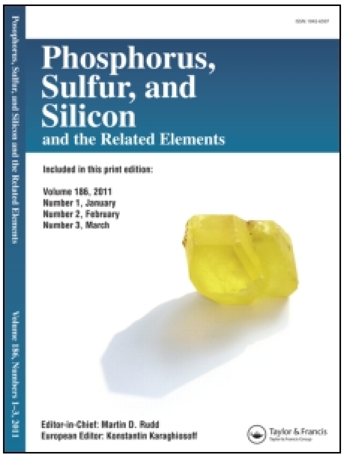

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Aspects of Organoselenium and Organotellurium Chemistry

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Aspects of Organoselenium and Organotellurium Chemistry

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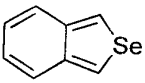
Alabama, USA

*The Chemistry of several condensed selenophenes, and tellurophenes (**1–4**) will be presented. The synthesis of mixed selenium-tellurium fulvenes (**5**) and generation of 2,4-bis-methyleneditelluretane (**6**) will be discussed.*



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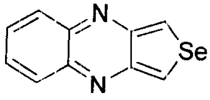

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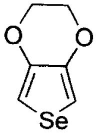

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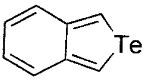

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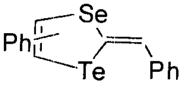

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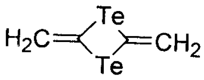

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Keywords Benzoselenophene; benzotellurophene

INTRODUCTION

During the past years work in the chemistry of organic selenium and tellurium chemistry in our group has been focused on quinonoid

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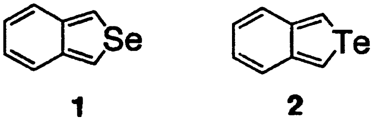
heterocycles, annelated selenophenes, 1,3-ditellurafulvenes, 1,3-ditelluretanes, and tellurium-containing heteropentalenes.

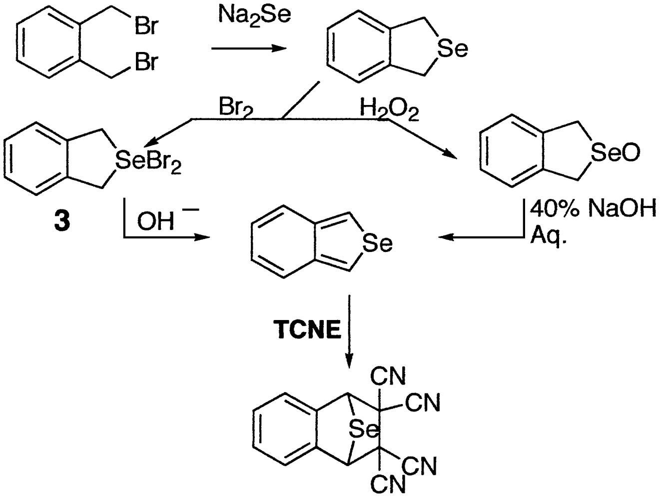
QUINONOID HETEROCYCLES

In contrast to benzo(c)thiophene, benzo(c)furan and isoindole, benzo(c)selenophene (**1**) and benzo(c)tellurophene (**2**) (Scheme 1) are less known.



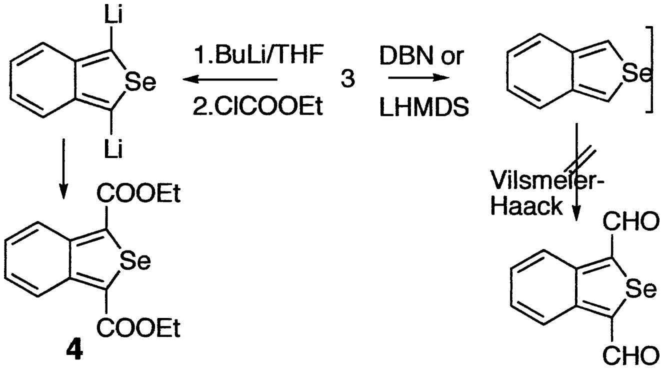
SCHEME 1

In 1976, benzo(c)selenophene was generated and trapped with tetracyanoethylene as shown in Scheme 2. It could never be isolated as a stable compound.[1]



