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Linear and Angular Heteroacenes from Double-Electrophilic Cyclization (DEC) and DEC-Reductive Elimination of Diynes

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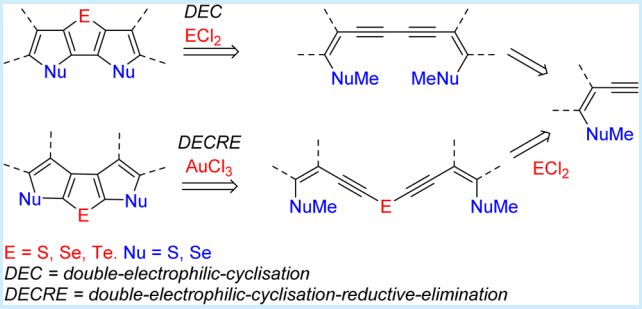
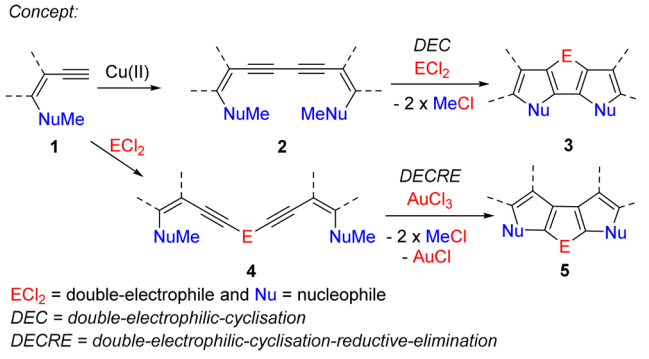
Supporting Information

ABSTRACT: Linear and angular heteroacenes are prepared from terminal alkynes bearing tethered nucleophiles in two steps. Linear heteroacenes are formed from the homocoupling of these alkynes followed by reaction with a double electrophile (ECl_2) to induce a tricyclization reaction cascade involving double-electrophilic cyclization (DEC). Related angular heteroacenes are formed from the prior substitution of the chloro groups in ECl_2 with the same terminal alkyne followed by reaction with $AuCl_3$ to produce a DEC-reductive-elimination (DECRE) reaction.

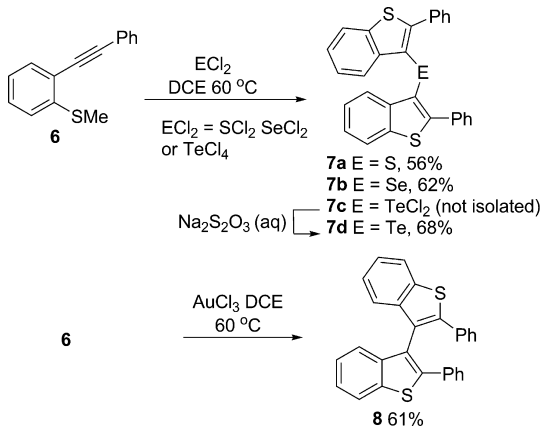


Interest in the electronic and photonic properties of π-rich heteroacenes of the general formula **3** and **5** (Scheme 1) has risen sharply in the last 10 years.[1,2] The general formula encompass a range of structures representing stable conjugated (**3**) and cross-conjugated (**5**) polyenes which are finding increasing applications in electronic and photonic materials, in particular, as organic semiconductors, light-emitting diodes, field-effect transistors, and photovoltaics.[2] Most usually, **3** and **5** are prepared from existing heterocycles,[2] though some other stepwise approaches involving alkyne cyclization have been reported.[3] Herein, we describe our investigations into the possibility of forming these heterocycles in a modular manner based on double-electrophilic-cyclization (DEC) (Scheme 1).[4] To access heterocycles **3**, **1** is converted into a 1,3-butadiyne **2** that is then reacted with a double electrophile ECl_2 (E = S, Se, Te) to initiate a DEC to produce **3** (involves electrofugal expulsion of MeCl). For heterocycles **5**, **1** is first reacted with ECl_2 to give a dialkynyl chalcogen **4** that is then reacted with double electrophile $AuCl_3$ in a related DEC-reductive-elimination (DECRE) process (Scheme 1).[5]

