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Generation of the First Tellurium-Containing Diheteropentalene

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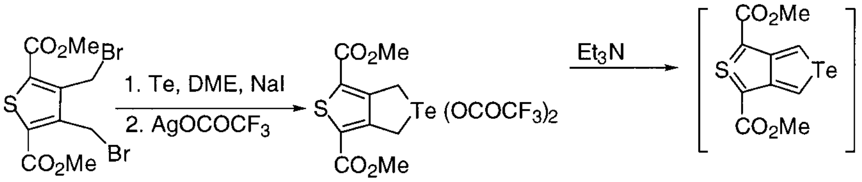
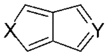
ABSTRACT



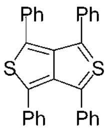
The known diester dibromomethylthiophene was converted to the tellurolo[3,4-*c*]thiophene, the first example of a diheteropentalene containing a tellurophene annelated across the 3,4-*c* position to thiophene. It is stable in solution and adds to DMAD across the 2,5-positions in tellurophene. The intermediate loses tellurium and collapses to a tetracarbomethoxy benzo[*c*]thiophene derivative.

The [3,4-*c*] annelated diheteropentalenes (**1**) form a very interesting class of heterocycles, attracting the attention of both theoretical and experimental chemists. Calculations on these systems, particularly **1** (X = Y = S) have been carried out in view of the possibility of low-lying sulfur d-orbital participation in bonding.[1−6] The preparation of the first stable derivative **2** was achieved in 1969, although the unstable members **3a,b** and **4a,b** were generated in solution and trapped with dimethyl acetylenedicarboxylate and *N*-methylmaleimide, etc.[7−9] We now report the synthesis of the novel tellurolo [3,4-*c*]thiophene **4c**, the first tellurium-containing heteropentalene.



1

X,Y = S, Se, Te



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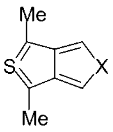
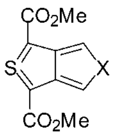


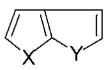
3a x=S
3b x=Se



4a x=S
4b x=Se
4c x=Te

A recent theoretical investigation of the relative stability of the four different diheteropentalenes viz. **1**, **5**, **6**, and **7** (X = Y = NH, O, S, Se, Te) has been carried out.

1



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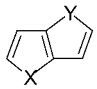

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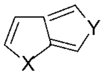

7

According to this study, **6** is thermodynamically the most stable entity in contrast to **1**, which is the least stable. However, aromaticity follows a different order, **1** being the most aromatic.[10] These predictions cannot be verified because only a small fraction of such molecules or derivatives thereof has been synthesized or generated.

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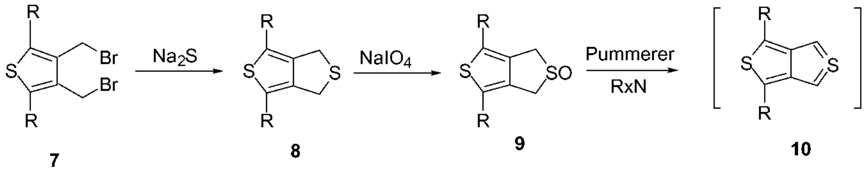
10.1021/ol0256466 CCC: $22.00

Scheme 1



Most of the synthetic studies during the past 3 decades have involved derivatives of **1** (X = Y = S). The parent heterocycles are unknown. A general strategy has been to prepare 3,4-dibromomethylthiophenes bearing substituents at the 2,5-positions. Treatment with sodium sulfide led to the 1,3-dihydrothieno[3,4-*c*]thiophene derivative **8**, which was oxidized to the sulfoxide **9**. The latter was subjected to a Pummerer dehydration with either acetic anhydride or base to give **10**. (Scheme 1)

This strategy was extended to generate selenium analogue **4b**.[11] However, this approach is not applicable to prepare tellurium analogues **4c** via intermediates such as **8**. Sodium telluride reduces the halogen in halomethyl compounds thereby leading to impractical yields of analogues of **8**.[12]

Since our objective was the preparation of the tellurium analogue **4c**, an alternate strategy was applied based on our protocol in the synthesis of benzo[*c*]tellurophene.[13] The known dibromomethyl compound **11** was reacted with tellurium metal in the presence of sodium iodide in DME to give the diiododihydrotellurophene annelated thiophene **12**. Replacement of the iodine by trifluoroacetate was achieved by treatment of **12** with silver trifluoroacetate to give **13**. Reaction with triethylamine was expected to give **14**. (Scheme 2).

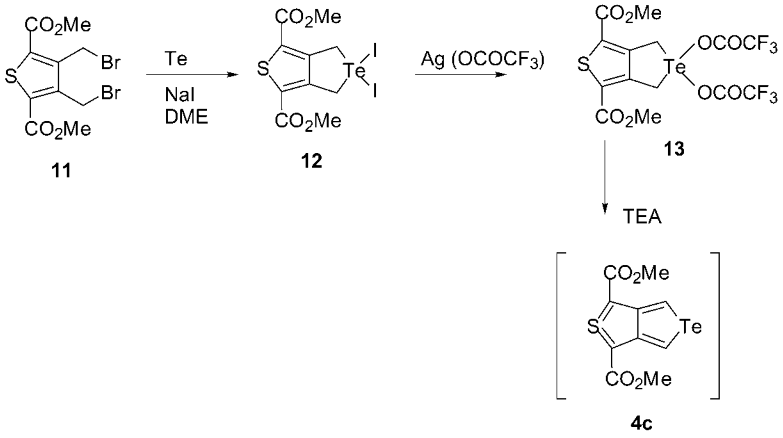
The triethylamine-catalyzed elimination of TFA from **13** was first studied by NMR spectroscopy. The benzylic hydrogens in **13** resonate at 4.65 and the ester methyl at 3.94 ppm, and within 10 min of addition of TEA, the diagnostic resonances of a tellurophene appear at δ 10.45 and 10.65, the latter disappearing soon, leaving only the δ 10.45 resonance. Furthermore, the solution turned purple. In addition several singlets from $-$COOMe and a singlet in the vinyl region at δ 5.42 were observed, which indicated the reaction was complex.

