Cycloaddition

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Strain-Promoted 1,3-Dithiolium-4-olates–Alkyne Cycloaddition

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Abstract: *Reported here is the reactivity of mesoionic 1,3-dithiolium-4-olates towards strained alkynes, leading to thiophene cycloaddition products. In the process, the potential of these dipoles towards orthogonal reaction with azides, allowing efficient double ligation reactions, was discovered. A versatile process to access benzo[c]thiophenes, in an unprecedented divergent fashion, was developed and provides a new entry to unconventional polyaromatic thiophenes.*

Mesoionics are an exotic class of dipoles holding much promise in cycloaddition reactions. Although their synthesis and reactivity have been reported since the 60's, their potential is far from being fully explored.[1] Mesoionic compounds represent a large family of five-membered heterocycles that cannot be represented by Lewis structures not involving charge separation. Over the last decade, the popularity of this exotic family of heterocycles has suddenly increased and caught much attention.[2] In particular, nitrogen-containing mesoionics such as münchnones and sydnones were reported to be competent dipole partners for strain-promoted cycloaddition reactions. Their reactivity with arynes, described by Larock and Shi,[3] Garg and Houk,[4] and others,[5] offered novel synthetic opportunities to access substituted pyrazoles and pyrroles, which are not trivial to assemble by traditional synthetic methodologies. Moreover, the use of the aryne–sydnone cycloaddition was recently described for the unconventional, direct assembly of helicene scaffolds.[6] In recent years, sydnones and imino-sydnones were identified as promising dipoles for strain-promoted ligation with cyclooctynes.[7,8] These transformations hold much promise for click and bioorthogonal chemistry and a variety of applications were reported in living cells[9] and organisms.[10]

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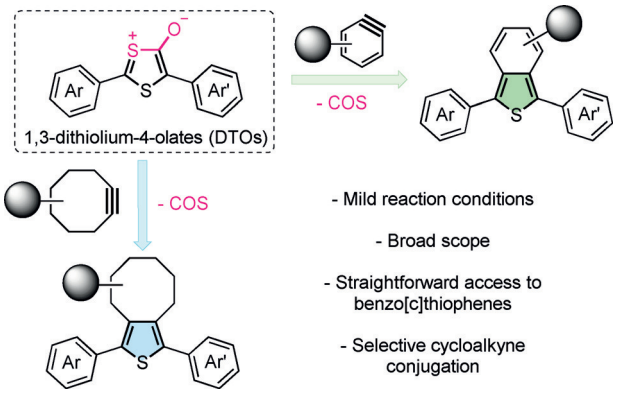
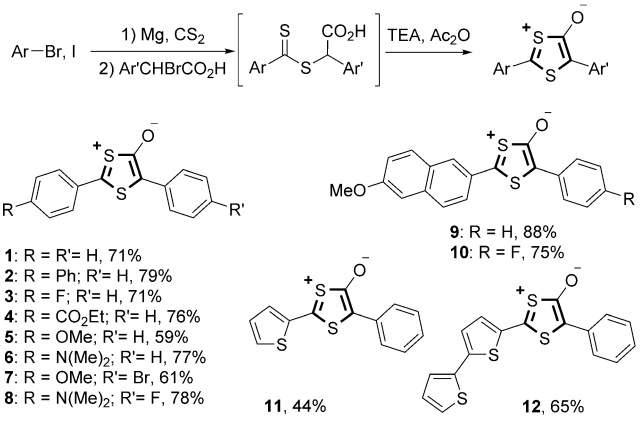
While the community has accepted nitrogen-containing mesoionics as a versatile platform in synthetic organic chemistry, sulfur-based derivatives remain a mere textbook curiosity and their reactivity is only partially explored. First reported in 1964,[11] 1,3-dithiolium-4-olates (DTOs) are essentially known to undergo thermal 1,3-dipolar cycloadditions in the presence of activated alkynes, followed by a retro-Diels–Alder reaction to deliver substituted thiophenes.[12] This thermal process has received limited attention, probably because of the poor regioselectivity, the limited scope, and the drastic reaction conditions required to assemble the thiophene unit. Their reactivity with activated alkenes such as fulvenes,[13] azirines,[14] maleimides,[15] and acenaphthylene[16] has also been sporadically reported. Surprisingly, less than twenty articles describe cycloaddition reactions with these dipoles. Given the fundamental importance of thiophenes in organic chemistry, in particular in medicinal and materials science, we decided to investigate in detail the reactivity of DTOs. In this report, we describe the cycloaddition between DTOs and strained alkynes, focusing on cyclooctynes and arynes. In the event, we unveil a novel ligation strategy, which is orthogonal to the well-established azide–cycloalkyne click reaction, as well as a complementary pathway to access a variety of substituted benzo[c]thiophenes with possible implications in materials science (Scheme 1).

