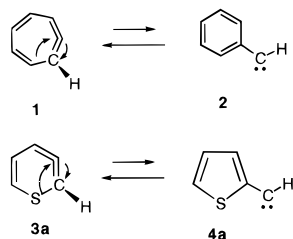


Communications to the Editor

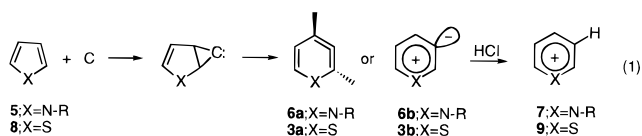
Thiacyclohexatriene–Thiophenylcarbene
Rearrangement. A Sulfur Analog of the
Cycloheptatetraene–Phenylcarbene RearrangementWeitao Pan, Metin Balci,[†] and Philip B. Shevlin*Department of Chemistry, Auburn University
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The interconversion of cycloheptatetraene (**1**) and phenylcarbene (**2**) along the C₇H₆ energy surface, providing a pathway for the interconversion of *o*-, *m*-, and *p*-substituted phenylcarbenes, has been the subject of intense scrutiny over many years.^{1,2} We now report evidence for a similar interconversion along the C₅H₄S energy surface connecting thiacyclohexa-2,3,5-triene (**3a**) with the thiophenylcarbene (**4a**) as well as evidence for several other interesting intermediates on this surface. Our



entry to the C₅H₄S energy surface employs a reaction analogous to our previously reported reaction of carbon with pyrrole (**5**) in which labeling studies (²H and ¹³C) demonstrate the intermediacy of a dehydropyridinium ylide, (**6b**).³ Subsequent protonation of **6b** leads to pyridinium ions **7** (eq 1). In the present case, we have cocondensed C atoms with thiophene (**8**) and HCl at 77 K.⁴ NMR analysis of the nonvolatile products in CF₃COOD solvent reveals the thiopyrylium ion, **9**, as the only detectable product in solution (eq 1).⁵



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(4) For reviews of the chemistry of atomic carbon, see: (a) Skell, P. S.; Havel J.; McGlinchey, M. J. *Acc. Chem. Res.* **1973**, *6*, 97. (b) MacKay, C. In *Carbenes*; Moss, R. A.; Jones, M., Jr., Eds.; Wiley-Interscience: New York, 1975; Vol. II, pp 1–42. (c) Shevlin, P. B. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. I, pp 1–36.

(5) The C atom reactor is modeled after that described by Skell, P. S.; Westcott, L. D., Jr.; Golstein, J. P.; Engel, R. R. *J. Am. Chem. Soc.* **1965**, *87*, 2829. Thiopyrylium ion **9** was identified by electrospray mass spectrometry and a comparison of its ¹H and ¹³C NMR spectra with those reported in the literature.⁶

Although it is tempting to propose the intermediacy of the 3-dehydrothiopyrylium ylide (**3b**) under these conditions, preliminary calculations (MP2/6-31G*) indicate that **3b** is actually a transition state connecting the two enantiomeric forms of **3a** and lies 8.5 kcal above **3a**.⁷ It is expected that both **3a** and **3b** would be protonated by HCl to give the aromatic thiopyrylium ion (**9**). For **6**, where planar dehydropyridinium ylid **6b** is calculated (MP2/6-31G*) to be the ground state,^{2a} reaction with CO₂ is observed.^{2b} However, in the present study, we observe no reaction of **3** with CO₂. Since an ylide is expected to react with CO₂ but a cummulene is not, we favor the nonplanar cummulene structure **3a** as the ground state in this system.^{7,8}

To further investigate the mechanism of the formation of **9** and to determine the point of attack of the carbon atoms on **8**, we have reacted ¹³C-enriched carbon vapor with thiophene in both the presence and absence of added H(D)Cl.¹⁰ The results of these reactions, which are summarized in Scheme 1 (*C = ¹³C), reveal far more complexity than was observed in the reaction of ¹³C atoms with pyrrole which gave a label only at C₃ in **7**.³ In the present case, trapping with HCl yields **9** with 54% of label at C₂, 40% at C₃ and 6% at C₄. The most reasonable pathway to **9** labeled at C₃ is addition to a double bond followed by ring expansion to generate **3a** (or **3b**) which is subsequently protonated.

To rationalize the label at C₂ of **9**, we postulate attack of ¹³C atoms at sulfur followed by ring expansion to generate **10**, which has both planar ylide **10a** and carbene **10b** resonance structures. Subsequent trapping of **10** by HCl would yield **9** labeled at C₂. The use of DCl as a trap shows approximately equal amounts of D at C₂ and C₃ as required by the intermediacy of **3** and **10**, ruling out a major route to **9**-¹³C involving rearrangement of carbene **4a** formed by initial C–H insertion.

