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A Plethora of Carbene Interconversions on the C_5H_4S Energy Surface: A Computational Study

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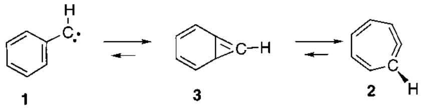
Abstract: The potential energy surface for the reaction of atomic carbon with thiophene has been studied computationally. Intermediates which are energetically viable include the 2- and 3-thienylcarbenes **8** and **11**, thiacyclohexa-3,5-dien-2-ylidene, **10**, and thiacyclohexa-2,3,5-triene, **6**. In accord with experimental data, **6** and **8** are in equilibrium. The lowest-energy pathway for rearrangement of **6** to **8**, which is endothermic by 14.5 kcal/mol, involves ring opening to *Z*-2-penten-4-ynthial which then recloses to carbene **8**. A 1,4 addition of C across the diene system in thiophene generates an ylid which rearranges with little or no barrier to cyclopentadienethione, the global minimum on this potential energy surface.

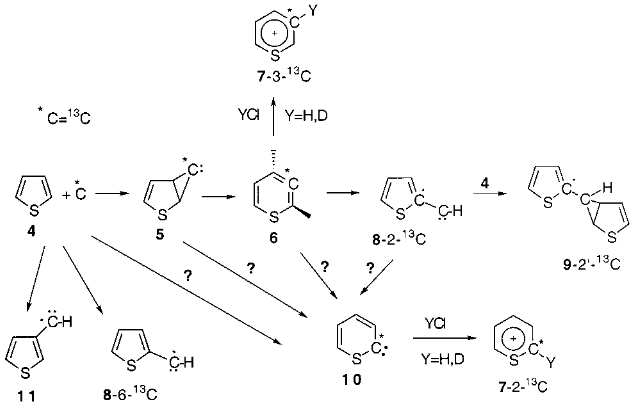
Introduction

The high energy associated with carbenes has facilitated the formation of many new high-energy molecules. Of particular interest are cases in which the energetic product of the carbene rearrangement lies close to the carbene in energy, and a reversible rearrangement is possible. A familiar example, which has been well-studied both experimentally[1,2] and computationally,[3] is the interconversion of phenylcarbene, **1**, and cycloheptatetraene, **2**, along the C_7H_6 energy surface. This reaction, which is thought to involve the intermediacy of bicyclo[4.1.0]hepta-1.3.6-triene, **3**, interconverts the *o*-, *m*-, and *p*-substituted phenylcarbenes. In this equilibrium, **2** is the thermodynamic sink and has been trapped in several ways.[2,4]



As summarized in Scheme 1, we have recently observed an analogue of the phenylcarbene rearrangement in the reaction of atomic carbon with thiophene, **4**, in which the use of ^{13}C atoms indicates that an important pathway involves addition of C to a double bond to give thiabicyclopropylidene, **5**, which ring-opens to thiacyclohexa-2,3,5-triene, **6**.[5,6] Addition of H(D)-Cl during the reaction traps **6** as the 3-labeled (^{13}C and D) thiopyrylium ion, **7**. When acid is absent, **6** rearranges to the 2-thienylcarbene, **8**, labeled predominately on the quaternary carbon, which is trapped by thiophene to give **9**. An additional product of acid trapping is the 2-labeled thiapyrylium ion **7** which was postulated to result from protonation of thiacyclohexa-3,5-dien-2-ylidene, **10**. Carbene **10** could lie on the energy surface connecting **6** and **8**, it could result directly from **5**, or it could arise independently in the reaction between C and **4**. Minor products are carbene **8**-6-^{13}C and the 3-thienylcarbene, **11**, whose labels indicate that they result from an initial C−H insertion by carbon on **4**.

Scheme 1. Major Products in the Reaction of ^{13}C Atoms with Thiophene, **4**



To determine the likely modes of interconversion of initially formed reactive intermediates in this system, we have carried out an extensive computational investigation of the C_5H_4S energy surface. These studies have uncovered a new low-energy pathway in the carbene−cumulene (**8**−**6**) interconversion which does not exist on the energy surface connecting **1** and **2**.

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These investigations have been designed to predict the most reasonable pathways to stable products from initially formed intermediates. Although we feel that we obtain reasonable estimates of the relative energies of initial intermediates, we cannot predict which of these intermediates is likely to predominate in the reaction of C with **4**. To make such predictions with confidence requires a detailed consideration of the trajectory of the attacking carbon and the fact that it is most likely in the ^{1}D state, requiring collapse of a multiconfigurational complex to the initial intermediates.

Computational Methods

Geometries were calculated at the B3LYP/6-31G(d) level of theory which has proven to be effective in reproducing geometries in a wide variety of bonding environments.[7,8] Vibrational frequencies have been computed at the B3LYP/6-31G(d) level to confirm the nature of the stationary points and to make zero-point corrections. The imaginary frequency (transition vector) was animated graphically for all transition states to ensure that the motion was appropriate for converting reactants to products. In cases in which the transition vector did not clearly indicate reactant and product, the transition state was displaced and optimized to confirm the identity of the reactant and product. Single-point calculations have been made at QCISD(T)/6-31G(d) and MP2/6-311+G(3df,2p) levels and combined with the additivity approximation[9] to estimate relative energies at the [QCISD(T)/6-311+G(3df,2p)] level (eq 1).

$$\Delta E(\text{QCISD(T)/6-311+G(3df,2p)}) = \Delta E(\text{QCISD(T)/6-31G(d)}) + \Delta E(\text{MP2/6-311+G(3df,2p)}) - \Delta E(\text{MP2/6-31G(d)}) \quad (1)$$

The approximation in eq 1 is similar to the one used in the G2(MP2,SVP) procedure[10a] except that geometries and zero-point energies (unscaled) are calculated at B3LYP/6-31G(d) rather than MP2/6-31G(d) (for geometry) and HF/6-31G(d) (for frequencies) and a higher-level correction term (ΔHLC) has not been included. The ΔHLC term is zero except when the number of a and b spin electrons is different from the reference compound. Thus, the target calculation [QCISD(T)/6-311+G(3df,2p)] is similar to the G2(MP2,SVP) method which has been shown by Radom and co-workers[10] to reproduce a number of molecular properties to within chemical accuracy (2 kcal/mol). However, it should be pointed out that for transition states the errors may be larger.