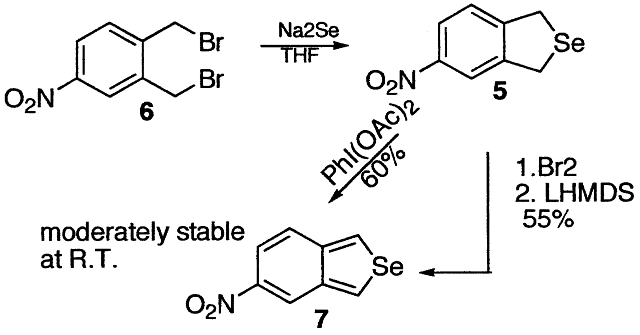
SCHEME 2

The only other reference to a polymer derived from benzo(c)selenophene is in a Japanese patent.[2] The problem was revisited in 2003. The aim at this time was to investigate if benzo(c)selenophene could be generated in an aprotic medium and if it could be functionalized. This was achieved by the use of butyllithium in tetrarofuran (THF) on the dihydrobenzo(c)selenophene dibromide **3**. Benzo(c)selenophene (**1**) thus liberated was dilithiated again in situ and treated with an electrophile. The use of chloroformic ester was successful and yielded the diester **4**. (Scheme 3). Direct reaction of the liberated benzo(c)selenophene with DMF/$POCl_3$ did not proceed as well (Scheme 2).[3]



SCHEME 3

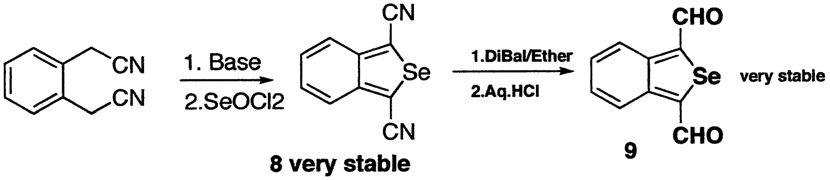
The structure of diester **4** was confirmed by X-ray. 5-Nitro-1,3-dihydro benzo(c)selenophene (**5**) was prepared readily by treatment of the 4-nitro-o-xylylenedibromide (**6**) with sodium selenide in THF. The dihydroselenophene **6** was readily oxidized fully to the aromatic selenophene **7** by phenyliodosoacetate. The dihydro compound **6** could also be brominated to the dibromide **8** which was subjected to dehydrobromination to give **7** (Scheme 4).



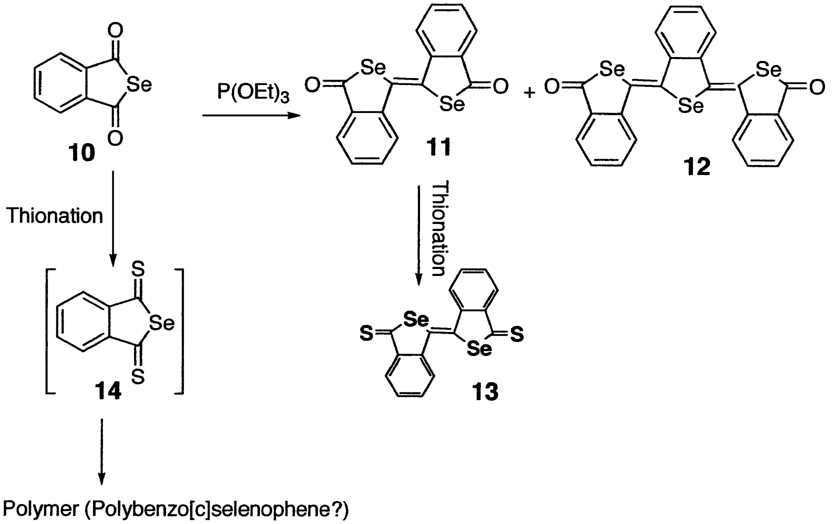
SCHEME 4

1,3-Dicyano-benzo(c)selenophene (**8**) was made in 2002 by an unusual reaction and was found to be very stable.[4] Dibal reduction of **8** yielded the dialdehyde **9** which was also very stable (Scheme 5)[3]

