in contrast to the protio carbene **3**, the IR and EPR signals of triplet 1-(3-thienyl)ethylidene-d_3 (**3**-d_3) do not change upon standing in the dark in an argon matrix at 10–15 K.

Photochemistry of 1-(2-Thienyl)diazoethane (22). Irradiation of 1-(2-thienyl)diazoethane (**22**) ($\lambda >$ 613 nm; Ar, 10 K) gives a mixture of 2-vinylthiophene (**7**) and a compound tentatively assigned as 2-thiabicyclo[3.2.0]hepta-3,6-diene (**16**) (Scheme 5) (Figure S4). Triplet 2-thienyl-1-ethylidene (**4**) is not observed by IR or EPR spectroscopy. Further irradiation ($\lambda >$ 280 nm) of the mixture led to a decrease in *s-Z* **7** and the growth of *s-E* **7** (Figure S5).

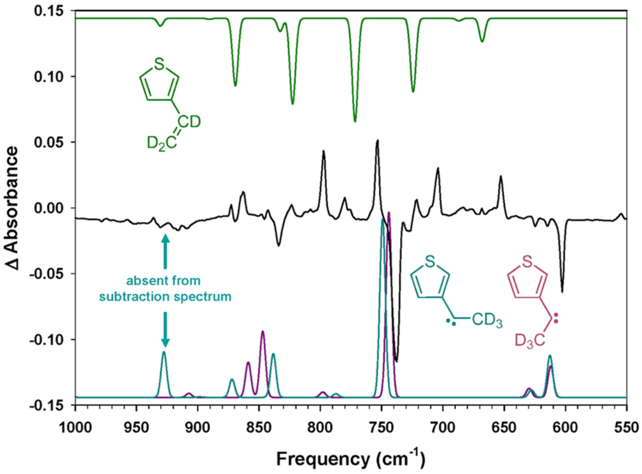
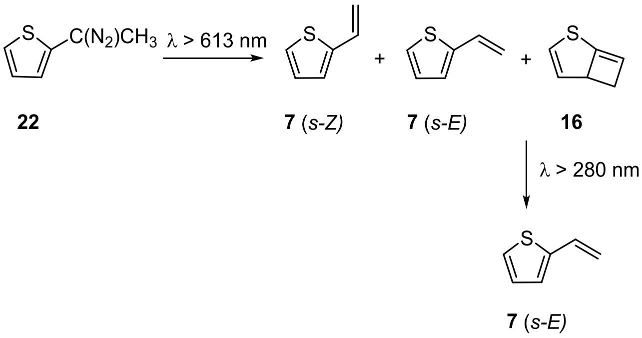


Figure 4. IR subtraction spectrum showing spectral changes observed upon irradiation at $\lambda >$ 444 nm (Ar, 10 K). The spectrum shows the disappearance of *s-E* 1-(3-thienyl)ethylidene-d_3 (**3**-d_3) and the growth of *s-E* 3-vinylthiophene-d_3 (**8**-d_3). Calculated spectra of *s-Z* and *s-E* **3**-d_3 are shown on the bottom of the spectrum, while the calculated spectrum of *s-E* 3-vinylthiophene-d_3 (**8**-d_3) is shown along the top. A major peak (925 cm^{-1}) in the calculated spectrum of *s-Z* **3**-d_3 is absent from the subtraction spectrum, supporting our assignment of the single rotamer present to *s-E* **3**-d_3.

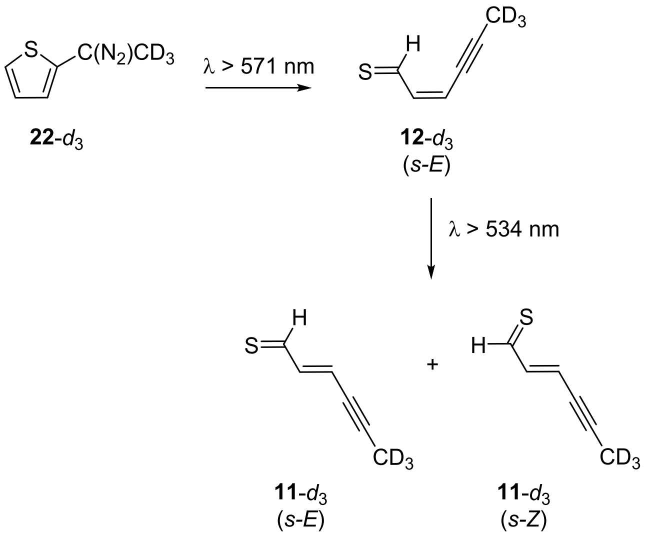
Scheme 5. Photochemistry of 1-(2-Thienyl)diazoethane (22) (Ar, 10 K)



Photochemistry of 1-(2-Thienyl)diazoethane-d_3 (22-d_3). Irradiation of 1-(2-thienyl)diazoethane-d_3 (**22-d_3**) ($\lambda >$ 571 nm; Ar, 10 K) gives the product of ring opening, *s-E Z*-hex-2-en-4-ynethial-d_3 (**12**-d_3) (Scheme 6) (Figure S6). Triplet 2-thienyl-1-ethylidene-d_3 (**4-d_3**) is not observed by IR or EPR spectroscopy. Irradiation ($\lambda >$ 534 nm, 21 h) of the matrix containing diazo compound **22**-d_3 and ring-opening product **12**-d_3 results in the disappearance of **22**-d_3, a decrease in the amount of **12**-d_3, and the corresponding growth of both *s-E* and *s-Z* conformers of *E*-hex-2-en-4-ynethial-d_3 (**11**-d_3) (Figure S7).