Since it is known that DFT underestimates barrier heights by a few kcal/mol,[11] reactions with small barriers may proceed without activation to products when calculated at B3LYP/6-31G(d). Therefore, wecalculated several transitions states (**TS27-28**, **TS28-24**, **TS28-10**) and intermediates (**27**, **28**) at the MP2/6-31G(d) level when such structures did not exist on the B3LYP/6-31G(d) potential energy surface. Thus, all energies in the text are at the [QCISD(T)/6-311+G(3df,2p)]//B3LYP/6-32(d)+ZPC or [QCISD(T)/6-311+G(3df,2p)]//MP2/6-31G(d)+ZPC levels. Energies calculated at the various levels of theory are shown in Table 1. Geometries and energies of relevant intermediates are shown in Figures 1 and 2. All calculations were made with the GAUSSIAN98 program.[12] The frozen core approximation was used in calculating MP2 and QCISD(T) energies.

Results and Discussion

In these investigations, we have focused our attention on the possible pathways leading to intermediates **6**, **8**, and **10**, the interconversion of these intermediates, and other reactions they may be expected to undergo. Our labeling experiments indicate that carbene **8**-6-^{13}C and it's regioisomer the 3-thienylcarbene, **11**, are also formed by a minor C−H insertion pathway. Thus, we have included the expected chemistry of **11** in our calculations. Since there are a number of viable pathways to **6**, **8**, and **10** in this system, we have divided the possibilities into several categories. We first consider the possibility that **6**, **8**, and **10** all arise from an initial double bond addition to give **5**. In this case, **5** could either directly generate **6**, **8**, and **10**, or it could ring-open to **6** from which **8** and **10** could form by several possible mechanisms. Both of these alternatives will be investigated. Next, we shall consider the possibility that **6** and **8** arise from **5**, while **10** is the result of an independent reaction between C and **4**. As we shall see, these computational investigations have led us to the consideration of multiple pathways and products in this system.

The Role of Thiabicyclopropylidene 5 in Product Formation. Since we calculate that carbene **5** has a singlet ground state 18.8 kcal/mol lower than the triplet, we have focused our attention on the singlet energy surface and briefly discuss the triplet surface later. The formation of **5** from C(^{1}D) is calculated to be exothermic by 83.5 kcal/mol.[13] An examination of its geometry, shown in Figure 1, reveals several interesting features. The carbene carbon is only 2.2 Å from the sulfur, indicating an interaction between the filled sulfur p-orbital and the empty p-orbital on the carbene. This interaction, which is a common mode of stabilization for singlet carbenes, is also revealed by an examination of the carbene LUMO. The fact that there is some bonding between the attacking carbon and sulfur in **5**, raises the possibility that this species could directly produce **8** and **10** as well as **6**. Carbene **10** could arise directly from **5** by retaining the C_1-S_8 interaction and breaking the C_2-S_8 and C_1-C_3 bonds. Direct formation of **8** from **5** could also be envisioned to occur by retaining the C_1-S_8 interaction and breaking the C_2-S_8 and C_2-C_3 bonds. However, when these three possible reactions of **5** were investigated, it was found that direct formation of **10** ($\Delta H^{\ddagger} = 16.8$ kcal/mol) or **8** ($\Delta H^{\ddagger} = 31.4$ kcal/mol) was not competitive with ring opening to **6** ($\Delta H^{\ddagger} = 6.6$ kcal/mol). Hence, if **5** is formed initially and its energy is uniformly distributed throughout the molecule, it is expected to cross the lowest barrier and rearrange only to **6**. Accordingly, we shall now consider the properties and reactions of **6**.

The Properties and Reactions of Cumulene 6. When we reacted carbon with pyrrole **12**, labeling studies (^{2}H and ^{13}C)

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Table 1. Total Energies (hartrees), Zero-Point Energies (kcal/mol), and Relative Energies (kcal/mol) for Structures Optimized at the B3LYP/6-31G(d) Level