Selenophthalic anhydride (**10**) appeared to be an attractive starting material to make benzo(c)selenophene polymer. Reaction of **10** with



SCHEME 5

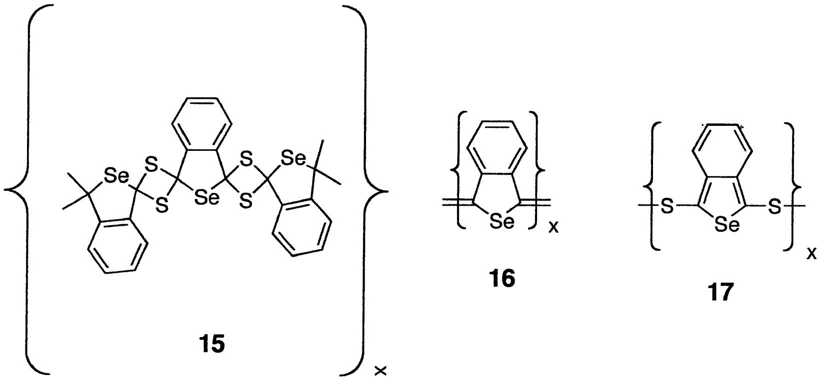


SCHEME 6

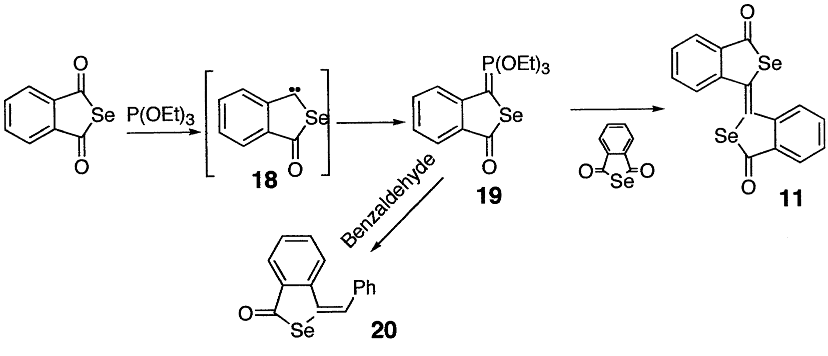
triethylphosphite afforded a mixture of the dimer **11** and trimer **12**. Thionation of dimer **11** with Lawesson's reagent gave the dithione **13** which was very stable. In contrast, thionation of anhydride **10** gave rise to an insoluble, dark polymeric material. Apparently seleno dithiophthalic anhydride **14** should have been formed and in analogy to trithiophthalic anhydride, must have polymerized (Scheme 6). The nature of this dark, insoluble material has not yet been established. It could have any of the structures **15–17** or it could be a mixture (Scheme 7).[5]

The reaction of **10** with triethylphosphite probably gives rise to the phosphorane **19** via the carbene **18** which reacts with more **10** to give **11**. If benzaldehyde was introduced into the deoxygenation mixture the benzylidene derivative **20** could be isolated (Scheme 8).

Benzo(c)tellurophene (**2**) posed a different problem. The known diiodide **21** does not undergo dehydroiodination with triethylamine. It undergoes deiodination to dihydrobenzo(c)-tellurophene. (**23**) On the other hand the trifluoroacetate **22** readily was prepared and upon