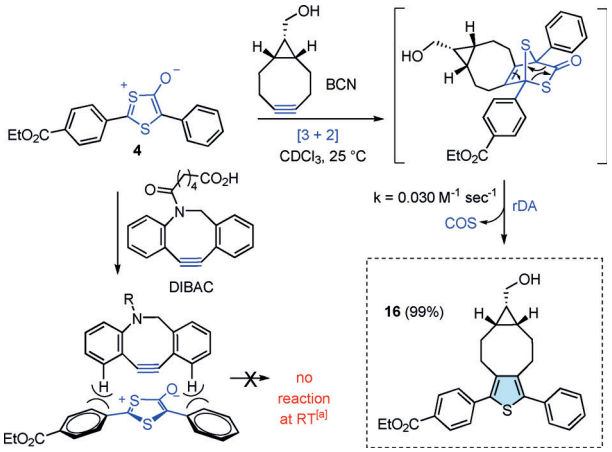


Scheme 1. Reactivity of 1,3-dithiolium-4-olates (DTOs) with strained alkynes.

At the outset, we prepared a library of DTOs, according to previous synthetic protocols developed by Potts[17] and Gotthardt,[18] in a three-step procedure (Scheme 2). Grignard reagents were reacted in presence of carbon disulphide at room temperature. The corresponding dithioic acids underwent nucleophilic substitution in presence of α-bromophenyl acetic acids under aqueous conditions. Without further purification, the phenyl acetic acid derivatives were cyclized



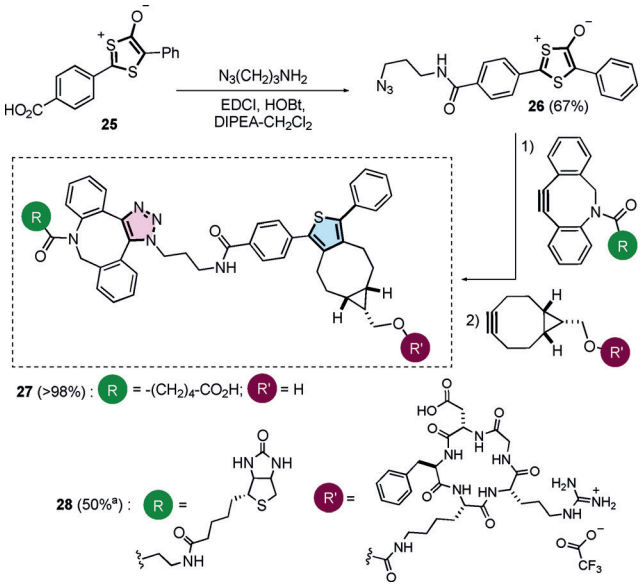
Scheme 2. Synthesis of 1,3-dithiolium-4-olates. Yields based on α-bromophenyl acetic acids as limiting reagents. TEA = triethylamine.