structure no.	B3LYP/6-31G(d)	MP2/6-31G(d)	QCISD(T)/6-31G(d)	MP2/6-311+G(3df,2p)	additivity^a	ZPE^b	rel *E* (kcal/mol)
C(^{3}P)+**4**	−590.84891	−589.65752	−589.74154	−589.93881	−590.02283	41.97	98.7
5	−590.92921	−589.73171	−589.81421	−590.02762	−590.11012	43.27	45.2
6	−591.01105	−589.81281	−589.89355	−590.10334	−590.18408	44.47	0.0
6MP2	-	−589.81354	−589.89352	−590.10450	−590.18448	44.99^f	0.3
8	−590.99046	−589.78395	−589.86524	−590.07790	−590.15919	43.39	14.5
10	−591.02650	−589.82427	−589.90329	−590.11794	−590.19696	45.06	−7.5
10MP2	-	−589.82498	−589.90264	−590.11947	−590.19713	45.65^f	−7.0
11	−590.97751	−589.77367	−589.85587	−590.06814	−590.15034	43.30	20.0
15	−590.99920	−589.79976	−589.87378	−590.09341	−590.16743	44.05	10.0
16a	−591.01370	−589.81380	−589.89310	−590.09928	−590.17858	43.42	2.4
16b	−591.02145	−589.82125	−589.90086	−590.10597	−590.18558	43.51	−1.9
C_2H_2	−77.32565	−77.06649	−77.09381	−77.15683	−77.18415	16.71	
20	−513.61045	−512.67675	−512.72982	−512.87340	−512.92647	22.04	
20+C_2H_2	−590.93610	−589.74329	−589.82363	−590.03023	−590.11062	38.75	25.9
21	−590.98896	−589.77879	−589.86471	−590.07136	−590.15728	43.73	16.1
22	−590.99481	−589.80701	−589.87748	−590.09759	−590.16806	45.03	10.6
23	−590.97901	−589.78912	−589.86519	−590.07812	−590.15419	44.13	18.4
24	−591.06766	−589.87067	−589.95096	−590.15479	−590.23508	45.40	−31.1
24MP2	-	−589.87087	−589.95091	−590.15505	−590.23509	45.47^f	−31.0
25	−590.87359	−589.66344	−589.75223	−589.97045	−590.05924	42.98	76.8
27MP2	-	−589.76214	−589.83788	−590.05964	−590.13537	45.00^f	31.1
28MP2	-	−589.81438	−589.88818	−590.10361	−590.17740	45.48^f	5.2
30	−590.99380	−589.78965	−589.87025	−590.08322	−590.16382	44.19	12.4
31	−590.98925	−589.79703	−589.87172	−590.08557	−590.16026	44.11	14.6
32	−590.92956	−589.73537	−589.81404	−590.03575	−590.11442	43.01	42.2
33	−591.01326	−589.81631	−589.89617	−590.10182	−590.18168	43.18	0.2
34	−590.99423	−589.79973	−589.87181	−590.09208	−590.16416	44.63	12.7
35	−591.00046	−589.79254	−589.87121	−590.07784	−590.15651	43.70	16.5
36	−591.01912	−589.81865	−589.89853	−590.10198	−590.18186	43.30	0.2
37a	−590.94614	−589.72954	−589.82120	−590.01557	−590.10723	42.06	45.8
37b	−590.94426	−589.73008	−589.82316	−590.01311	−590.10619	42.15	46.6
TS^c							
TS5−6	−590.92480	−589.72220	−589.80802	−590.01277	−590.09859	42.59	51.8
TS5−8	−590.87294	−589.66990	−589.75134	−589.97714	−590.05858	42.30	76.6
TS5−10	−590.90237	−589.70490	−589.78234	−590.00426	−590.08170	42.18	62.0
TS6−8	−590.95625	−589.75586	−589.83027	−590.05629	−590.13070	42.66	31.7
TS6−10	−590.90350	−589.70133	−589.78012	−589.99951	−590.07830	40.26	62.2
TS6−16a	−590.98914	−589.78796	−589.86476	−590.07601	−590.15281	43.30	18.4
TS6−20+C_2H_2	−590.90638	−589.71343	−589.78765	−590.00579	−590.08001	40.01	60.8
TS6−30	−590.89810	−589.69320	−589.77638	−589.99140	−590.07458	40.33	64.6
TS8−21	−590.91342	−589.70694	−589.78644	−590.00368	−590.08318	40.43	59.3
TS8−23	−590.96286	−589.76357	−589.84245	−590.05492	−590.13380	43.20	30.3
TS10−24	−590.95597	−589.76815	−589.84318	−590.06278	−590.13781	43.50	28.1
TS11−6	−590.92980	−589.73464	−589.80792	−590.03179	−590.10507	42.50	47.6
TS11−20+C_2H_2	−590.87187	−589.65446	−589.76594	−589.95531	−590.06679	39.39	68.5
TS11−31	−590.96197	−589.76052	−589.84053	−590.05354	−590.13355	43.04	30.3
TS11−33	−590.89310	−589.68656	−589.76529	−589.98705	−590.06578	40.02	69.8
TS16a-16b	−591.00257	−589.80713	−589.88766	−590.09234	−590.17287	42.65	5.2
TS16a-8	−590.98651	−589.77146	−589.85803	−590.06314	−590.14971	42.77	19.9
TS21−22	−590.96666	−589.76465	−589.84691	−590.05660	−590.13886	43.65	27.6
TS23−10	−590.96908	−589.77790	−589.85278	−590.07047	−590.14535	43.26	23.1
TS25−10	−590.83437	−589.62376	−589.71491	−589.93115	−590.02230	41.87	98.9
TS25−C_2H_2	−590.79783	−589.60722	−589.68406	−589.90706	−589.98390	37.75	118.9
TS27−28MP2	-	−589.76076	−589.83760	−590.05778	−590.13462	44.77^f	31.3
TS28−10MP2	-	−589.76865	−589.84341	−590.06434	−590.13910	43.97^f	27.7
TS28−24MP2	-	−589.81226	−589.88569	−590.10147	−590.17489	44.99^f	6.3
TS30−32	−590.92956	−589.72189	−589.81024	−590.01462	−590.10297	42.10	48.5
TS31−30	−590.96731	−589.77535	−589.84895	−590.06842	−590.14202	43.06	25.0
TS31−35	−590.97543	−589.76841	−589.81284	−590.05633	−590.10076	43.36	51.2
TS33−34	−590.94471	−589.74481	−589.82589	−590.04200	−590.12308	43.12	36.9
TS35−16a	−590.91393	−589.70470	−589.78663	−589.99640	−590.07833	40.75	62.6
TS35−36	−590.91768	−589.70787	−589.79043	−589.99846	−590.08102	40.78	61.0
Triplets^d							
T-5	−590.91284	−589.70571	−589.79487	−589.99104	−590.08020	43.30	64.0
T-6	−590.99185	−589.75981	−589.86388	−590.04646	−590.15053	43.61	20.2
T-8	−590.98993	−589.76374	−589.86623	−590.04925	−590.15174	42.78	18.6
T-10	−590.98997	−589.75522	−589.86373	−590.03836	−590.14687	43.86	22.7
T-11	−590.98392	−589.76083	−589.86237	−590.04751	−590.14905	43.01	20.5
T-25	−590.87468	−589.66691	−589.75287	−589.96258	−590.04854	42.68	83.3
T-30	−590.98820	−589.75493	−589.86258	−590.03914	−590.14679	43.70	22.6
T-38	−590.89807	−589.67488	−589.77419	−589.96788	−590.06719	42.05	70.9
T-TS5−6	−590.90921	−589.68098	−589.78672	−589.97102	−590.07676	42.34	65.2
T-TS25−38	−590.86458	−589.63000	−589.74068	−589.92619	−590.03687	42.01	89.9
T-TS38−10	−590.89561	−589.66916	−589.76918	−589.96315	−590.06317	41.64	73.0

Table 1. (Continued)

structure no.	B3LYP/6-31G(d)	MP2/6-31G(d)	QCISD(T)/6-31G(d)	MP2/6-311+G(3df,2p)	additivity[a]	ZPE[b]	rel *E* (kcal/mol)
			Cations[e]				
7	−591.45608	−590.25581	−590.33267	−590.53732	−590.61418	53.87	−34.9
39	−591.38033	−590.17730	−590.25748	−590.45899	−590.53917	52.80	11.1
40	−591.39008	−590.18033	−590.26867	−590.46577	−590.55411	51.09	0.0
41	−591.29637	−590.08169	−590.16912	−590.37534	−590.46277	50.56	56.8
TS39−7	−591.32741	−590.11916	−590.20718	−590.40250	−590.49052	50.83	39.6
TS40−41	−591.27438	−590.06147	−590.14558	−590.35881	−590.44292	48.47	67.2
TS41−7	−591.24820	−590.04595	−590.13187	−590.34510	−590.43102	49.39	75.5

[a] ΔE(additivity) = ΔE(QCISD(T)/6-31G(d)) + ΔE(MP2/6-311+G(3df,2p)) − ΔE(MP2/6-31G(d)). [b] Zero-point energy is calculated at the B3LYP/6-31G(d) level except where noted. [c] All transition states have one imaginary frequency at the B3LYP/6-31G(d) level. [d] The next 11 entries are triplet spin states. [e] The next seven entries are $SC_5H_5^+$ cations. Energies are relative to **40**. [f] Zero-point energy is calculated at the MP2/6-31G(d) level.