Scheme 1. DEC and DECRE Reaction Pathways



Scheme 2. DEC and DECRE Reactions of Alkyne 6



Our investigations began with a preliminary examination of the utility of SCl_2, $SeCl_2$ and $TeCl_4$ as double-electrophiles in the proposed DEC reaction on a simple alkyne substrate **6** (Scheme 2).[6] $TeCl_4$ was used in this study instead of $TeCl_2$ in view of the former's greater commercial availability and lower cost. All three electrophiles performed well in the double-electrophilic cyclization of methyl 2-(phenylethynyl)phenyl sulfide **6** when reacted in 1,2-dichloroenthane (DCE) at 60 °C to give the dibenzo[*b*]-thiophenyl sulfide **7a**, selenide **7b**, and telluride **7d**, respectively (56−68%). The reaction performed best upon slow addition of ECl_2 to a heated solution of **6**, and this became an even more important criterium in its application to the tricyclization reactions involving butadiynes (see below). In the reaction of **6** with $TeCl_4$, the initial product formed was the dibenzo[*b*]thiophenyl

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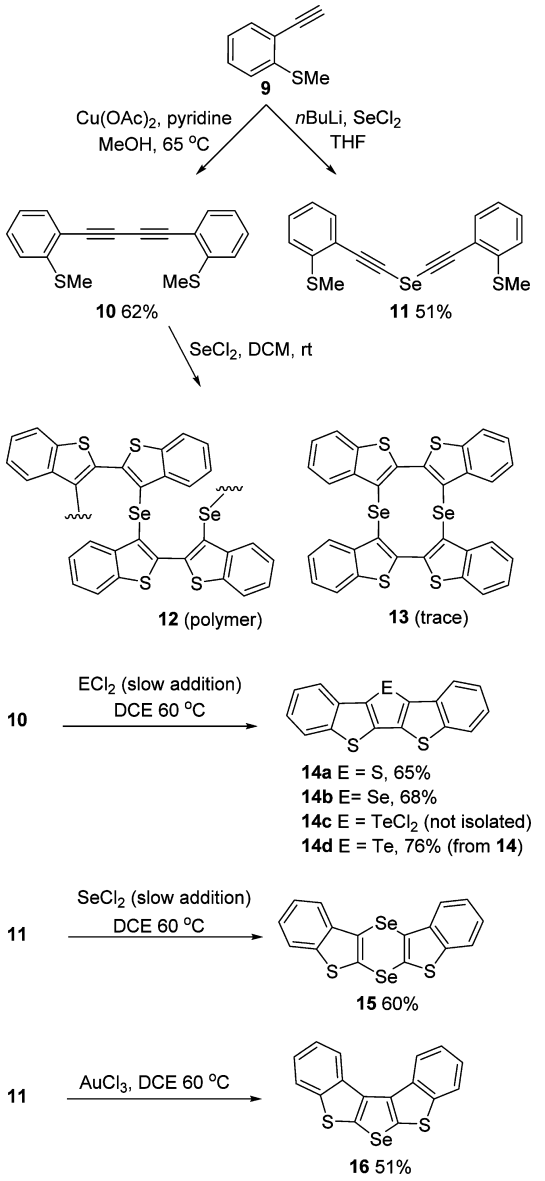
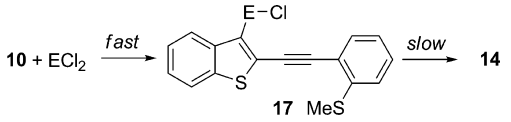
Scheme 3. DEC and DECRE in Heteroacene Synthesis