SCHEME 7



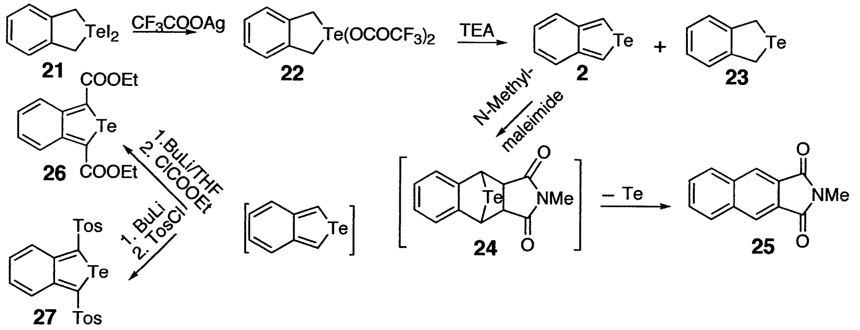
SCHEME 8

treatment with triethylamine in benzene gave a mixture of the reduced product as well as **2**. The quinonoid **2** could be trapped with N-methylmaleimide and the resulting adduct **24** lost tellurium spontaneously to give N-methyl-2,3-naphthalimide **25**.^{6} Benzo(c)tellurophene (**2**) could also be generated using BuLi/THF on **23**, and further dilithiated. The dilithio derivative could be converted to the diester **26**. Surprisingly, acetyl chloride, CNBr, TBDMSCl, etc., did not react with the dilithio derivative. The only other electrophile to react successfully to give **27** was tosyl chloride (Scheme 9).^{7}

One can conclude that benzo(c)selenophene (**1**) and benzo(c)-tellurophene (**2**) substituted either on the heterocyclic ring or on the benzene ring with electronegative substituents are stable.

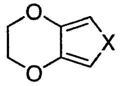
ANNELATED SELENOPHENES

In recent times 3,4-ethylenedioxythiophene (EDOT, **28**) has received great attention, in view of the solid-state properties of the polymer

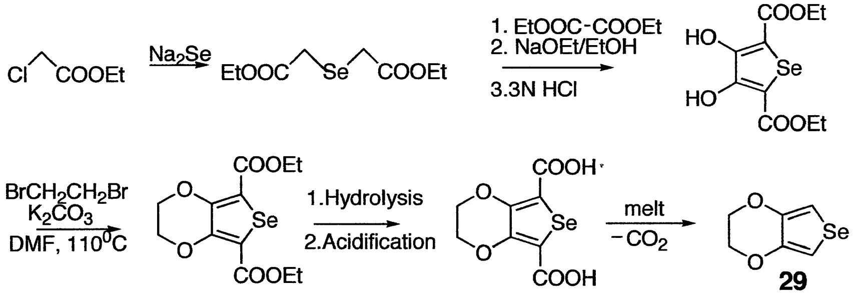


SCHEME 9

derived from it, almost thirty years after its synthesis by Gogte et al.[8,9] Since the selenium analog of **29**, viz. 3,4-ethylenedioxyselenophene (EDOS, **29**) was not known, it was synthesized in our laboratory starting from methyl chloroacetate as shown in Scheme 10.



28 X = S, EDOT
29 X =Se, EDOS

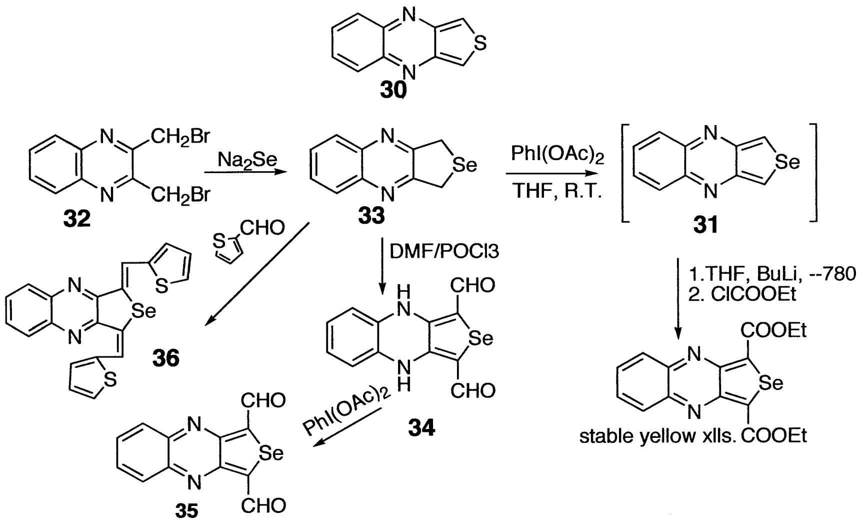


SCHEME 10

EDOS (**29**) exhibits a slightly lower oxidation potential (1.18 V) than EDOT (**28**; 1.44 V). It readily polymerizes both electrochemically and chemically. Repetitive cyclic voltammetry leads to a blue film of poly EDOS showing redox behavior. When a thin film of the oxidized polymer was deposited on an ITO glass it showed an absorption band at 6480 cm^{-1}. EDOS also was oxidized chemically. An acetonitrile solution of the chemically oxidized material showed λmax at 594 nm for the neutral polymer.[10]

