

Toward 2-Thiophyne: Ketocarbene versus Hetaryne Intermediates from 2-(Trimethylsilyl)thiophen-3-yl Triflate

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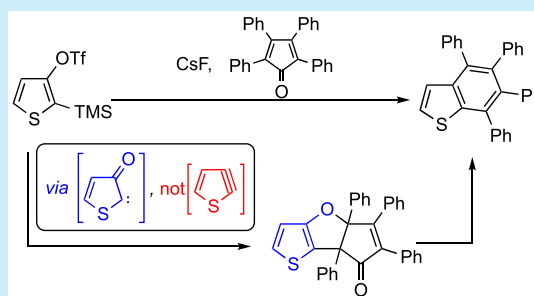


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ABSTRACT: The reaction of 2-(trimethylsilyl)thiophen-3-yl triflate with CsF in the presence of 2,3,4,5-tetraphenylcyclopentadienone affords 4,5,6,7-tetraphenylbenzo[*b*]thiophene, as it would be expected from the hypothesized generation and trapping of 2-thiophyne. However, a detailed experimental and computational study discards the intermediacy of this elusive 5-membered hetaryne. Instead, a complex mechanism involving the generation of an intermediate ketocarbene, which adds to the cyclopentadienone to give an isolable tricyclic intermediate, followed by thermal rearrangements, is proposed.



Around 120 years ago, Störmer and Kahlert postulated, for the first time, the generation of a didehydroaromatic intermediate, 2,3-didehydrobenzofuran,¹ although the general acceptance of arynes was not firmly established until the 1950s.² Since then, a large number of arynes have been proposed, including carbocyclic³ and heterocyclic⁴ species. While the existence of six-membered arynes has been firmly established and even proved by STM/AFM imaging,⁵ the formation of most 5-membered heterocyclic arynes,^{6–8} and particularly, 2,3-didehydrothiophene (2-thiophyne, **1**, see Figure 1),⁹ has been a matter of debate. In fact, although

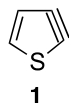


Figure 1. 2,3-Didehydrothiophene or 2-thiophyne (**1**).

metal complexes of η^2 -2-thiophyne are well-known,¹⁰ the existence and reactivity of the free hetaryne species has not been unambiguously proven.

Pionering work on the attempted generation and trapping of 2-thiophyne (**1**) was performed by Wittig and Rings, who heated the organomercuric derivative **2** in the presence of cyclopentadienone **3**, isolating benzothiophene **4** (see Figure 2).^{11a} Although this product was the one expected from the cycloaddition of the hetaryne **1** to diene **3**, followed by cheletropic extrusion of CO from adduct **5a**, additional experimental evidence led the authors to suggest an alternative mechanism involving the cycloaddition of cyclopentadienone **3** to the C2–C3 double bond of 3-iodothiophene leading to intermediate **6a**.^{11b} Some years later, Reinecke and co-workers studied the flash vacuum pyrolysis (FVP) of anhydride **7** in the presence of dienes such as thiophene, obtaining benzothio-

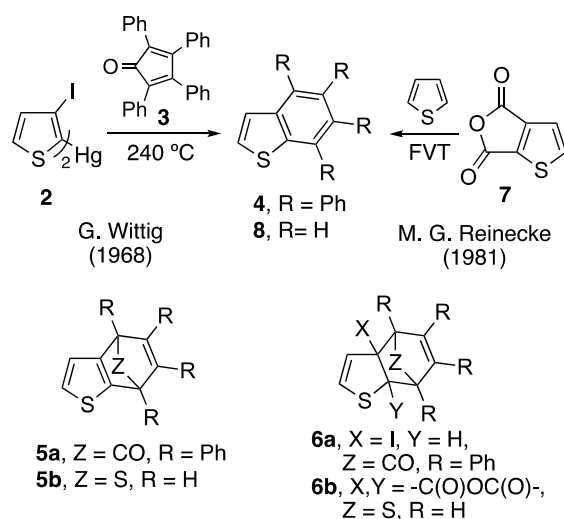


Figure 2. Previous attempts to generate and trap 2-thiophyne (**1**).

phene **8**.¹² Their detailed study concluded that the best explanation for the results is the one based on the involvement of 2-thiophyne (**1**) and adduct **5b**, although the direct reaction of the diene with anhydride **7** (to give **6b**) or with some decomposition product of **7**, must also be considered. Further attempts to unambiguously demonstrate the generation of 2-