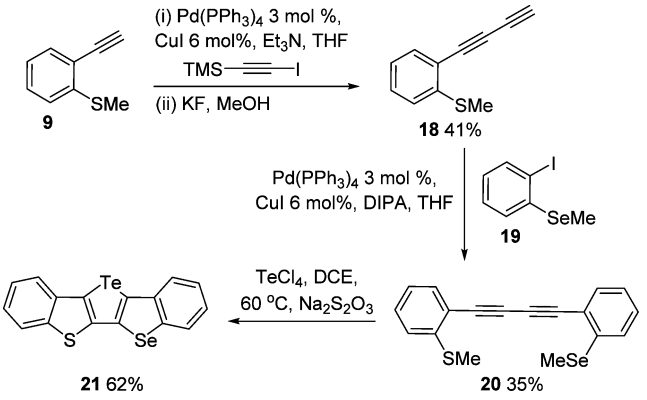
Scheme 4. Formation of Key Intermediate 17



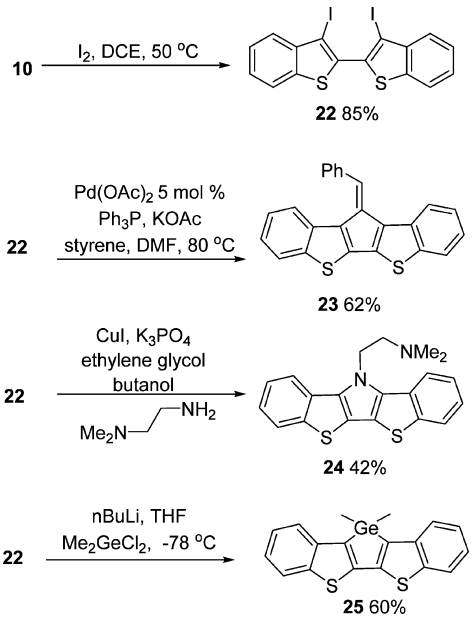
dichlorotelluride **7c**, which converted to **7d** upon reductive workup ($Na_2S_2O_3$). Reaction of **6** with $AuCl_3$ proceeded as planned and gave the DECRE product **8** (61%).

To investigate the potential for the DEC and DECRE reactions to be used in the conversion of diynes to heteroacenes, we converted (2-ethynylphenyl)(methyl)sulfane (**9**) to 1,3-butadiyne **10** and dialkynylselenide **11**. Initial attempts to achieve a DEC by reaction of **10** with $SeCl_2$ in dichloromethane (DCM) at room temperature gave rapid formation of a white solid (precipitate). The mass of the precipitate accounted for the total amount of reactants added, and there was no discernible material in the filtrate. This solid proved insoluble in most solvents, was not characterizable by NMR, and was considered to be a polymer of the type **12** (unconfirmed). Electron ionization−mass spectrometry

Scheme 5. DEC of an Unsymmetrical Butadiyne



Scheme 6. Double Iodocyclization



(EI-MS) gave a base peak corresponding to the macrocyclic dimer **13**; however, it is most likely that this material was only formed in trace amounts or as a fragment in the EI-MS of the polymer **12**, as **13** would be expected to have suitable solubility in NMR solvents ($CDCl_3$ or DMSO-d_6). Formation of the polymer **12** was avoided by slow addition of both the electrophile (ECl_2) and the diyne **10** to a solution of 1,2-dicloroethane heated to 60 °C (Scheme 3). These conditions gave the heteroacenes **14a−d** in good yield (65−76%). The slow addition of both reagents at elevated temperature favors unimolecular cyclization of the key intermediate **17** to **14** over its reaction with another molecule of diyne **10** or ECl_2 (Scheme 4). The dialkynyl selenide **11** was also subjected to DEC with $SeCl_2$ to give the bis(benzo[*b*]thiopheno)-1,4-diselinine **15** (60%). Reaction of **11** with $AuCl_3$ was successful in producing a DECRE process to give the angular heteroacenes **16** (51%), presumably via an intermediate gold(III) ring (not shown).