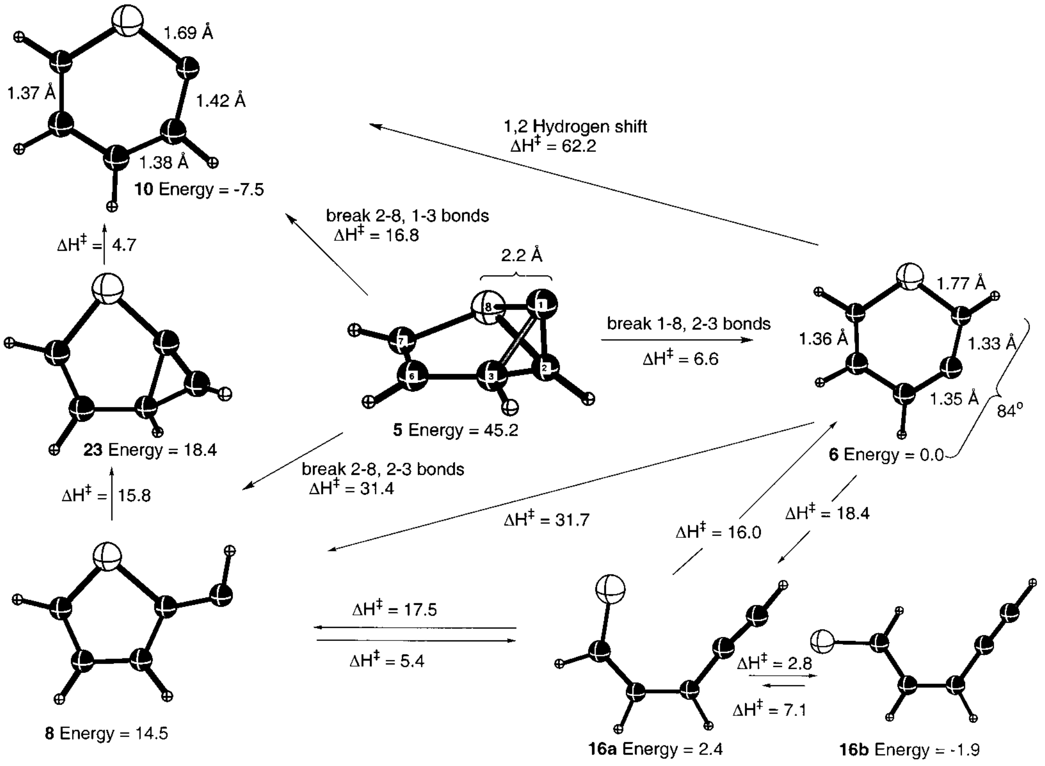
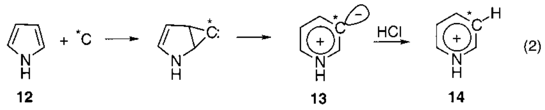


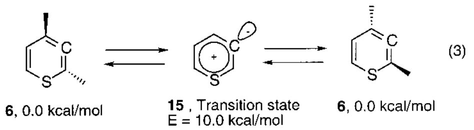
Figure 1. Geometries (B3LYP/6-31G(d)) of intermediates leading to the major products from the initial addition of C to a double bond in **4**. Energies (kcal/mol) are relative to **6**, while $\Delta H^‡$s are actual activation energies (kcal/mol) for the pathways connecting the intermediates.

demonstrated the intermediacy of a dehydropyridinium ylid, **13**.[14] Subsequent protonation of **13** leads to pyridinium ion **14** (eq 2).



(2)

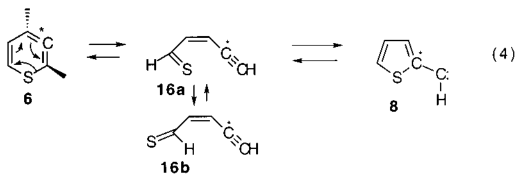
Although it is tempting to propose the intermediacy of the 3-dehydrothiopyrylium ylid **15** in the present case, our calculations indicate that **15** is actually a transition state connecting the two enantiomeric forms of **6** and lies 10.0 kcal/mol above **6** (eq 3).[15] It is expected that both **6** and **15** would be protonated by HCl to give the aromatic thiopyrylium ion, **7**. Thus, **6** appears to be similar to **2** in which both experiment and calculations indicate enantiomeric cycloheptatetraenes separated by a planar transition state.



(3)

Since **6** is similar to **2** in structure, we have investigated the energetics of its rearrangement to **8** in a reaction formally analogous to the rearrangement of **2** to **1**. While we find a pathway from **6** to **8** ($\Delta H^‡ = 31.7$ kcal/mol), it differs from the **2**-to-**1** rearrangement in that there is no bicyclic intermediate (indeed the electronic structure precludes one). Rather, the transition state resembles that for a carbon analogue of the Wolf rearrangement.

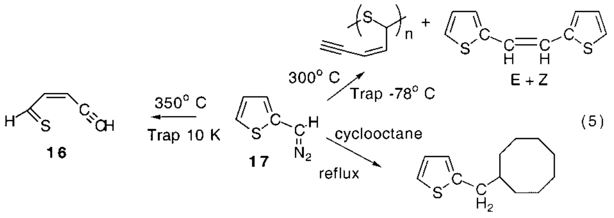
In examining possible reactions of **6**, we have uncovered an interesting lower-energy pathway for the interconversion of **6** and **8**. This reaction begins with the ring opening of **6** to *Z*-pent-2-en-4-ynthial, **16a**, which then closes to carbene **8** as shown in eq 4. Although **16a** is formed initially from both **6** and **8**,



(4)

the most stable conformer is **16b**. Since the barrier connecting **16a** and **16b** is lower than those connecting it with **6** or **8**, it is expected that **16b** will form during the rearrangement of **6** to **8** along this pathway. Thus, the energy difference between **16a** and **16b** of 4.3 kcal/mol must be added to the **16a** → **8** barrier, giving a value of 21.8 kcal/mol for the rate-determining step in the **6** → **8** rearrangement. Ring opening of **8** to **16a** traverses a barrier of 5.4 kcal/mol. Closure of **16a** to **6** crosses a barrier of $16.0 + 4.3 = 20.3$ kcal/mol. Hence, the interconversion of **6** and **8** via **16a,16b** requires surmounting a barrier of 21.8 kcal/mol. In contrast, we calculate a barrier of 31.7 kcal/mol for the direct interconversion of **6** and **8**. Thus, under conditions in which energetic **6** or **8** are generated, we would predict that these species would interconvert by the ring opening−reclosure pathway involving the intermediacy of **16** rather that by a direct rearrangement.