Scheme 3. Reactivity of the DTO **4** with cyclic alkynes. [a] Reaction between DTOs and DIBAC could only be observed when the temperature was higher than 90 °C.

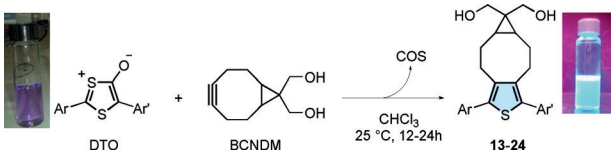
in the presence of acetic anhydride and triethylamine to deliver the desired DTOs **1**–**12** as dark-blue solids in 44 to 88 % yields. Products are bench-stable and display strong absorbance properties. With this series of DTOs, we next started the investigation of their reactivity with cyclooctynes. When the 2,5-diphenyl DTO **1** was mixed with bicyclo-[6.1.0]non-4-yne-9,9-diyldimethanol (BCNDM)[19] a smooth conversion was observed at room temperature in chloroform, and the thiophene cycloadduct **13** was isolated in quantitative yield (Table 1). It should be noted that the retro-Diels–Alder step generates the desired thiophene with equimolar amounts of carbonyl sulfide (COS), whose relevance has been recently described for the therapeutic delivery of H_2S.[20] The evolution of the reaction could be easily visualized by the discoloration of the dark mesoionic solution: while **1** has characteristic dark color but displays no fluorescence, **13** is a colorless fluorescent molecule.

Turn-on probes based on bioorthogonal ligation and click reactions are remarkable chemical tools to label, visualize, and study drugs and biomolecules. These transformations have been extensively studied and several fluorogenic azide,[21] tetrazine,[22] and sydnone probes[23] have been developed. In light of their promising optical properties, **1**–**12** were reacted with BCNDM to afford quantitatively the corresponding thiophene products (Table 1; see Figure S6 in the Supporting Information). The photophysical properties of both DTOs and thiophenes were measured and second-order kinetics were determined. All reactions were found fluorogenic, showing high fluorescence enhancement upon formation of the thiophene products. Comparative kinetics (Table 1) highlighted the importance of both substituents on positions 2 and 5 of the mesoionic core. Kinetic values of the strain-promoted 1,3-dithiolium-4-olates–alkyne cycloaddition (SPDAC) reaction, ranging from 0.016 to 0.180 $M^{-1}s^{-1}$, are comparable to the well-known strain-promoted azide–alkyne cycloaddition (SPAAC) click reaction. While for azides and sydnones the use of highly strained cyclooctynes increases the reaction rates, in striking contrast, no reaction occurred between **4** and DIBAC at room temperature, even after prolonged stirring (Scheme 3). This unexpected lack of reactivity might be rationalized by the steric hindrance resulting from the 2,5-diaryl substituents of the mesoionic and the aromatic rings adjacent to the alkyne. Given this peculiar orthogonal behavior, we designed the dual probe **26**,[24] bearing an alkyl azide connected to the DTO, and it was synthetized in 67 % yield from **25** (Scheme 4). In a proof-of-concept experiment, **26** reacted exclusively at the azide moiety with DIBAC, and sequential addition of BCN allowed the clean formation of **27** in a quantitative fashion.[24] Similar results were obtained with functionalized cyclooctynes: complete orthogonal ligations after sequential addition of a DIBAC-biotin conjugate and a BCN bearing the cyclic RGD peptide, afforded **28** selectively. This experiment shows the potential of DTO as competent dipoles for orthogonal ligations with azides.



Scheme 4. Orthogonality between dithiolium SPDAC and azide SPAAC cycloaddition reactions (only one regioisomer of triazole product is represented). [a] Yield of product isolated after HPLC purification. EDCI = 1-(3-dimethylaminopropyl)-3-ethyl-carbodiimide, DIPEA = diisopropylethylamine.