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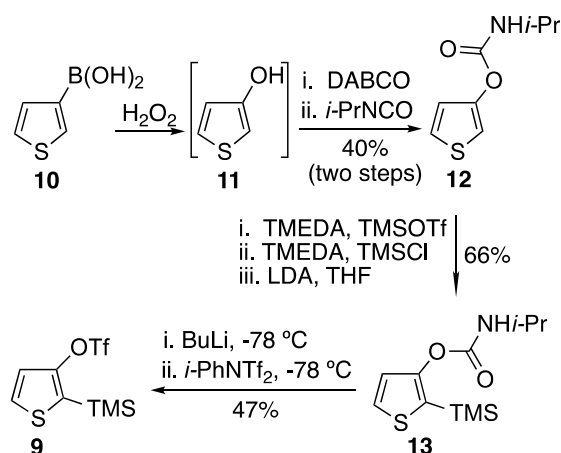


thiophyne (**1**) from anhydride **7** were also inconclusive.¹³ More recently, the generation of a 2-thiophyne by treatment of a 2-thiophenyltriflate with base was claimed,¹⁴ but the detailed study of this transformation has been not reported.

Although the aforementioned unsuccessful results were attributed to the high strain and the lack of stability of 2-thiophyne (**1**), recent computational work identified this hetaryne intermediate as synthetically accessible.¹⁵ This prospect, and our long-term experience in aryne chemistry, led us to explore the possibility to generate **1** from a Kobayashi-type precursor,¹⁶ the previously undescribed 2-(trimethylsilyl)thiophen-3-yl triflate (**9**).

For the synthesis of triflate **9**, depicted in Scheme 1, (thiophen-3-yl)boronic acid (**10**) was treated with hydrogen

Scheme 1. Synthesis of 2-(Trimethylsilyl)thiophen-3-yl Triflate (**9**)

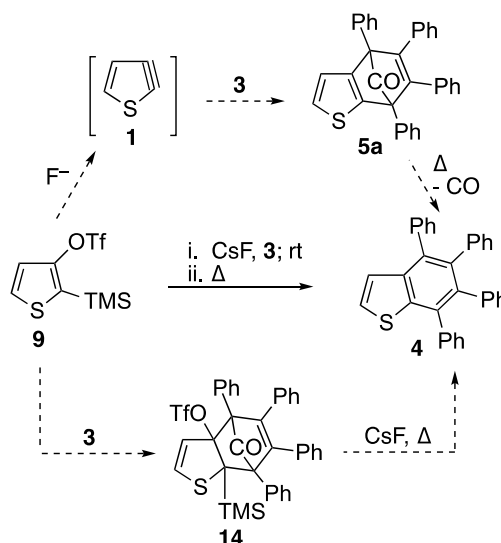


peroxide to afford thiophen-3-ol (**11**),¹⁷ which was reacted in situ with DABCO and isopropyl isocyanate to give carbamate **12** in 40% yield. Then, the *o*-lithiation/silylation protocol described by Hoppe and coworkers¹⁸ for *N*-silylated *O*-aryl *N*-isopropylcarbamates was used to obtain compound **13** in 66% yield. A subsequent one-pot deprotection/triflation procedure, previously utilized by Houk and Garg for the synthesis of other hetaryne precursors,^{4b,19} afforded silyl triflate **9** in 47% yield.

The ability of triflate **9** as precursor of 2-thiophyne (**1**) was tested by trapping experiments with different dienes. While treatment of **9** with CsF in the presence of furan, 1,3-diphenylisobenzofuran, or anthracene did not afford the expected adducts, the reaction with 2,3,4,5-tetraphenylcyclopentadienone (**3**) at room temperature in THF/ACN, followed by heating under reflux for 16 h, successfully allowed us to detect and isolate 4,5,6,7-tetraphenylbenzo[*b*]thiophene (**4**), albeit in low yield (<5%). Although this result was consistent with the expected generation of 2-thiophyne (**1**) and its trapping as the Diels–Alder adduct **5a**, which should lead to **4** by cheletropic extrusion of CO upon heating, alternative nonaryne pathways such as the one involving intermediate **14** (Scheme 2) could not be ruled out, particularly considering the precedents discussed above (see Figure 2).

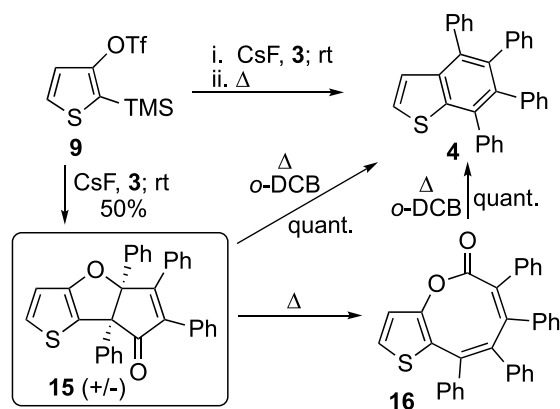
To shed light on the reaction mechanism, a careful experimental study was performed, focusing on the identification of intermediate species such as the hypothesized adducts **5a** or **14**. Thus, we monitored the reaction of triflate **9** with CsF in the presence of **3**, performed this time at room