The reaction was carried out in benzene for 5$-$6 h under nitrogen at 55$-$60 °C. The intense purple color was stable only in solution under nitrogen for about 2 h, and attempts to isolate the product proved futile. The benzene solution showed λ_{max} at 558 nm similar to known thieno[3,4-*c*]-thiophenes. Workup led to the isolation of a dimeric product **14**, mp 116° (dec), in 29% yield and the reduced compound **15** in 15% yield, identified by comparison with an authentic sample made by the reduction of diiodide **12**. The structure of **14** was assigned on the basis of its NMR spectrum, which showed two singlets (1:3) at δ 10.45 and 3.97. The mass spectrum of **14** did not show its M^+ under electron impact but exhibited *m*/*e* at 355 (16%) corresponding to the M^+ of the monomer **4c**. This behavior is not unprecedented and has been observed in the case of an analogous dimer derived from a thieno[3,4-*c*]thiophene derivative (Scheme 3).

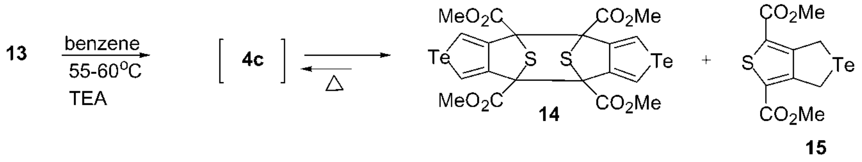
The dissociation of dimer **14** was studied by NMR spectroscopy in DMSO solution. Upon heating, a new singlet appeared at δ 9.55, upfield from the signal of the dimer at 10.29. Upon cooling, the peak at δ 9.55 disappeared, leaving only the peak due to the dimer. Therefore, clearly the resonance at δ 9.55 in DMSO should be that of the monomer.

Dimer **14** was heated with DMAD at 110$-$115 °C to trap the generated monomeric product **4c** to give the adduct **16**, mp 180 °C, in 11.0% yield (Scheme 4). The NMR spectrum was in accord with structure **16**, the aromatic protons

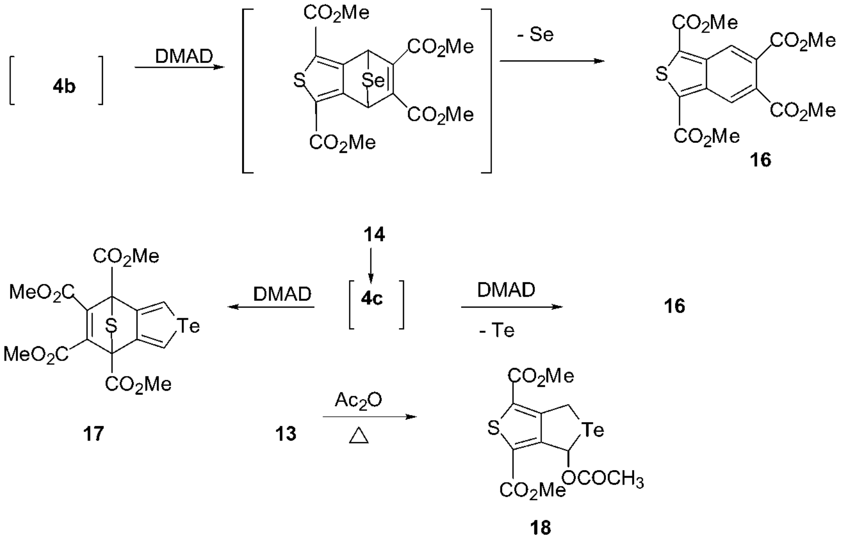
Scheme 2



Scheme 3



Scheme 4



appearing at δ 8.85 (s) and the ester methyl resonances at δ 4.02 and 3.94 in the ratio of 1:3:3. The mass spectrum showed a M^+ peak at *m*/*e* 366 (55%). The adduct **16** could also be isolated by carrying out the base-catalyzed telluro-Pummerer reaction in the presence of DMAD, albeit in low yield due to the degradation of DMAD by TEA and the instability of **4c**. Adduct **16** was identical to the known product from **4b** and DMAD.[11]

Product **17**, anticipated if the addition of DMAD had occurred on the thiophene portion of **4c**, was not detected. Attempts to carry out the Ac_2O-catalyzed Pummerer reaction on **13** led to the isolation of **18** in low yield, identified by NMR and mass spectrometry (Scheme 4). To our knowledge, this is the first example of an acetic anhydride-catalyzed telluro-Pummerer reaction.

The first diheteropentalene bearing the tellurolo[3,4-*c*]-thiophene framework, viz., **4c**, has been generated. It appears to be stable in dilute solution for no more than 1−2 h. Its visible spectrum is shifted bathochromically 60 nm from that of the corresponding thieno[3,4-*c*] analogue, **4a**, and ~24 nm from the selenium analogue **4b**. The reaction with DMAD is similar to the behavior of **4b**, or benzo[*c*]-tellurophene, where addition to the selenophene ring and tellurophene ring respectively takes place.

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