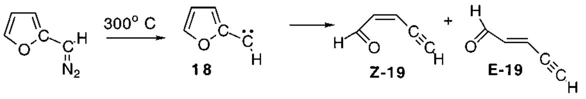
The finding that carbene **8** easily opens to **16a** is not surprising and is in accord with experimental observation. Thus, Albers and Sander[16] have reported that thermolysis of diazo-(2-thienyl)methane **17** at 350 °C followed by trapping at 10 K gives **16**. When Hoffman, Orphanides, and Shechter[17] pyrolyzed **17** at 300 °C, trapped products at −78 °C, and analyzed them by conventional means, they found dimers of carbene **8** along with smaller amounts of a polymer corresponding to **16**. These authors also pyrolyzed **17** in cyclooctane and isolated the C−H insertion product (eq 5).



16 **17** (5)

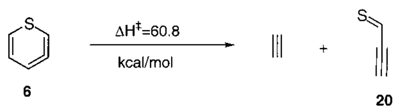
These findings are consistent with an initial formation of carbene **8** which is in equilibrium with **16**. On a low-temperature matrix, **16** is isolated, while conventional trapping leads mainly to products from carbene **8**. Of course, our results indicate that cumulene **6** is also present in the equilibrium mixture but not trapped in the above experiments. It is anticipated that pyrolysis of **17** followed by trapping with acid would yield thiopyrylium ion **7**. While our ^{13}C labeling results cannot distinguish between a direct formation of **8** from **6** or a pathway involving **16**, they are consistent with predominate formation of **8** from **6**.

The cleavage of (2-heteryl)carbenes is also observed in the thermolysis of 2-furylcarbene, **18**, which results in formation of *Z*- and *E*-pent-2-en-4-ynal, **19**.[17] That no difficulty is encountered in isolating **19** in this reaction most probably results from the fact that ring opening in **18** is considerably more exothermic than in **8** and that reversal to the carbene does not occur. Indeed, we calculate a barrier of 2.2 kcal/mol for the ring opening of **18** to ***Z*-19** in a reaction exothermic by 28.3 kcal/mol.[18]



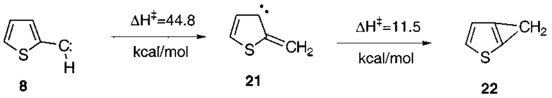
18 **Z-19** **E-19**

An alternate reaction of cumulene **6**, cleavage to acetylene and propynethial **20**, has a barrier of 60.8 kcal/mol and would not be competitive.



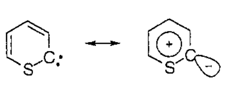
6 **20**

An interesting, although higher-energy, reaction of carbene **8** is 1,3 hydrogen migration to generate the butadienylidene **21** which subsequently closes to bicyclopropene **22**.

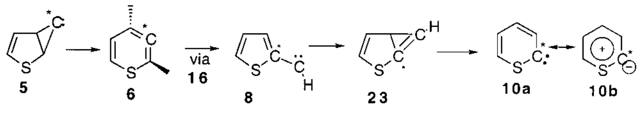


8 **21** **22**

The Energetics of the Formation and Reactions of 10. We now turn our attention to the ways in which intermediate **10** could form in the C + **4** system and the chemical reactions of this interesting reactive intermediate. It is apparent from the structure of **10** that this species may be considered either a carbene or an yild as exemplified by resonance structures **10a** and **10b**. The ylid form **10b** would have the advantage of aromatic stabilization similar to that observed in the thiopyrylium ion. Evidence for substantial contribution of yild **10b**, with its C−S double bond, is provided by the rather short $C_{carbene}$−S bond length of 1.69 Å compared to 1.77 Å in **6** and 1.73 Å calculated in **4**. Of the reactive intermediates implicated in the C + **4** reaction, **10** is calculated to be the most stable.


10a **10b**

As mentioned earlier, formation of **10** from **5**, with randomized energy, is not expected to be competitive with ring opening of **5** to **6**. The formation of **10** directly from **6** by a 1,2 hydrogen shift is problematic as it involves migration of the hydride into a filled p orbital, and this process is calculated to have a prohibitively high barrier of 62.2 kcal/mol. We have calculated a route to **10** by rearrangement of carbene **8** and find a reasonable route to this intermediate in the C + **4** reaction (Figure 1). This reaction appears to follow a pathway which is quite similar to that observed in the rearrangement of **1** to **2**. Thus, carbene **8** first closes to 2-thiabicyclo[3.1.0]-hexa-3,6-diene, **23**, a compound analogous to **3**, with a barrier of 15.8 kcal/mol. Subsequent ring opening of **23** with a barrier of 4.7 kcal/mol generates **10.** There is no experimental evidence for trapping of **23** in any of the reactions of carbene **8**, and the fact that it lies in an energy well only 4.7 kcal/mol deep would seem to preclude trapping. The label distribution that we observe in **7** from the reaction of C + **4** followed by acid trapping is consistent with the sequence of reactions in Figure 1 in which **10** is formed from **8** via **23**.



5 **6** **8** **23** **10a** **10b**

An examination of the chemistry of **10** reveals a ring contraction to cyclopentadienethione, **24**, which appears to be

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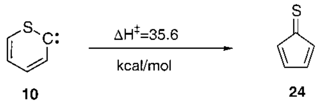
[14] (a) Emanuel, C. J.; Shevlin, P. B. *J. Am. Chem. Soc.* **1994**, *116*, 5991. (b) Pan, W.; Shevlin, P. B. *J. Am. Chem. Soc.* **1997**, *119*, 5091.

[15] We have considered the possibility that **15** may have strong biradical character. UDFT calculations on the singlet biradical allow us to estimate that this $^1A''$ species is about 17 kcal/mol above **6**.

[16] Albers, R.; Sander, W. *J. Org. Chem.* **1997**, *62*, 761.

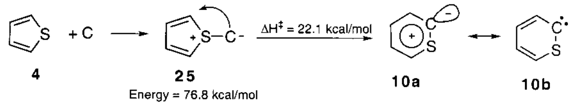
[17] Hoffman, R. V.; Orphanides, G. G.; Shechter, H. *J. Am. Chem. Soc.* **1978**, *100*, 7927.

the global minimum on the C_5H_4S energy surface, over a barrier of 35.6 kcal/mol.