Yet another annelated selenophene is selenolo[3,4-b]quinoxaline (**31**). The sulfur analog **30** was generated and studied during the nineteenseventies.[11] In 1995, thieno[3,4-b]quinoxaline was isolated in the free state in our lab.[12] The synthesis of **31** was achieved as shown in Scheme 11 starting from the readily available bisbromomethylquinoxaline (**32**), via the dihydroselenophene **33**.

Dihydroselenophene **33** undergoes Vilsmeier-Haack formylation in its tautomeric form to give the annelated diformyl derivative **34**. Oxidation of **34** using phenyl iodosoacetate yields diformyl seleno[3,4-b]quionoxaline **35**. Dihydroselenophene **33** condenses with aromatic aldehydes readily in the presence of base to give stilbenoid derivatives, exemplified by **36** (Scheme 11).[13]



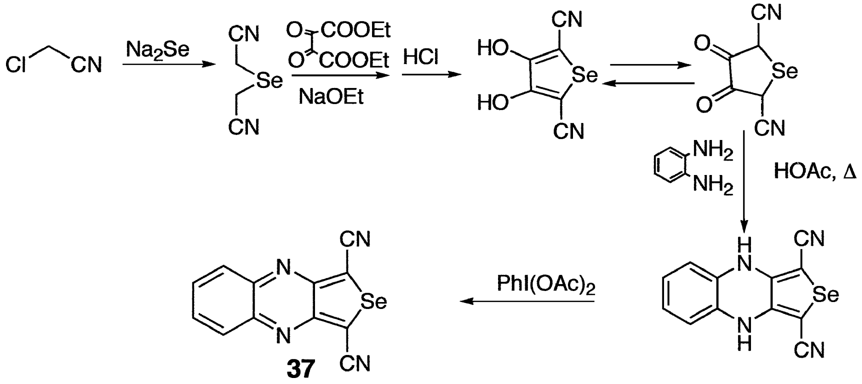
SCHEME 11

Our attention was turned on the dicyanoderivative **37**. It was prepared as shown in Scheme 12.[12]

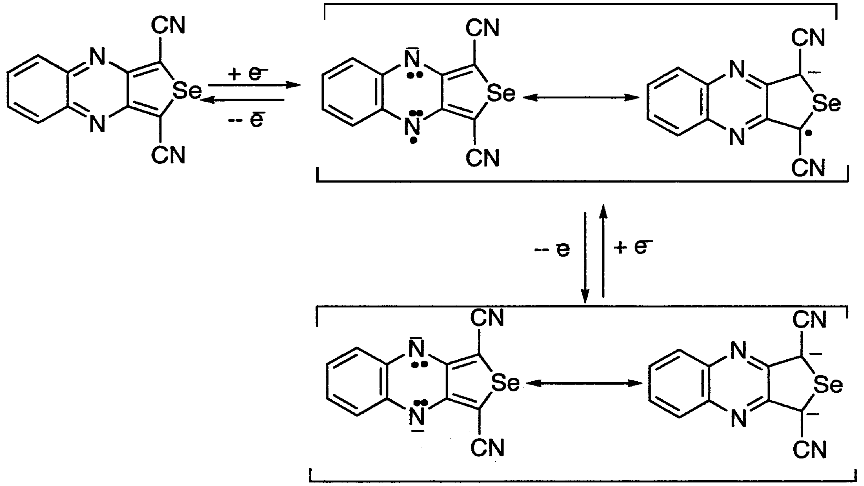
The interest in this compound was due to the nature of its potential acceptor properties. The radical anion and dianion derivable from **37** are depicted in Scheme 13. Both species are highly delocalized. The cyclic voltammogram of **37** confirms this expectation.