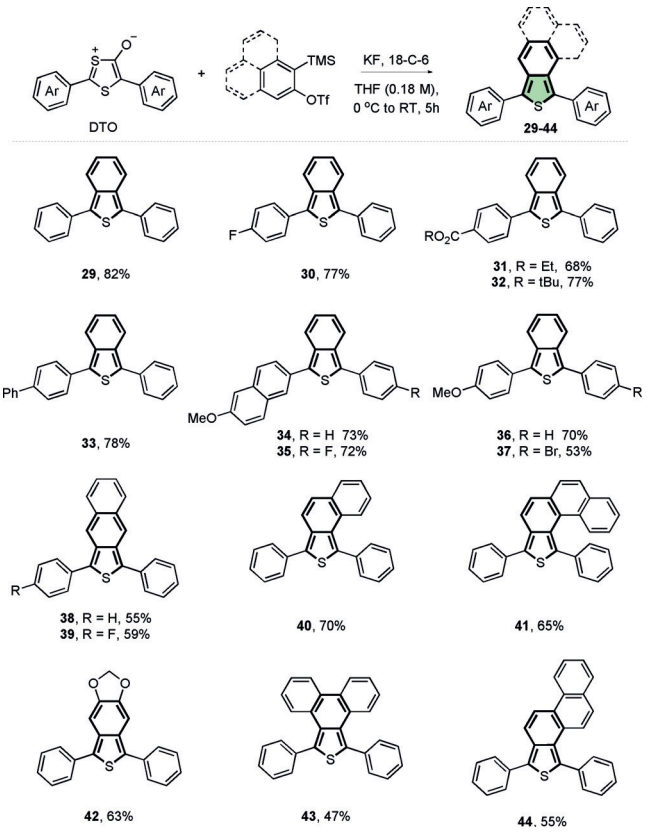
Table 1: Photophysical data of DTOs and their cycloadducts, and kinetic studies on cycloaddition reactions.[a]



Ar	Ar′	DTO: λ_{max} (ε)[b]	Adduct: yield[c] $\lambda_{ex}/\lambda_{em}$[d]	k[e]
		1: 543 (10200)	**13**:97% 296/381	0.071 ± 0.005
Ph		**2**: 559 (20200)	**14**:99% 312/397	0.099 ± 0.002
F		**3**: 548 (8400)	**15**:96% 293/379	0.128 ± 0.004
EtO_2C		**4**: 560 (11800)	**16**:98% 324/424	0.030 ± 0.004
MeO		**5**: 557 (12600)	**17**:90% 299/390	0.082 ± 0.002
N		**6**: 595 (22700)	**18**:99% 316/401	0.016 ± 0.001
MeO	Br	**7**: 563 (11900)	**19**:96% 303/396	0.054 ± 0.001
N	F	**8**: 595 (17900)	**20**:97% 316/392	nd
MeO		**9**: 566 (17300)	**21**:96% 310/392	0.071 ± 0.001
MeO	F	**10**: 568 (16300)	**22**:99% 310/387	0.101 ± 0.001
S		**11**: 576 (10800)	**23**:97% 311/411	0.184 ± 0.003
S S		**12**: 625 (12300)	**24**:98% 361/460	nd

[a] Kinetics were conducted with 150 μM of DTO and BCNDM in $CHCl_3$. [b] λ_{max}: nm ε : $M^{-1}cm^{-1}$. [c] Yields of isolated products. [d] λ_{ex} and λ_{em} of thiophene cycloadduct (nm), see Figures S7 and S8 for fluorescence spectra. [e] $M^{-1}s^{-1}$.