Photochemistry of (3-Methyl-2-thienyl)diazomethane (23). Irradiation of (3-methyl-2-thienyl)diazomethane (**23**) ($\lambda >$ 571 nm; Ar, 10 K) gives the products of ring opening, *s-Z* and *s-E Z*-3-methylpent-2-en-4-ynethial (**14**) and *s-Z* and *s-E E*-3-methylpent-2-en-4-ynethial (**15**) (Scheme 7) (Figure S8). Triplet 3-methyl-2-thienylcarbene (**6**) is not observed by IR or EPR spectroscopy. Further irradiation ($\lambda >$ 300 nm) of the matrix leads to the partial conversion of *E*-3-methylpent-2-en-4-ynethial (**15**) to *Z*-3-methylpent-2-en-4-ynethial (**14**) (Figure S9).

Scheme 6. Photochemistry of 1-(2-Thienyl)diazoethane-d_3 (22-d_3) (Ar, 10 K)



Spectroscopic Data for C_6H_6S Isomers. *s-E* 1-(3-Thienyl)ethylidene (**3**): UV/vis (N_2, 10 K) λ_{max} 444, 471, 473 nm; EPR (Ar, 15 K), $|D/hc|$= 0.5028 cm^{-1}, $|E/hc|$= 0.0541 cm^{-1}, Z_1 = 1837.3 G, X_2 = 4338.0 G, Y_2 = 6573.0 G, Z_2 = 8823.0 G, microwave frequency = 9.654 GHz. *s-Z* 2-Vinylthiophene (**7**): IR (Ar, 10 K): 1628 s, 1608 w, 1368 w, 1205 s, 1049 m, 978 m, 893 m, 852 m, 826 w, 704 w, 696 s, 682 w, 566 m, 505 w, 500 w, 490 m, 487 w, 477 w, 445 w, 416 m, 394 m, 390 m, 384 m cm^{-1}. *s-E* 2-Vinylthiophene (**7**): IR (Ar, 10 K): 1623 m, 1608 m, 1409 s, 1361 m, 1243 s, 1129 w, 1075 w, 1037 m, 987 w, 981 m, 855 s, 822 w, 713 w, 697 s, 670 m, 522 w, 494 m, 484 w, 479 m, 440 w, 436 m, 421 w cm^{-1}. *s-Z* 3-Vinylthiophene (**8**): IR (N_2, 10 K) 1635 m, 1414 w, 1359 w, 1215 w, 989 m, 905 s, 875 m, 833 m, 790 s, 702 w, 658 w, 549 w cm^{-1}. *s-E* 3-Vinylthiophene (**8**): IR (N_2, 10 K) 1635 m, 989 m, 905 s, 867 w, 827 w, 794 s, 702 w, 664 w, 549 w cm^{-1}. 2-Thiabicyclo[3.2.0]hepta-3,5-diene (**13**): IR (N_2, 10 K) 1691 s, 1597 s, 1283 m, 1218 m, 1108 m, 1000 m, 896 w, 878 w, 769 w, 764 w, 638 m cm^{-1}. *s-Z Z*-3-Methyl-pent-2-en-4-ynethial (*s-Z* **14**): IR (Ar, 10 K): 3321 m, 2138 m, 1604 s, 1369 m, 1232 s, 732 s, 678 w, 640 m, 602 s, 542 w cm^{-1}. *s-E Z*-3-Methyl-pent-2-en-4-ynethial (s-E **14**): IR (Ar, 10 K) 3321, 2122, 1604 s, 1422 w, 1312 w, 1232 s, 974 w, 971 w, 880 s, 719 m, 617 m cm^{-1}. *s-Z E*-3-Methyl-pent-2-en-4-ynethial (s-Z **15**): IR (Ar, 10 K): 3313 s, 1573 s, 1433 w, 1380 w, 1364 w, 1183 m, 871 m, 634 m cm^{-1}. *s-E E*-3-Methyl-pent-2-en-4-ynethial (s-E **15**): IR (Ar, 10 K) 3313, 1573, 1450, 1301, 1183, 1171, 1013, 642 m cm^{-1}. 2-Thiabicyclo[3.2.0]hepta-3,6-diene (**16**): IR (Ar, 10 K): 1576 s, 1564 w, 1160 s, 1106 w, 958 w cm^{-1}.