Although these H(D)Cl-trapping experiments and ¹³C-labeling results provide evidence for the intermediacy of **3** and **10** in the reaction of atomic carbon with **8**, they say little concerning the possible intermediacy of the isomeric 2- and 3-thiophenylcarbenes (**4a** and **4b**). Although carbenes **4a** and **4b** have been prepared from the corresponding tosylhydrazone salts and observed to dimerize¹¹ and **4b** has recently been generated on a 10 K Ar matrix,¹² the fate of these carbenes under the present HCl-trapping conditions and subsequent extraction with CF₃COOD is unclear. Accordingly, we have carried out an experiment in which we condensed C with **8** in the absence of HCl and extracted the reactor bottom with hexane after the reaction. The residue insoluble in hexane was then dissolved in CF₃COOH. The results of this experiment are striking. The hexane fraction contained the two new compounds *exo*-2-thia-6-(2-thiophenyl)bicyclo[3.1.0]hex-3-ene (**11**) and *exo*-2-thia-

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(7) Thus, **3** appears to be similar to **1** where both experiment and calculations indicate enantiomeric cycloheptatetraenes separated by a planar transition state. However, we point out that the situation regarding **1** has only recently been clarified after many years of work culminating in several recent sophisticated theoretical treatments.² We are presently in the process conducting a similar computational study of the C₅H₄S energy surface. Pending the results of these studies, conclusions regarding the energetics of **3a** and **3b** must be regarded as preliminary.

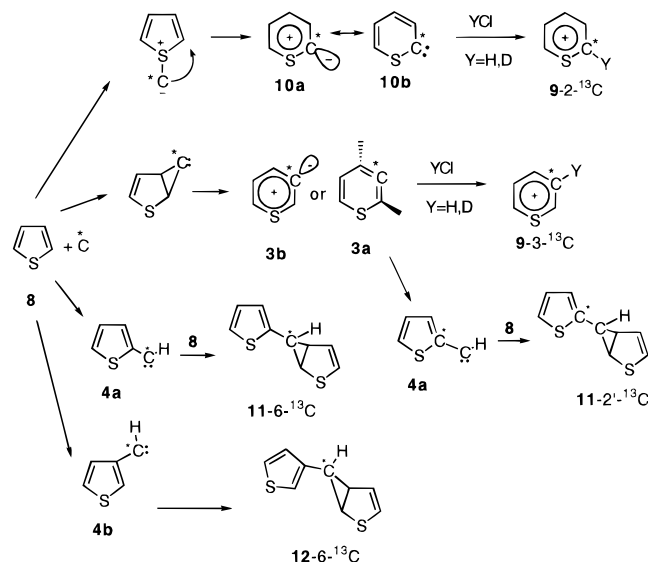
(8) Although cummulene **3a** is expected to have considerable strain energy, we note that 3,4-dehydrothiophene, a cyclic cummulene with one less carbon, has been trapped.⁹

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(10) Carbon vapor enriched in ¹³C was generated as described in ref 3a. (11) Hoffman, R. V.; Orphanides, G. G.; Shechter, H. *J. Am. Chem. Soc.* **1978**, *100*, 7927.

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Scheme 1



6-(3-thiophenyl)bicyclo[3.1.0]hex-3-ene (**12**) in a 2.5:1 ratio (Scheme 1).¹³ Analysis of the CF₃COOH solution of the residue remaining after hexane extraction revealed the presence of **9** (**9/11/12** = 2.2:2.5:1).

Since **11** and **12** are likely result from the reaction of **8** with carbenes **4a** and **4b**, respectively, the intermediacy of these carbenes is indicated. If carbene **4a** is involved in the formation of **11**, it could arise by the cummulene-carbene rearrangement (**3a** → **4a**) or by a simple C-H insertion by C atoms on **8** (Scheme 1). To distinguish between these pathways to **4a**, we have reacted ¹³C atoms with **8** using the conditions described above. This experiment reveals that **11** is labeled in the 2' and 6 positions in a 5:1 ratio while **12** is labeled exclusively in the 6 position. Since the majority of the label in **11** is in the 2' position, we conclude that a substantial fraction of this compound results from the reaction of **8** with **4a** which has been produced by the cummulene to carbene rearrangement of initially formed **3a** as shown in Scheme 1. The fact that **11** is also labeled in the 6 position and **12** is exclusively 6-labeled indicates that C-H insertions by carbon also produce **4a** and **4b** which then react with **8** to produce appropriately labeled **11** and **12** (Scheme 1).