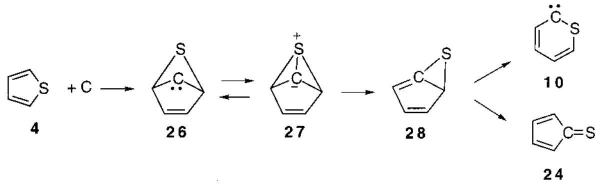


We have also examined the possibility that **10** arises directly from the C + **4** reaction via intermediates distinct from **5**. In particular, we have examined the consequences of an initial attack by C at sulfur and 1,4-addition of carbon across the diene system in **4**.

While we do find an energy minimum for **25** in which carbon attacks **4** at the sulfur, this species is 31.6 kcal/mol higher in energy than **5**. Furthermore, rearrangement of **25** to **10** requires traversing a barrier of 22.1 kcal/mol. Although formation of **10** via **25** would give the experimentally observed label distribution, this pathway lies at higher energy than that in which **10** results from **8**. An alternate reaction of **25**, cleavage to two molecules of acetylene and CS, has a higher barrier of 42.1 kcal/mol.



We next turn to the possibility that carbon attacks **4** at the π system by a 1,4 addition to generate 6-thiabicyclo[2.1.1]hex-2-en-5-ylidene, **26**, which could rearrange via ylid **27** to 6-thiabicyclo[3.1.0]hexa-1,3-diene, **28**.[19] Subsequent ring opening of **28** would generate **10** with the experimentally observed label distribution.



When we attempted a geometry optimization of carbene **26** at the B3LYP/6-31G(d) level, a stationary point corresponding to yild **27** with a $C_{carbene}-S$ bond length of 1.92 Å was generated. However, a frequency calculation on this structure revealed it to be a transition state with C_s symmetry. When this symmetry was removed by lengthening one CH−S bond and shortening the other, a reoptimization generated cyclopentadienethione, **24**.

Thus, the DFT calculation identifies a low-energy pathway leading to **24** without barrier. Since it is common for DFT calculations to underestimate small barriers,[11] we have reoptimized carbene **26** at the MP2/6-31G(d) level. As in the DFT calculation, this procedure led to ylid **27** now with a $C_{carbene}-S$ bond length of 1.89 Å. At the MP2/6-31G(d) level however, a frequency calculation indicated that **27** was an energy minimum. Additional calculations at the MP2/6-31G(d) level indicated that 6-thiabicyclo[3.1.0]hexa-1,3-diene, **28**, was an energy minimum and identified transition states from **27** to **28** and from **28** to **10** and **24**. These MP2 geometries were then used to calculate energies at the [QCISD(T)/6-311+G(3df,2p)]//MP2/6-31G(d)+ZPC level which are included in Table 1 and summarized in Figure 2 with relevant geometries. An examination of these energies in Table 1 and in Figure 2 reveals that the lowest-energy pathway from ylid **27** is rearrangement to thiabicyclohexadiene **28** with a barrier of 0.2 kcal/mol and thence to thioketone **24** with a barrier of 1.1 kcal/mol. While we do calculate a transition state from **28** to **10**, this rearrangement proceeds with the considerably higher barrier of 22.5 kcal/mol and would not be competitive with the rearrangement of **28** to **24**.

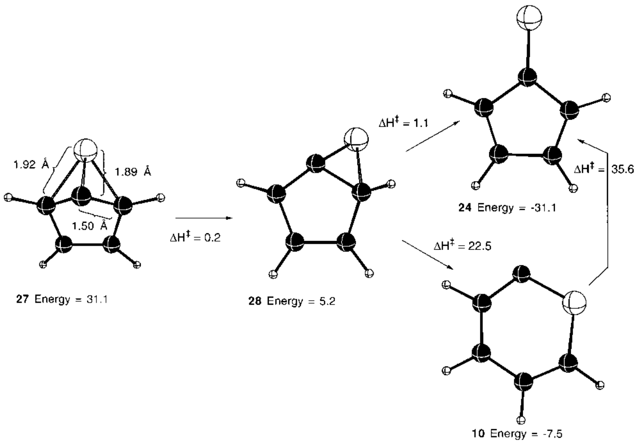
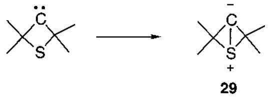


Figure 2. Geometries (MP2/6-31G(d)) of intermediates leading to the major products from the initial 1,4 addition of C to **4**. Energies (kcal/mol) are relative to **6**, while $\Delta H^{\ddagger}$s are actual activation energies (kcal/mol) for the pathways connecting the intermediates.

Although it may seem problematic to compare higher-level energies calculated from MP2/6-31G(d) geometries with those calculated using B3LYP/6-31G(d) geometries, both methods give qualitatively the same conclusion: If C atoms add 1,4 across the diene system in **4**, the initial product will rearrange with little or no barrier to thioketone **24**. We note also that there is little difference in higher level energies regardless of the geometry used. Thus, the energy of **6** differs by only 0.3 kcal/mol at the two geometries, and that of **10**, by only 0.5 kcal/mol. The rearrangement of ylid **27** to thioketone **24** is of interest, as one might expect a least-motion pathway, in which both CH−S bonds in **27** are broken simultaneously, to provide an efficient route to **24**. However, this pathway is orbital symmetry-forbidden, and a nonsynchronous breaking of the two CH−S bonds is required. Once this symmetry distortion is achieved, the rearrangement to **24** proceeds with little (via **28**, MP2 geometry) or no barrier (B3LYP geometry).

The fact that ylid **27** rather than carbene **26** is the energy minimum for this intermediate finds analogy in the recent report by Snoonian and Platz[21] in which evidence for bridged ground state **29** for 2,2,4,4-tetramethyl-3-thietan-1-ylidene is reported.



The Chemistry of 3-Thienylcarbene, 11. As mentioned earlier, experimental evidence indicates that carbenes **8** and **11**

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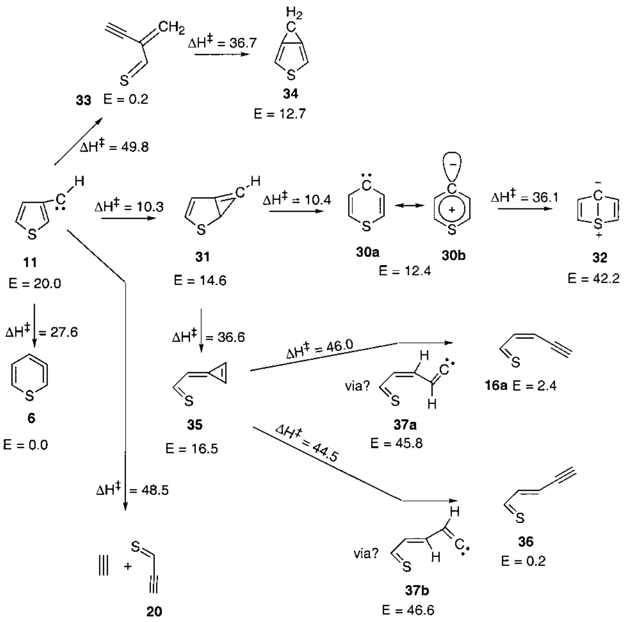
(18) Similar barriers and exothermicities have been calculated previously: (a) Khasanova, T.; Sheridan, R. S. *J. Am. Chem. Soc.* **1998**, *120*, 233. (b) Sun, Y.; Wong, M. W. *J. Org. Chem.* **1999**, *64*, 9170. (c) Birney, D. M. *J. Am. Chem. Soc.* **2000**, *122*, 10917.