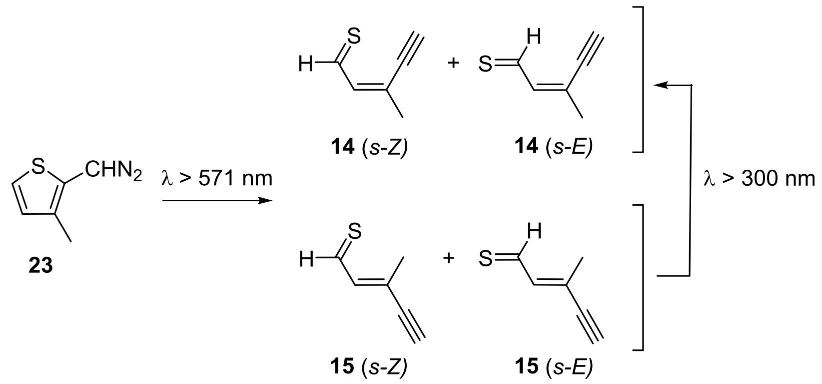
Spectroscopic Data for $C_6H_3D_3S$ Isomers. *s-E* 1-(3-Thienyl)ethylidene-d_3 (**3**-d_3): IR (Ar, 10 K) 2045 w, 834 m, 739 s, 603 m cm^{-1}; UV/vis (Ar, 10 K) λ_{max} 444, 471, 473 nm; EPR (Ar, 15 K), $|D/hc|$ = 0.5019 cm^{-1}, $|E/hc|$ = 0.0547 cm^{-1}, Z_1 = 1827.5 G, X_2 = 4324.0 G, Y_2 = 6617.0.0 G, Z_2 = 8813.0 G, microwave frequency = 9.670 GHz. *s-Z* 3-Vinylthiophene-d_3 (**8**-d_3): IR (Ar, 10 K): 1587 m, 1410 m, 1367 w, 1033 w, 780 m, 721 m, 653 m cm^{-1}. *s-E* 3-Vinylthiophene-d_3 (**8**-d_3): IR (Ar, 10 K): 1587 m, 1410 m, 1246 w, 1033 w, 862 m, 798 s, 753 s, 721 m, 704 s, 653 m, cm^{-1}. *s-Z E*-Hex-2-en-4-ynethial-d_3 (**11**-d_3): IR (Ar, 10 K): 2230 s, 1577 s, 1368 w, 1164 s, 961 w, 700 w cm^{-1}. *s-E E*-Hex-2-en-4-ynethial-d_3 (**11**-d_3): IR (Ar, 10 K): 2230 s, 1577 s, 1362 w, 1263w, 1126 m, 961 w cm^{-1}. *s-E Z*-Hex-2-en-4-ynethial-d_3 (**12**-d_3): IR (Ar, 10 K): 2236 s, 1564 s, 1417 m, 1386 w, 1297 w, 1228 m, 1180 m, 1124 s, 783 w, 752 w cm^{-1}.

■ DISCUSSION

Triplet 1-(3-Thienyl)ethylidene (3). Generating and detecting a triplet ethylidene species, i.e., a triplet carbene bearing a methyl substituent, represent challenges in carbene chemistry because the intramolecular 1,2-hydrogen migration reaction of ethylidenes is so facile. The ability to detect an ethylidene derivative, whether by matrix-isolation techniques or by time-resolved spectroscopy, is strongly dependent on particular characteristics of the structure and photochemistry of the carbene and its precursor. The study of heteroaromatic carbenes, such as 3-thienylcarbene (**1**),[16] is similarly challenging because of the propensity of these species to undergo fragmentation of the ring. Because the current study involves both of these factors, we were not particularly confident that our efforts to detect triplet 1-(3-thienyl)-ethylidene would be successful. Nevertheless, our investigations led to the characterization of 1-(3-thienyl)ethylidene (**3**) and (**3**-d_3).

In previous work, we observed two geometric isomers of triplet 3-thienylcarbene (**1**) by EPR spectroscopy. The signals attributed to *s-Z* and *s-E* 3-thienylcarbene are atypical for carbene rotamers in that the signals are unusually different for the two rotamers. These differences were rationalized on the basis of an NBO analysis.[16] In the current study, we observed only a single geometric isomer in the case of the methyl- and

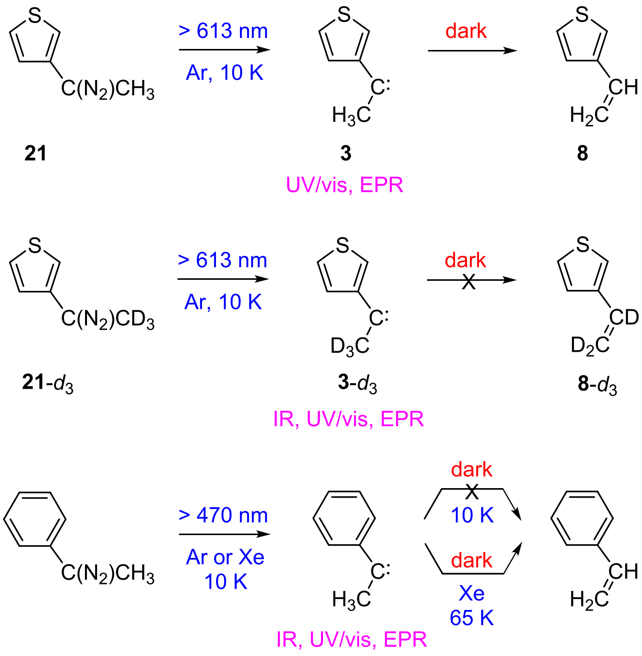
Scheme 7. Photochemistry of (3-Methyl-2-thienyl)diazomethane (23) (Ar, 10 K)