Scheme 2. Hypothesized Pathways for the Reaction of Triflate **9** with CsF and Cyclopentadienone **3**



temperature, and stopped the reaction once the starting triflate **9** was consumed. After workup and chromatographic purification, we isolated a major product that proved to be NMR- and IR-data-compatible with **5a**, but showed a mass spectrum whose molecular ion peak was 16 mass units larger than expected. Fortunately, we were able to grow single crystals of this new compound, thus allowing us to perform X-ray diffraction (XRD) analysis that unambiguously revealed the totally unexpected structure **15** (Scheme 3 and Figure 3; see the Supporting Information for details).

Scheme 3. Experimentally Detected Intermediate Species in the Formation of Benzo[*b*]thiophene **4** from Triflate **9**, CsF, and **3**



Remarkably, when a solution of **15** in *o*-dichlorobenzene was heated at 180 °C for a week, benzo[*b*]thiophene **4** was isolated in quantitative yield, proving that **15** is a real intermediate in the formation of **4**. Furthermore, stopping this reaction before complete conversion allowed us to isolate a new intermediate which was tentatively identified as **16**. This new compound was also quantitatively converted into **4** by refluxing in *o*-dichlorobenzene (Scheme 3).

These results and, particularly, the isolation and unambiguous characterization of the tricyclic intermediate **15**, suggest that benzo[*b*]thiophene **4** was formed through a complex

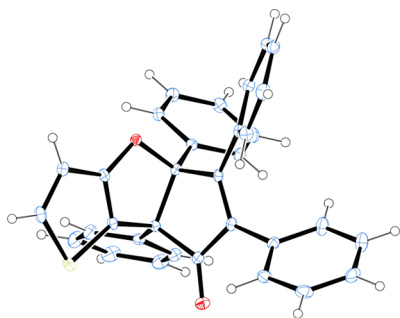
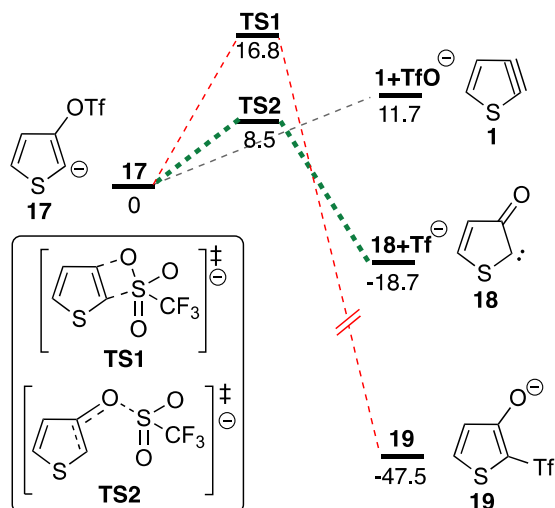


Figure 3. Structure and ORTEP drawing of intermediate 15.

mechanism not involving hetaryne **1**. We decided to study this reaction computationally and, thus, we first performed B3LYP/6-31++G(d,p) calculations²⁰ on the decomposition of triflate **9** (see the Supporting Information for details). Assuming that the anionic intermediate **17** is formed from **9**,²¹ several pathways can be envisaged, as depicted in Scheme 4.

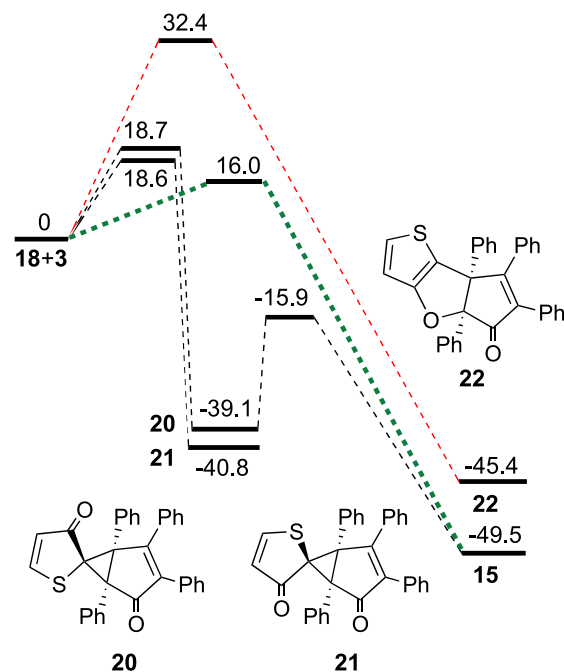
Scheme 4. Computed Energy Profiles (ΔG , kcal mol⁻¹) for the Evolution Pathways of Intermediate **17**