(19) A perceptive reviewer has pointed out that the rearrangement of **26** to **28** resembles the ring contraction of cyclobutylidene to methylenecyclopropane. It is interesting that, like cyclobutylidene,[20] **26** is stabilized by unusual intramolecular interactions.

(20) (a) Stracener, L. L.; Halter, R. J.; McMahon, R. J.; Castro, C.; William L. Karney, W. L. *J. Org. Chem.* **2000**, *65*, 199. (b) Schoeller, W. W. *J. Am. Chem. Soc.* **1979**, *101*, 4811. (c) Sulzbach, H. M.; Platz, M. S.; Schaefer, H. F.; Hadad, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 5682.

(21) Snoonian, J. R.; Platz, M. S. *J. Phys. Chem. A* **2001**, *105*, 2106.

Scheme 2. Reaction Pathways Calculated for Carbene **11**[a]



[a] Energies (kcal/mol) are relative to **6**, and $\Delta H^{\ddagger}$s represent energy barriers connecting the intermediates

are formed by C−H insertion in the reaction between C and **4**. Since the chemistry of **8** has been discussed, we shall briefly discuss the expected reactions of **11** which are outlined in Scheme 2. In analogy with phenylcarbene, the lowest-energy pathway for **11** is ring expansion to thiacyclohexa-2,5-dien-4-ylidene **30** which proceeds via the intermediacy of thiabicyclohexadiene **31**. Carbene **30** like **10**, enjoys the possibility of aromatic stabilization via resonance structure **30b**, and the rearrangement of **11** to **30** is exothermic by 7.6 kcal/mol. In analogy with ylids **27** and **29** one might expect that **30** would be stabilized by sulfur-bridging in ylid **32**. However ylid **32**, although an energy minimum, is calculated to be 29.8 kcal/mol higher in energy than **30** which must cross a barrier, 36.1 kcal/mol, to reach the ylid. In this case, it is presumably the strain associated with the two fused thiacyclobutene rings and the aromaticity of **30** which favors this species in the **30**−**32** equilibrium. A higher-energy pathway ($\Delta H^{\ddagger} = 27.6$ kcal/mol) connects carbene **11** with cumulene **6** via a transition state with considerable bonding between the carbene carbon and C_4 of the ring and provides the final link in a pathway for the interconversion of carbenes **8**, **10**, **11**, and **30**. Thus, given enough energy, we would expect that carbenes **6**, **8**, **11**, and **30**, regardless of their precursor, would eventually find their way to **10**. At still higher energies, we find that cleavage of **11** will generate acetylene and **20** ($\Delta H^{\ddagger} = 48.5$ kcal/mol), while ring opening of **11** with concomitant hydrogen migration will generate 2-ethynyl-2-butenthial, **33** ($\Delta H^{\ddagger} = 49.8$ kcal/mol). Rearrangement of **33** to bicyclic thiophene **34** crosses a barrier of 36.7 kcal/mol.

When Albers and Sander[16] photolyzed the diazo precursor of carbene **11** at 10 K, they observed the interesting rearrangement to α-thial methylenecyclopropene **35** which they postulated to occur via **11** and **31.** Subsequent photolysis of **35** generated *Z*- and *E*-pent-2-en-4-ynthial, **16** and **36**. Accordingly, we have calculated the PES connecting **31** to **35** and thence to **16** and **36** as shown in Scheme 2. The fact that the barrier for the thermal rearrangement of **31** to **35** is relatively high at 36.6 kcal/mol and subsequent ring openings to **16** and **36** are even higher (46.0 and 44.5 kcal/mol respectively) indicates that the rearrangements observed by Albers and Sander[16] are photochemical rather than thermal, a conclusion also reached by these authors. Although the ring opening of **35** occurs with hydrogen migration and C−C bond cleavage, an interesting feature is the fact that the C−C bond is cleaved at the carbon at the migration origin and appears to generate the intermediate vinylidenes **37a** and **37b** which rapidly migrate to a hydrogen.

The Reaction of C(^{3}P) with 4. In our experimental investigations of the co-condensation of C atoms arc-generated with **4** at 77 K, we find no evidence for the reaction of C(^{3}P). Thus, addition of oxygen, an efficient scavenger of C(^{3}P), does not effect product yields. We do not think lack of products from triplet carbon reflects the absence of this species which is the ground state of atomic carbon. Instead, we feel that the reaction conditions (condensed phase, 77 K) are not conducive to the reaction of C(^{3}P) with substrate. Rather, reaction of triplet carbon with itself leads to the copious amount of amorphus carbon we see in these reactions. However, there is extensive documentation of the reactions of C(^{3}P) in gas-phase molecular beam studies,[22] and we shall briefly discuss the expected reactivity of triplet C with **4** which is summarized in Scheme 3.

It is perhaps not surprising that carbene **10**, with its empty p orbital stabilized by electron donation from the adjacent sulfur and double bonds has a singlet ground state ($S-T = -30.2$ kcal/mol). We do however, find a low-energy pathway to ^{3}**10** via the intermediacy of ^{3}**25** ($S-T = -6.5$ kcal/mol) and monovalent triplet **38**. An alternate pathway leads from initial ^{3}**5** ($S-T = -18.8$ kcal/mol) to ^{3}**6** ($S-T = -20.2$ kcal/mol). In contrast to ^{1}**6**, the triplet is a planar molecule. This brief exploration of the triplet surface in the C + **4** reaction leads us to conclude that the most likely pathways in this system will lead to triplet forms of **6** and **10** which will then decay to their corresponding singlet states. It should be pointed out that gas-phase studies of the reactions of C(^{3}P) lead to energetic intermediates which, lacking collisional stabilization, invariably cleave a C−H bond.[22a−e] We have not considered this subsequent reaction channel in our calculations on the initial intermediates in the C(^{3}P) + **4** system.