trideuteriomethyl-substituted derivatives 1-(3-thienyl)-ethylidene (**3**) and 1-(3-thienyl)ethylidene-d_3 (**3**-d_3). Upon comparison of EPR spectra of the methyl-substituted compounds to that of the parent compound, it can be seen that the transitions of **3** and **3**-d_3 correlate very well with those of the *s-E* conformer of 3-thienylcarbene (Figure 3). Given that methyl substitution does not significantly perturb the zero-field splitting parameters of triplet carbenes,[17−20] we assign the observed EPR spectra to arise from a single, *s-E*, geometric isomer of the triplet carbenes 1-(3-thienyl)ethylidene (**3** and **3**-d_3). Further evidence for this assignment is seen in the IR subtraction spectrum resulting from the irradiation of a diazo compound (**21**-d_3) at $\lambda > 444$ nm (Figure 4). A major peak (925 cm^{-1}) in the calculated spectrum of triplet carbene *s-Z* **3**-d_3 is absent from the subtraction spectrum, supporting our assignment of the single rotamer present to triplet carbene *s-E* **3**-d_3. The reason for the absence of the *s-Z* conformer is uncertain. A plausible explanation is that the conformation of the diazo compound precursor that would lead to the *s-Z* conformer of the carbene undergoes H or D migration in the excited state of the diazo compound. Such a process, involving the reaction in the excited state (RIES),[21,22] bypasses the carbene intermediate and produces the product of 1,2-shift, directly. Other explanations are possible, and additional, detailed studies would be required to probe this somewhat subtle point. The electronic absorption spectra of 1-(3-thienyl)ethylidene (**3** and **3**-d_3), involving weak visible transitions with vibronic coupling, are characteristic of triplet aryl carbenes (and benzyl radicals).[20]

Tunneling Reaction. Beyond the spectroscopic characterization of triplet 1-(3-thienyl)ethylidene (**3**), the most significant observation of the current study involves the intramolecular rearrangement of triplet carbene **3** in a low-temperature matrix at 10 K. The EPR and UV/vis signals of triplet 1-(3-thienyl)ethylidene (**3**) decrease slowly in intensity upon standing in the dark in argon at 10 K (Figures 1 and 2). Notably, the trideuteriomethyl analogue, **3**-d_3, is completely stable upon standing in the dark under comparable conditions. These observations are highly suggestive of a process in which the protio triplet carbene **3** undergoes an intramolecular 1,2-hydrogen migration reaction to yield singlet 3-vinylthiophene (**8**) (Scheme 8), a formally spin-forbidden tunneling reaction. The migration reaction in the corresponding deuterium-substituted carbene **3**-d_3 is effectively quenched by virtue of a very large primary kinetic isotope effect (k_H/k_D), which renders carbene **3**-d_3 stable in the dark at 10 K. In the current case, the low proportion of protio carbene **3** in the matrix precludes a positive identification of the product of the dark reaction. The IR spectrum of 3-vinylthiophene (**8**) is unequivocally observed in the matrix during the initial photolysis of diazo compound **21**, but an increase in intensity upon standing in the dark cannot be reliably detected because of the very small proportion of carbene **3** in the matrix.

Scheme 8. 1,2-Hydrogen Migration Reactions in Ethylidene Derivatives



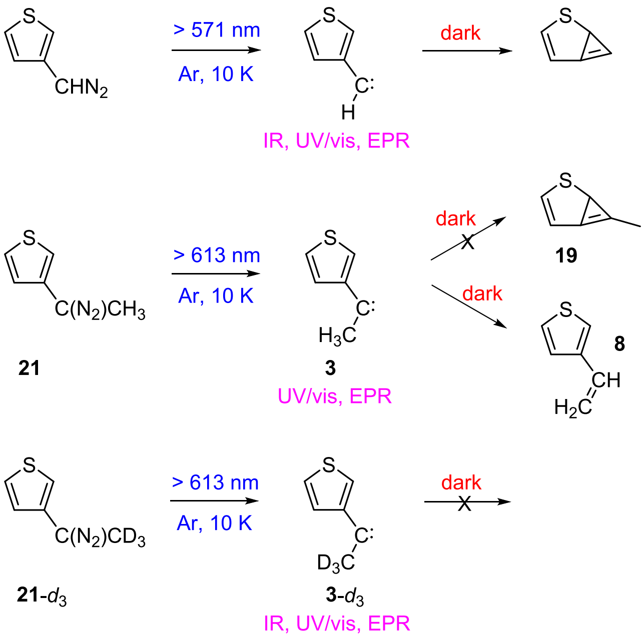
The reactivity displayed by triplet 1-(3-thienyl)ethylidene (**3**) contrasts with that observed for the close analogue, 1-phenylethylidene (Scheme 8). Triplet 1-phenylethylidene is stable in rare gas matrices at 10 K. The 1,2-hydrogen migration reaction to produce styrene occurs only upon warming a xenon matrix to ca. 65 K, and it was speculated that the hydrogen migration reaction originated in the thermally populated singlet state of the carbene.[18] To facilitate the comparison of these systems, we computed the singlet−triplet energy gap for 1-(3-thienyl)ethylidene (**3**) (1.3 kcal/mol) and 1-phenylethylidene (5.2 kcal/mol) at the B3LYP/6-311+G(2d,p) level of theory (ZPVE included). (This computational methodology is expected to afford a somewhat better estimate of the singlet−triplet gap than the B3LYP/6-31G(d) results reported in Scheme 2.) The singlet−triplet gaps of these carbenes differ in magnitude by 3.9 kcal/mol, which could have a pronounced effect on the carbene reactivity under certain conditions. The question, however, is whether the singlet state of 1-(3-thienyl)ethylidene (**3**) is truly low enough in energy to have sufficient thermal population at 10 K to account for the observed reactivity. Our experimental data do not provide an unambiguous assessment of this point. For this mechanism to be operative, the singlet−triplet gap in 1-(3-thienyl)ethylidene (**3**) would have to be exceedingly small. This possibility cannot be excluded.