Calculations show that elimination of the triflate to afford the aryne (2-thiophyne, **1**) is a barrierless process, endergonic by 11.7 kcal/mol.²² An alternative anionic thia-Fries rearrangement, which has been observed in some attempts of aryne generation from aryl triflates,²³ is also unlikely to happen, because of the relatively high activation barrier for the formation of **19** (16.8 kcal mol⁻¹). Surprisingly, we found that the most kinetically favorable process, with an activation barrier of 8.5 kcal mol⁻¹, is the formation of the ketocarbene **18** (see the Supporting Information) by cleavage of an O–S bond of the triflate groups.

Interestingly, the unexpectedly found ketocarbene **18** could reasonably explain the formation of the previously isolated tricyclic intermediate **15** and, thus, we computed the reaction of **18** with cyclopentadienone **3**, as shown in Scheme 5. One possible mechanistic pathway could involve the [2 + 1] cycloaddition of the carbene to one of the double bonds of **3**, leading to the spirocompounds **20** and/or **21**. In fact, we could find transition states for the formation of both isomers, given that the barriers (18.6 and 18.7 kcal mol⁻¹) and the reaction energies (−39.1 and −40.8 kcal mol⁻¹, respectively) were quite

Scheme 5. Energy Profile (ΔG , kcal mol⁻¹) for the Reaction Ketocarbene **18** with Cyclopentadienone **3**



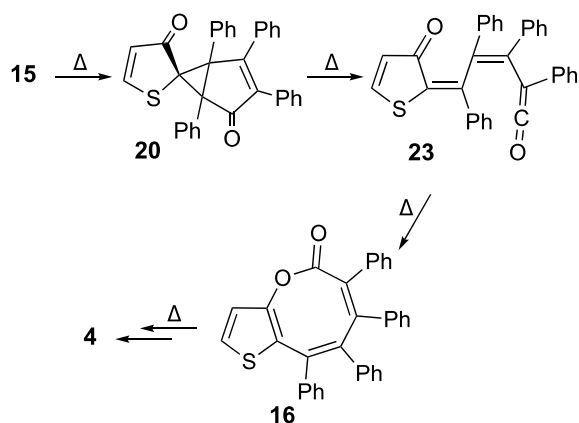
similar, and also found a transition state for the oxavinylcyclopropane rearrangement²⁴ of isomer **20** to give the isolated compound **15** (barrier = 23 kcal mol⁻¹). However, the study showed that the alternative pathway that leads directly to **15** through a concerted formal 1,3-dipolar addition is more favorable. This reaction would proceed through a very asynchronous transition state, with a barrier of 16 kcal mol⁻¹ (2.6 kcal mol⁻¹ lower than the barrier for the cyclopropanation reaction). Note that the alternative regioisomeric adduct **22** resulted to be lightly less stable than **15**, and the barrier for its formation is substantially higher (32.4 kcal/mol).

Once the viability of the generation of ketocarbene **18** and its reasonable reaction with cyclopentadienone **3** to afford the fully characterized compound **15** were demonstrated, we focused our attention on the transformation of this intermediate product to the final benzothiophene **4**.

As previously mentioned, **15** is thermally converted to **4**, with the loss of CO₂, by prolonged heating in refluxing *o*-dichlorobenzene. To gain insight into this transformation, we performed a density functional theory (DFT) study (see the Supporting Information) that led us to propose the mechanism outlined in Scheme 6. Thus, compound **15** can suffer a rearrangement to give spirane **20**, which might be a key intermediate in this transformation, since DFT calculations show that it easily undergoes ring-opening to give ketene **23**. A subsequent 8 π electrocyclicization would generate compound **16**, which evolves with the loss of CO₂ to afford benzo[*b*]thiophene **4**.²⁵

To summarize, 2-(trimethylsilyl)thiophen-3-yl triflate has been synthesized as a potential Kobayashi-type precursor of the elusive five-membered hetaryne 2-thiophyne (**1**). Although the reaction of this triflate with 1,2,3,4-tetraphenylcyclopentadienone under aryne forming conditions afforded the expected trapping product, computational and experimental studies, including the isolation and characterization of unexpected intermediate products, ruled out the formation of the hetaryne. Instead, our results revealed an unprecedented mechanism

Scheme 6. Mechanistic Proposal for the Transformation of 15 into Benzo[*b*]thiophene 4



involving the generation and subsequent reaction of a ketocarbene intermediate.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.1c02552>.

Experimental procedures, characterization of new compounds, including NMR spectra, computational methods and results, including Cartesian coordinates (PDF)

Accession Codes

CCDC 1837531 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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