Conclusions and Relationship of these Calculations to the Experimental Reaction of Arc-Generated Carbon with 4

As stated in the Introduction, trapping and labeling studies of the reaction of arc-generated carbon with **4** provide evidence for the intermediacy of **6**, **8**, **10**, and **11**. The label in **6** indicates that it comes from an initial double bond addition followed by ring opening, a route calculated to be energetically viable. Trapping products from carbene **8** indicate that it arises from both a C−H insertion and rearrangement of **6**. Our calculations have identified a previously unknown low-energy pathway for this rearrangement. Trapping products of carbene **11** indicate that this carbene arises solely by C−H insertion with no evidence of a carbene rearrangement route to **11**. The calculations indicate that rearrangement of **6** to **11** ($\Delta H^{\ddagger} = 47.6$ kcal/

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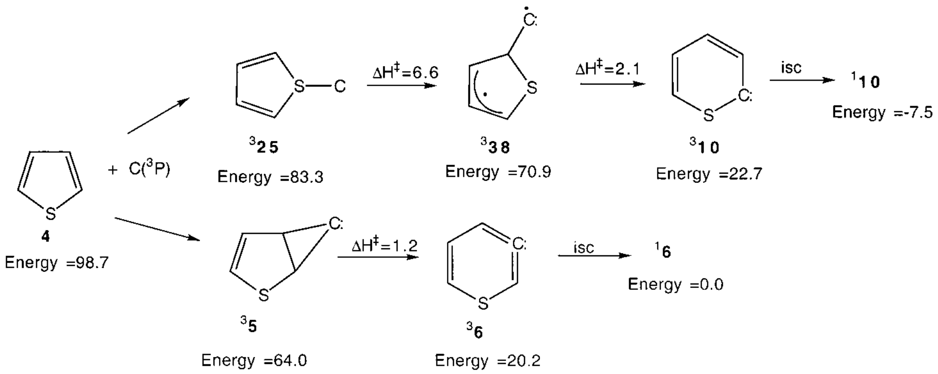
(22) Recent examples include: (a) Le, T. N.; Lee, H.; Mebel, A. M.; Kaiser, R. I. *J. Phys. Chem.* A **2001**, *105*, 1847. (b) Bettinger, H. F.; Schleyer, P. v. R.; Schaefer, H. F., III; Schreiner, P. R.; Kaiser, R. I.; Lee, Y. T. *J. Chem. Phys.* **2000**, *113*, 4520. (c) Huang, L. C. L.; Lee, H. Y.; Mebel, A. M.; Lin, S. H.; Lee, Y. T.; Kaiser, R. I. *J. Chem. Phys.* **2000**, *113*, 9637. (d) Kaiser, R. I.; Mebel, A. M.; Chang, A. H. H.; Lin, S. H.; Lee, Y. T. *J. Chem. Phys.* **1999**, *110*, 10330. (e) Kaiser, R. I.; Hahndorf, I.; Huang, L. C. L.; Lee, Y. T.; Bettinger, H. F.; Schleyer, P. v. R.; Schaefer, H. F., III; Schreiner, P. R. *J. Chem. Phys.* **1999**, *110*, 6091. (f) Kaiser, R. I.; Ochsenfeld, C.; Head-Gordon, M.; Lee, Y. T. *J. Chem. Phys.* **1999**, *110*, 2391. (g) Chastaing, D.; Le Picard, S. D.; Sims, I. R. *J. Chem. Phys.* **2000**, *112*, 8466. (h) Chastaing, D.; James, P. L.; Sims, I. R.; Smith, I. W. M. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2247. (i) Geppert, W. D.; Naulin, C.; Costes, M. *Chem. Phys. Lett.* **2001**, *333*, 51.

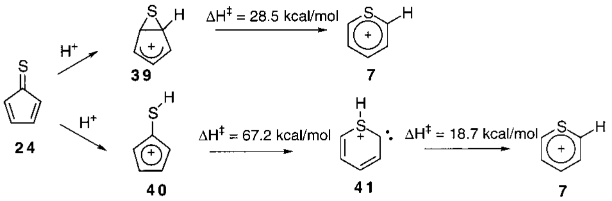
Scheme 3. Major Products Expected in the Reaction of C(^{3}P) Atoms with Thiophene, **4**[a]



[a] Energies (kcal/mol) are relative to ^{1}**6** and $\Delta H^{\ddagger}$'s, represent energy barriers (kcal/mol) connecting the intermediates

mol) would not be competitive with rearrangement of **6** to **8** ($\Delta H^{\ddagger} = 31.7$ kcal/mol). However, rearrangement of **11** (generated by C−H insertion) to **6** ($\Delta H^{\ddagger} = 27.6$ kcal/mol) may be possible. This rearrangement would generate **6** labeled at C_4, and we do report 6% of the label in this position. The lowest-energy pathway for rearrangement of **11** is to **31** ($\Delta H^{\ddagger} = 10.3$ kcal/mol) This pathway generates **30** which upon protonation produces **7**-3-^{13}C which is indistinguishable from **7** from protonation of **6**. The calculations identify a pathway from **6** to **10** which would generate **7**-2^{13}C as is observed.

However, the calculations identify an additional low-energy pathway in the reaction of C with **4** which has not been previously considered. This is the initial 1,4 addition to give ylid **27** which rearranges with little or no barrier to thioketone **24**, a species not analyzed for in the experimental work. Although the spectral properties of **24** have been measured in the gas phase,[23] the compound has not been isolated, and it is not clear that it would have survived addition of acid to the products of the C + **4** reaction. It is possible that protonation of **24** would provide a pathway to the observed **7**-2-^{13}C. In fact, we calculate that protonation of **24** on carbon generates bridged carbocation **39** which ring-opens to **7** with a barrier of 28.5 kcal/mol. In contrast, protonation of **24** on sulfur generates **40** which, although 11.1 kcal/mol lower in energy than **39**, ring-expands to **41** with a barrier of 67.2 kcal/mol. Subsequent H migration in **41** over a barrier of 18.7 kcal/mol gives **7**. Thus, if it is assumed that **24**-1-^{13}C is generated in the ^{13}C + **4** reaction, acid trapping would generate **7**-2-^{13}C as observed.



Our calculations clearly indicate that a reexamination of the products of the C + **4** reaction for the presence of **24** is in order. We plan to undertake this reexamination. As is often the case, the application of computational methods to the interpretation of the experimental results points the way toward additional experiments.

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Supporting Information Available: Geometries of the species listed in Table 1 (PDF). This material is available free of charge via the Internet at http://www.acs.org.

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(23) Schulz, R.; Schweig, A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 570.