A second plausible mechanism for the conversion of triplet 1-(3-thienyl)ethylidene (**3**) to 3-vinylthiophene (**8**) (Scheme 8) involves 1,2-hydrogen migration in the triplet state of carbene **3** to afford triplet 3-vinylthiophene (**8**), followed by either phosphorescence or intersystem crossing. DFT calculations suggest that this pathway is energetically viable, with the triplet state of 3-vinylthiophene (**8**) (*s-E*, 53.2 kcal/mol) lying 4.9 kcal/mol below the triplet 1-(3-thienyl)ethylidene (**3**) (*s-E*, 58.1 kcal/mol) in energy (Scheme 2). There are other instances in which intramolecular hydrogen migration reactions of triplet carbenes[23] or nitrenes[24] are postulated to occur on the triplet surface.

A third plausible mechanism for the conversion of triplet 1-(3-thienyl)ethylidene (**3**) to 3-vinylthiophene (**8**) involves 1,2-hydrogen migration near the point of intersection of the triplet and singlet energy surfaces. The burgeoning interest in tunneling reactions notwithstanding,[8,12−15] detailed kinetic modeling and analysis of tunneling reactions that occur with concomitant change of spin multiplicity remain highly challenging problems. Few examples involving tunneling between triplet and singlet surfaces have been studied in detail.[25,26] We have not attempted to model the current system because it is simply not a favorable case in which both the reactant and product can be experimentally monitored over a significant fraction of the reaction course.

In the earlier study of 3-thienylcarbene (**1**), the EPR transitions of the *s-E* conformer of triplet carbene **1** displayed a very small decrease in intensity upon standing for a prolonged period (30−80 h) in the dark in argon at 15 K.[16] As in the case presented here, the low proportion of carbene in the matrix precluded the identification of the reaction product. We speculated that it might be the bicyclic compound resulting from cyclization (Scheme 9). This cyclization reaction is conceivable for the methyl- and trideuteriomethyl-substituted carbenes, and DFT calculations suggest that the cyclization reaction of triplet **3** to singlet **19** is slightly exothermic (ca. 2.5 kcal/mol; Scheme 3). We do not believe, however, that this reaction is responsible for the current observations because (i) the reaction observed for 1-(3-thienyl)ethylidene (**3**) is qualitatively faster than the reaction observed for 3-thienylcarbene (**1**) and (ii) the cyclization reaction is not expected to exhibit the pronounced kinetic isotope effect that is observed for carbenes **3** and **3**-d_3.

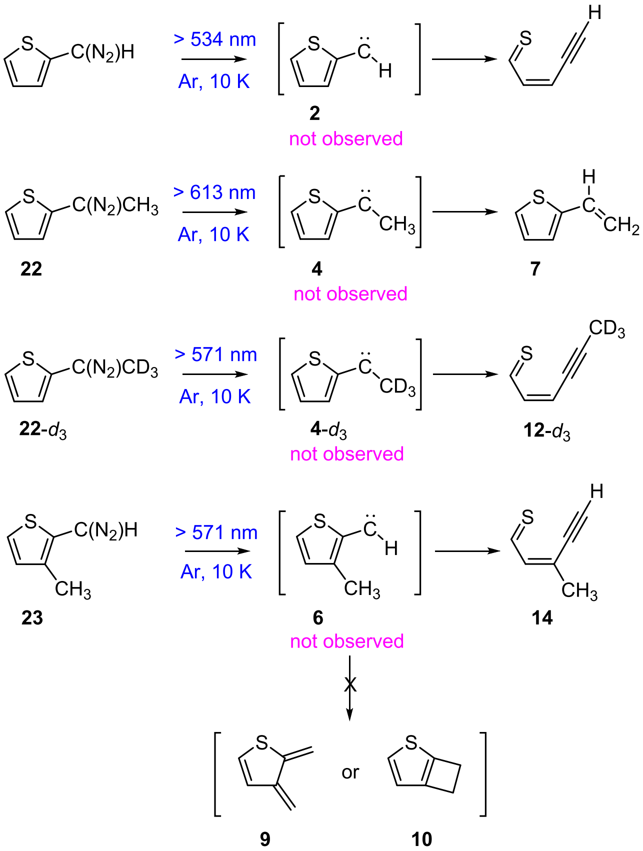
Scheme 9. Putative Cyclization Reactions in 3-Thienylcarbene Derivatives



1-(3-Thienyl)diazoethane Photochemistry. The photochemical products observed upon irradiation of the methyl- and trideuteriomethyl-substituted diazo compounds **21** and **21**-d_3 are qualitatively distinct from those observed from the unsubstituted diazo compound. The dominant products seen upon irradiation of 1-(3-thienyl)diazoethanes **21** and **21**-d_3 are 3-vinylthiophenes (**8** and **8**-d_3, respectively), while the dominant photoproduct seen upon irradiation of 3-thienyldiazomethane is thialmethylenecyclopropene.[16,27,28] The analogous methyl-substituted thialmethylenecyclopropene products (**18**) were not observed in the photochemistry of 1-(3-thienyl)diazoethanes **21** and **21**-d_3. The computed energies of the cyclopropane-containing products (**18**) are significantly higher in energy, ∼46 kcal/mol, than the observed hydrogen shift products (**8**). We also note that there is a slight shift in the electronic absorption spectrum of the diazo compound upon methyl substitution, which leads to a difference in the wavelength for the onset of photochemistry. Under our experimental conditions, 3-thienyldiazomethane requires slightly shorter wavelength irradiation ($\lambda > 534$ nm vs $\lambda > 613$ nm) for photochemical conversion, relative to diazo compounds **21** and **21**-d_3.