(13) Compounds **11** and **12** were separated by flash chromatography on alumina with pentane eluent and characterized by NMR spectroscopy. For **11**: ¹H NMR (δ, CDCl₃) 7.11 (dd, 1H, *J* = 5.1, 1.2 Hz), 6.93 (dd, 1H, *J* = 5.1, 3.5 Hz), 6.73 (ddd, 1H, *J* = 3.5, 1.2, 0.7 Hz), 6.12 (dd, 1H, *J* = 5.7, 1.6 Hz), 5.93 (dd, 1H, *J* = 5.7, 2.8 Hz), 3.20 (ddd, 1H, *J* = 7.3, 3.5, 1.6 Hz), 2.83 (1H, 4d, *J* = 7.3, 2.5, 2.8 Hz), 1.77 (brt, 1H, *J* = 3.5 Hz); ¹³C NMR (δ, CDCl₃) 145.21 (s), 127.24 (d, *J*_{CH} = 167.9 Hz), 126.56 (d, *J*_{CH} = 180.5 Hz), 124.06 (d, *J*_{CH} = 171.3 Hz), 122.90 (d, *J*_{CH} = 184.2 Hz), 122.39 (d, *J*_{CH} = 171.8 Hz), 40.90 (d, *J*_{CH} = 167.9 Hz), 34.82 (d, *J*_{CH} = 179.9 Hz), 23.64 (d, *J*_{CH} = 167.3 Hz); HRMS for C₉H₈S₂, calcd 180.0067, found 180.0060. For **12**: ¹H NMR (δ, CDCl₃) 7.28 (dd, 1H, *J* = 5.0, 3.6 Hz), 6.83 (m, 2H), 6.10 (ddd, 1H, *J* = 5.7, 1.6, 0.4 Hz), 5.92 (dd, 1H, *J* = 5.7, 2.8 Hz), 3.14 (ddd, 1H, *J* = 7.3, 3.5, 1.6 Hz), 2.76 (1H, 4d, *J* = 7.3, 2.5, 2.8 Hz), 1.62 (brt, 1H, *J* = 3.5 Hz); ¹³C NMR (δ, CDCl₃) 126.20, 126.03, 125.93, 124.37, 117.66, 39.67, 33.68, 23.79; GCMS *m/z* = 180.

Analysis of the CF₃COOH soluble residue generated in this experiment shows that **9** contains 90% of its excess ¹³C in the 2 position with the remainder in the 3 position. This is in contrast to **9** formed by cocondensation of HCl with ¹³C and **8** which was labeled in the 2 and 3 positions in a 1.35:1 ratio. The fact that **9** is labeled 90% in the 2 position in the absence of cocondensed HCl indicates that **10** lives long enough to accept a proton while most of **3a** rearranges to **4a** which is subsequently trapped by **8**. In the absence of HCl, it is probable that the vinyl protons on **8** serve to protonate **10**. We have previously obtained evidence for protonation of dehydropyrindinium ylids by the vinyl protons in *N*-methylpyrrole,^{3b} and it is expected that the vinyl protons on thiophene will be more acidic than those on *N*-methylpyrrole.¹⁴

These results, which demonstrate that atomic carbon reacts with thiophene by double bond addition, attack at sulfur, and insertion into both C-H bonds, stand in marked contrast to the reaction of C with pyrrole in which only addition to the double bond and subsequent ring opening to the dehydro aromatic ylide **6b** occurs. Although the reasons for the differing reactivity of C atoms toward **5** and **8** are not completely clear, we have rationalized the regiochemistry of carbon reactions by postulating that carbon attacks at the point of highest electron density in the highest occupied molecular orbital (HOMO).^{3a,15} Given this consideration, it is not surprising that pyrrole, which has no electron density on N in the HOMO and a HOMO-HOMO-1 gap of 1 eV,¹⁶ is not attacked at nitrogen. However, for **8**, the HOMO-HOMO-1 gap of 0.65 eV¹⁷ may bring about a less-regiospecific attack by carbon and allow attack at sulfur.

These investigations further demonstrate the unique ability of atomic carbon to provide facile routes to interesting reactive intermediates. Here, the generation of a small ring cummulene with ¹³C atoms reveals a cyclic cummulene-carbene interconversion which is analogous to that occurring in the well-known phenylcarbene rearrangement.

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Supporting Information Available: NMR spectra and assignments for compounds **11** and **12** (9 pages). See any current masthead page for ordering and Internet access instructions.

JA970241F

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(18) Furan, an apparently analogous system, reacts rather differently. We have observed C atoms to react with furan in the gas phase by predominate addition to the double bond followed by ring opening.¹⁵ In the present case, HCl trapping does not result in pyrylium ion (although the analysis is complicated by extensive polymerization of the furan) and ring-opened products are not observed in either the reaction of furan or **8**.