The unsymmetrical butadiyne **20** was formed from **9** by initial Pd coupling of iodo(trimethylsilyl)acetylene followed by desilylation to give **18** (41%) and Pd coupling to (2-iodophenyl)-(methyl)selane **19** to give **20** (35%) (Scheme 5). DEC of **20** with $TeCl_4$ followed by reductive workup ($Na_2S_2O_3$) produced **21** (62%) as the first reported heteroacene containing all three thiophene, selenophene, and tellurophene heterocycles.

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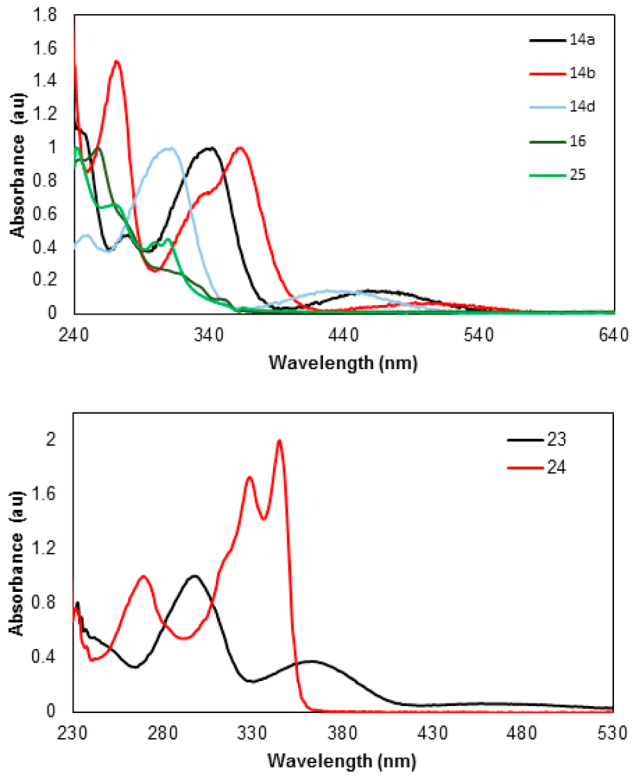

Figure 1. Absorption spectra of key intermediates in their chloroform solutions (solution concentration 2 μM).

The double-iodocyclization of butadiynes can also be used to generate heteroacenes in a separate step.[3f,7] Thus, conversion of **10** to diiodide **22**[7] gives access to the fulvene **23** (62%) by double-Heck[8] reaction, the pyrroloheteroacene **24** (42%) by a double-Ullman-type reaction,[9] and the germole **25** (60%) by lithiation and reaction with Me_2GeCl_2 (Scheme 6).[10]

Given the importance of these heterocycles, we investigated the optical properties of key targets by measuring their UV−vis absorption spectra in chloroform solution (Figure 1). Most of the materials absorbed strongly in the high energy area, i.e., <400 nm (typically 250−380 nm), with few materials exhibiting weak absorption in the visible region (~450 nm; **14a−d**). The longest wavelength absorption maximum (λ_{max}) of **14b** was red-shifted more than **14a**, which in turn exerted more red-shift than **14d**, thus indicating that changing a heteroatom can alter the absorption profile, and hence optical band gap, of a target chromophore. The chemistry proposed herein provides such flexibility, and the target chromophores it generated can be utilized for organic electronic applications, for example, organic field-effect transistors.

In conclusion, the DEC of butadiynes bearing internal nucleophiles **2** with ECl_2 (SCl_2, $SeCl_2$, and $TeCl_4$) provides concise, modular access to linear heteroacenes **3**. This is complimented by the double-iodocyclization of the same butadiyne substrates to enable access to other linear heteroacenes and by the DECRE cyclization that enables related substrates **4** to form angular heteroacenes **5**.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00265.

Experimental details, synthetic procedures, and ^1H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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