Attempted Generation of a 2-Thienylcarbene Derivative (4 or 6). The successful generation of triplet 1-(3-thienyl)ethylidene (**3**) encouraged us to attempt the generation of the isomer, 1-(2-thienyl)ethylidene (**4**). Computations predict that both geometric isomers of 1-(2-thienyl)ethylidene (**4**) should exhibit a triplet ground state (Scheme 3). Irradiation of 1-(2-thienyl)diazoethane (**22**) ($\lambda > 613$ nm; Ar, 10 K), however, affords 2-vinylthiophene (**7**), the product of 1,2-hydrogen migration, as the primary product (Schemes 5 and 10). The EPR spectrum is completely devoid of any signals that can be attributed to triplet 1-(2-thienyl)ethylidene (**4**). The presence of the methyl substituent opens a new reaction pathway, such that the photochemical fragmentation reaction that is observed for the parent 2-thienyldiazomethane is completely suppressed (Scheme 10).[16] Again, it is plausible that the hydrogen migration reaction to form **7** occurs in the excited state of diazo compound **22**, but other explanations are also possible. Interestingly, the photochemistry of the trideuteriomethyl-substituted diazo compound **22**-d_3 is qualitatively different. Rather than 1,2-migration of deuterium, irradiation of 1-(2-thienyl)diazoethane-d_3 (**22**-d_3) ($\lambda > 571$ nm; Ar, 10 K) leads to the photochemical fragmentation reaction (Schemes 6 and 10)

Scheme 10. Attempts to Generate 2-Thienylcarbene Derivatives



that is characteristic of the parent 2-thienyldiazomethane. Thus, deuterium substitution alters the chemistry, as we had hoped, but the consequence of the perturbation did not result in the ability to observe the triplet carbene spectroscopically. Once again, the EPR spectrum is completely devoid of any signals that can be attributed to triplet 1-(2-thienyl)ethylidene-d_3 (**4**-d_3).

In a final attempt to generate a 2-thienylcarbene derivative, or at least intercept it via an intramolecular reaction, we sought to generate 3-methyl-2-thienylcarbene (**6**). In phenyl- and naphthylcarbenes, an *ortho*-methyl substituent serves as an effective intramolecular trap for the proximal carbene center.[18,23,29] Irradiation of (3-methyl-2-thienyl)diazomethane (**23**) (λ > 571 nm; Ar, 10 K), however, leads to the photochemical fragmentation reaction (Schemes 7 and 10) that is characteristic of the parent 2-thienyldiazomethane. The EPR spectrum did not provide direct evidence for the generation of triplet 3-methyl-2-thienylcarbene (**6**), and the IR spectrum did not provide indirect evidence for carbene **6** in the form of signals that could be attributed to the products of intramolecular trapping, *o*-quinodimethane **9** or thienacyclobutene **10** (Scheme 10).

It should be noted that 2-furylcarbene, which is closely related to the 2-thienylcarbenes **4**, **4**-d_3, and **6** targeted herein, has been the subject of considerable experimental, computational, and theoretical interest. 2-Furylcarbene reacts via ring fragmentation[30,31] and has not been detected, experimentally. Herges[32] characterized the ring fragmentation of the 2-furylcarbene intermediate as a coarctate reaction pathway, while Birney[33] later computed a planar transition state, suggesting a pseudopericyclic reaction pathway. 2-Furylcarbene[16,33,34] as well as (2-furyl)chlorocarbene[35] has been calculated to have singlet ground states, at multiple levels of theory, by various groups. 2-Thienylcarbene and derivatives (**2**, **4**, **6**) are computed to have triplet ground states, although the computed singlet−triplet energy gaps are small (Scheme 2) and the absolute accuracy of the calculation may be slightly compromised by the presence of the sulfur atom.

CONCLUSIONS

Triplet carbenes 1-(3-thienyl)ethylidene (**3**) and 1-(3-thienyl)ethylidene-d_3 (**3**-d_3) have been generated and spectroscopically characterized under matrix isolation conditions at cryogenic temperature. Ethylidene **3** is not stable in the dark at 10 K, disappearing slowly over tens of hours. The trideuteriomethyl derivative **3**-d_3 is completely unreactive under similar conditions, implicating an intramolecular 1,2-hydrogen migration reaction as the cause for the disappearance of protio carbene **3**. It is likely that the reaction originates from the triplet state of **3** and occurs via a quantum mechanical tunneling process. Although there are now numerous examples of hydrogen atom transfer reactions that occur by quantum mechanical tunneling mechanisms in spin-allowed systems (radicals, singlet carbenes, etc.), there are few examples that occur as formally spin-forbidden processes. A close analogue for the rearrangement of triplet 1-(3-thienyl)ethylidene (**3**) to 3-vinylthiophene (**8**) is the rearrangement of triplet 1-phenylethylidene to styrene (Scheme 8), but the differences in reactivity are significant, not well understood at this time, and deserving of further study. Despite considerable effort, attempts to secure direct or even indirect evidence for derivatives of triplet 2-thienylcarbene were unsuccessful.