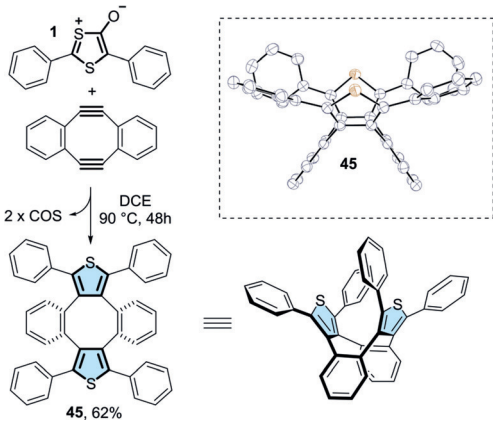
After showcasing the SPDAC as a potential tool for orthogonal cycloadditions with cyclooctynes, we next explored the reactivity of these sulphur-based mesoionics with arynes.[25] The importance of benzo[c]thiophenes in materials science, in particular for their nonlinear optical (NLO) properties,[26] low band gap conjugated polymers,[27] and their use as near-infrared fluorophore subunits is well-established.[28] Nonetheless, synthetic access to benzo-[c]thiophenes and derived S-heteroacenes still remains challenging and requires time-consuming, multistep convergent approaches. It is somehow surprising that the most common strategy still relies on the venerable Paal–Knorr cyclization, from the corresponding 1,4-diketone precursors in the presence of an excess of a sulfur source.[29] In this context, the SPDAC with arynes would provide a divergent entry to benzo[c]thiophenes and streamline access to unconventional derivatives. After careful optimization,[24] **29** was isolated in 82% yield from **1** and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate, in the presence of KF (4 equiv) and 18-crown-6 ether (4.5 equiv) in THF (Scheme 5).[30] With this



Scheme 5. Exploring the SPDAC for the synthesis of benzo-[c]thiophenes. Tf = trifluoromethanesulfonyl, THF = tetrahydrofuran, TMS = trimethylsilyl.

optimized set of reaction conditions, the benzo[c]thiophenes **29**–**37** were isolated in 53 to 82% yields from the corresponding DTOs. To investigate the versatility of the transformation, we next reacted the mesoionics with previously reported polyaromatic arynes.[31] In presence of 2,3-naphthyne precursor, the desired S-heteroacenes **38** and **39** were isolated in 55 and 59% yield, respectively. Interestingly, the acenothiophenes **29** and **38** were recently reported by the group of Chi, by means of a Paal–Knorr sequence in 65 and 50% yield, respectively, from the corresponding diketones.[32] These results show the divergence of SPDAC over current available methods. The reaction with *ortho*-fused 1,2-naphthyne and 3,4-phenanthryne precursors delivered the helical derivatives **40** and **41**, respectively, in good yields. Finally, the thiophenes **42**–**44** were isolated in 47 to 63% yield. The use of 9,10-phenanthryne is particularly interesting because it generates phenanthro[9,10-c]thiophenes such as **43**, whose synthesis has so far only been preliminarily explored.[33]

Finally, we investigated a double SPDAC reaction of **1** with the Sondheimer–Wong diyne (Scheme 6).[34] Similar to DIBAC, the reaction with this diyne was slower than with BCNDM, however a clean formation of the dithiophene-diphenylene **45** was observed upon heating at 90 °C during 48 hours. As highlighted by X-ray analysis, **45** adopts a unique saddle-shaped structure with the two thiophene moieties on the same side of the molecule.[35] This new skeleton might therefore represent a promising candidate for the development of chiral functional molecules.[36]



Scheme 6. Synthesis of **45** from DTO **1** and the Sondheimer-Wong diyne. DCE = 1,2-dichloroethane.

In conclusion, we have studied the virtually unexplored reactivity of DTO towards strained alkynes. These mesoionics can be successfully used for orthogonal double click reactions and provide a versatile platform to access benzo[c]thiophenes and dithiophene-diphenylene structures in an unprecedented divergent fashion, and will provide a new entry to unconventional polyaromatic thiophenes. Further work on these molecules is currently ongoing.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: click chemistry · cycloaddition · strained molecules · synthetic methods · thiophenes

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[35] CCDC 1937085 (**45**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. The structure of was confirmed by X-ray analysis.

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