METHOD SECTION

General Methods. ^{1}H NMR spectra (300 MHz) and ^{13}C{^{1}H} NMR spectra (75 MHz) were obtained in $CDCl_3$ or Me_2SO-d_6; chemical shifts (δ) are reported as ppm downfield from internal $SiMe_4$. Mass spectra and exact mass measurement (EMM) were obtained on a time-of-flight instrument using electrospray ionization (ESI) or atmospheric solid analysis probe ionization (ASAPI). 3-Acetylthiophene, 2-acetylthiophene, and 3-methyl-2-thiophenecarboxaldehyde were purchased from commercial sources. The matrix isolation apparatus and technique have been described previously.[16,36,37]

Computational Methods. Optimized geometries, energies, harmonic vibrational frequencies, and infrared intensities were obtained at the B3LYP/6-31G(d) level of theory and for selected species at the B3LYP/6-311+G(2d,p) level of theory using the Gaussian software package.[38] The nature of stationary points was confirmed by calculation of the harmonic vibrational frequencies, which also provided zero-point vibrational energy (ZPVE) corrections. Vibrational frequencies were not scaled. Computed IR spectra were generated from the predicted IR frequencies and intensities by applying a Gaussian line shape and a nominal line width that is representative of our experiments. Natural bond orbital (NBO) calculations were performed at the B3LYP/6-31G(d) level of theory using the NBO program.[39]

Deuteriation of 2- and 3-Acetylthiophene. 2- and 3-Acetylthiophene were deuteriated via an exchange reaction in a modified method given by De Maria et al.[40] The acetylthiophene (2 g, 0.016 mol) was dissolved in a small amount of dry diethyl ether (5 mL). To this solution were added 12 mL of deuterium oxide and two pellets of NaOH. The solution was stirred at room temperature overnight to give 97−98% deuteration of the acyl methyl group. The product was purified by recrystallization from methanol.

3-Acetylthiophene-*d*$_3$. White crystals. Yield 0.82 g (40%); ^{1}H NMR ($CDCl_3$) 8.04 (dd, *J* = 2.7, 1.1 Hz, 1H), 7.55 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.32 (m, 1H); ^{13}C{^{1}H} NMR (Me_2SO-d_6) δ 192.2, 142.2, 134.0, 127.4, 127.2, 126.4 ppm.

2-Acetylthiophene-*d*$_3$. White crystals. Yield 1.0 g (50%); ^{1}H NMR ($CDCl_3$) 7.69 (dd, *J* = 3.8, 1.0 Hz, 1H), 7.65 (dd, *J* = 5.0, 0.9 Hz, 1H), 7.13 (m, 1H); MS (EI) *m*/*z*: 129.0 (M$^+$); HRMS (ASAPI) *m*/*z*: [M]$^+$ calcd for $C_6H_3D_3OS^+$ 129.0328, Found 129.0332.

General Procedure for Preparation of Tosylhydrazones. The *p*-tosylhydrazone precursors to compounds **21**, **21**-***d***$_3$, **22**, **22**-***d***$_3$, and **23** were synthesized using a modified method given by Katritzky *et al.*[41] *p*-Toluenesulfonhydrazide (4.65 g, 0.025 mol) was added to a corresponding carbonyl compound (0.025 mol) in 30 mL of methanol and refluxed for 12 h using a heating mantle. The solution was diluted with water (50 mL), and the precipitate was collected by suction filtration. The crude product was recrystallized from methanol. Verification that H/D exchange did not occur during *p*-tosylhydrazone formation was obtained by ^{1}H NMR analysis.

3-Acetylthiophene Tosylhydrazone. White crystals. Yield 6.6 g (90%); mp 185−187 °C; ^{1}H NMR (Me_2SO-d_6) δ 10.38 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.79 (dd, *J* = 2.7, 1.3 Hz, 1H), 7.48 (dd, *J* = 5.0, 3.8 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.33 (dd, *J* = 5.0, 1.1 Hz, 1H), 2.34 (s, 3H), 2.16 (s, 3H); ^{13}C{^{1}H} NMR (Me_2SO-d_6) δ 150.1, 143.2, 140.4, 136.7, 136.1, 129.3, 127.6, 125.5, 125.2, 20.9, 14.7 ppm; MS (ESI) *m*/*z*: [MH]$^+$ 295.4; HRMS (ESI) *m*/*z*: [M + Na]$^+$ calcd for $C_{13}H_{14}N_2O_2S_2Na^+$ 317.0394, Found 317.0402.

3-Acetylthiophene-*d*$_3$ Tosylhydrazone. White crystals. Yield 5.7 g (77%); mp 184−186 °C; ^{1}H NMR (Me_2SO-d_6) δ 10.36 (s, 1H), 7.95 (m, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.49 (dd, *J* = 5.2, 2.9 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.31 (dd, *J* = 5.0, 0.9 Hz, 1H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (Me_2SO-d_6) δ 150.0, 143.2, 140.4, 136.1, 129.3, 127.6, 126.7, 125.5, 25.1, 20.9 ppm (CD_3 carbon does not show up); MS (EI) *m*/*z*: [M]$^{+\cdot}$ 297.0; HRMS (ASAPI) *m*/*z*: [M]$^+$ calcd for $C_{13}H_{11}D_3N_2O_2S_2^+$ 297.0680, Found 297.0680.

2-Acetylthiophene Tosylhydrazone. White crystals. Yield 6.3 g (86%); mp 206−208 °C;[31] ^{1}H NMR (Me_2SO-d_6) δ 10.45 (s, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 5.1 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.38 (d, *J* = 3.7 Hz, 1H), 7.02 (dd, *J* = 5.1, 3.7 Hz, 1H), 2.36 (s, 3H), 2.17 (s, 3H); $^{13}C\{^1H\}$ NMR (Me_2SO-d_6) δ 149.6, 143.3 (may be two overlapping peaks), 142.5, 136.6, 129.3, 128.6, 127.6, 127.4, 20.9, 14.4 ppm; MS (ESI) *m/z*: $[MH]^+$ 295.2; HRMS (ESI) *m/z*: $[MH]^+$ calcd for $C_{13}H_{11}D_3N_2O_2S_2H^+$ 295.0575, Found 295.0577.

2-Acetylthiophene-d_3 Tosylhydrazone. White crystals. Yield 5.2 g (70%); mp 207−209 °C;[31] ^1H NMR (Me_2SO-d_6) δ 10.75 (s, 1H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.51 (dd, *J* = 5.0, 1.0 Hz 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.36 (dd, *J* = 3.7, 1.0 Hz, 1H), 7.02 (dd, *J* = 5.0, 3.6 Hz, 1H), 2.34 (s, 3H); $^{13}C\{^1H\}$ NMR (Me_2SO-d_6) δ 149.7, 143.4, 142.5 (may be two overlapping peaks), 136.0, 129.3, 128.6, 127.6, 127.4, 20.9 (CD_3 carbon does not show up) ppm; MS (ESI) *m/z*: $[M]^+$ 297.1; HRMS (ASAPI) *m/z*: $[M]^+$ calcd for $C_{13}H_{11}D_3N_2O_2S_2^+$ 297.0685, Found 297.0678.

3-Methyl-2-thiophenecarboxaldehyde Tosylhydrazone. Light-orange crystals. Yield 5.8 g (79%); mp 151−153 °C; ^1H NMR (Me_2SO-d_6) δ 11.22 (s, 1H), 8.09 (s, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 4.8 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 6.89 (d, *J* = 5.1 Hz, 1H), 2.36 (s, 3H), 2.21 (s, 3H); $^{13}C\{^1H\}$ NMR (Me_2SO-d_6) δ 143.4, 141.2, 139.6, 136.0, 131.6, 130.8, 129.5, 127.7, 127.2, 20.9, 13.4 ppm.

Preparation of Tosylhydrazone Sodium Salts. Sodium hydride (1.1 equiv, 60% suspension in mineral oil) was added to the corresponding *p*-tosylhydrazone (1 equiv) in THF and allowed to stir at room temperature for 1 h. The resulting precipitate was filtered and dried on a vacuum line. The reaction was run on a 500 mg scale with respect to the tosylhydrazone.

Caution! Diazo compounds present the risk of explosive decomposition under thermal or photochemical conditions. Proper safety precautions must be taken when handling these compounds, especially as neat materials. Manipulations were performed on the smallest practical scale. Samples were maintained at low temperature, under a vacuum or inert atmosphere, whenever possible. We did not encounter any problems in handling the aryl diazo compounds described in this study.

Preparation of the Thienyl Diazo Compounds 21, 21-d_3, 22, 22-d_3, and 23. The diazo compounds were formed by heating the corresponding *p*-tosylhydrazone sodium salt to 110 °C under vacuum using an oil bath. The diazo compound (red, pink, or purple) was collected on a cold finger at −78 °C and rinsed into a deposition tube with dry methylene chloride. After the methylene chloride was removed under vacuum, the diazo compound was deposited onto a cold window (IR, UV/vis) or copper rod (EPR) with a constant flow of argon. This procedure yields the matrix-isolated diazo compounds **21**, **21-d_3**, **22**, **22-d_3**, and **23**.

1-(3-Thienyl)diazoethane (21). Hot pink liquid. IR (N_2, 10 K) 2048 s, 2044 s, 1626 w, 1597 w, 1540 m, 1471 w, 1466 w, 1440 w, 1398 w, 1384 w, 1075 w, 961 w, 900 w, 857 w, 761 m, 709 w, 621 w cm^{-1}.

1-(3-Thienyl)diazoethane-d_3 (21-d_3). Hot pink liquid. IR (Ar, 10 K): 2044 s, 1600 w, 1535 w, 863 w, 754 w, 619 w cm^{-1}.

1-(2-Thienyl)diazoethane (22).[31,42,43] Red/purple liquid. IR (Ar, 10 K): 2051 s, 2044 s, 1623 w, 1521 w, 1468 w, 1445 w, 1439 w, 1028 w, 847 w, 793 w, 675 w cm^{-1}.

1-(2-Thienyl)diazoethane-d_3 (22-d_3). Red/purple liquid. IR (Ar, 10 K) 2046 s, 2040 s, 1623 w, 1518 w, 1447 w, 1441 w, 1342 w, 846 w, 794 w, 738 w, 703 w, 681 w cm^{-1}.

(3-Methyl-2-thienyl)diazomethane (23). Red liquid. IR (Ar, 10 K): 2063 s, 1709 m, 1459 w, 1365 w, 1230 w, 1059 w, 737 m, 701 w cm^{-1}.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its online Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.3c01639.

Matrix isolation spectra (IR, UV/vis, EPR); ^1H and $^{13}C\{^1H\}$ NMR spectra of synthesized compounds; computed energies; harmonic vibrational frequencies; infrared intensities; and Cartesian coordinates (PDF)

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Notes

The authors declare no competing financial interest.

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