DICHALCOGENOFULVENES

Dichalcogenofulvenes form an interesting class of heterocycles. The exosubstituted fulvenes also bearing an identical ring substituent, of general structure **38** where X = S, Se, Te and R = alkyl, aryl are known. The sulfur analogs were first reported in the late fifties,[14] the selenium analogs in the midsixties,[15] and the tellurium analog (R = Ph) in



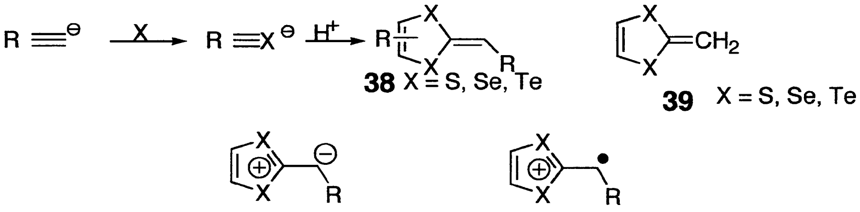
SCHEME 12



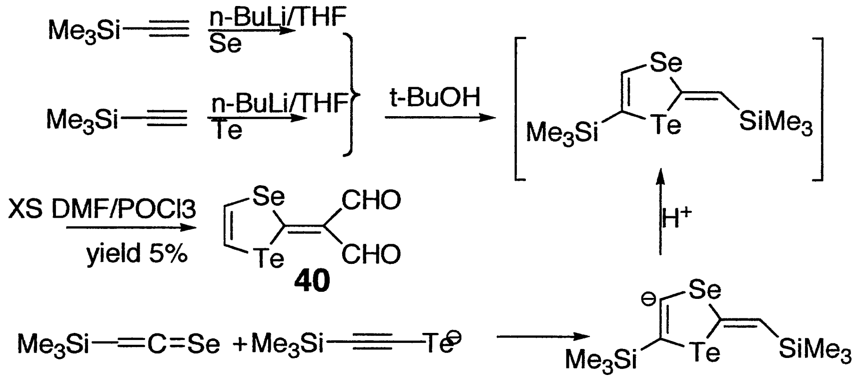
SCHEME 13

the early eightees.[16] The methylene derivatives **39**, (X = Se, Te) were reported in 1980 and 1991 repectively. Fulvene **39**, (X = Se) was isolated in the free state by us in 1980,[17] and **39** (X = Te) was made by Amosova et al in 1991.[18] The sulfur analog is still not known. The reactivity of **38** and **39** is dominated by dipolar and ion-radical contributors (Scheme 14).

Protonation of a mixture of trimethylsilylethynyl selenolate and teimethylsilylethynyl tellurolate gave in very low yield the diformyl Se-Te fulvene **40** after treatment with DMF/$POCl_3$ (Scheme 15).[19]



SCHEME 14



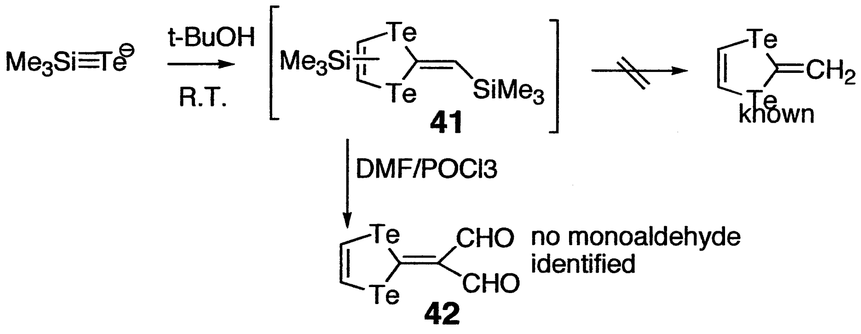
SCHEME 15

Both ethynyl thiolates and ethynyl selenolates protonate under mild conditions to give the 1,3-dithia and 1,3-diselenafulvenes respectively. Howerver, the reaction of an ethynyl tellurolate with a proton source depends on the nature of the H^+ as well as the temperature of reaction. For example, trimethylsilylethynyl tellurolate upon treatment with t-butanol at room-temperature generates the fulvene **41** (not isolable in the pure state). It reacts with DMF/$POCl_3$ to give the dialdehyde **42**, no monoaldehyde being detectable (Scheme 16).

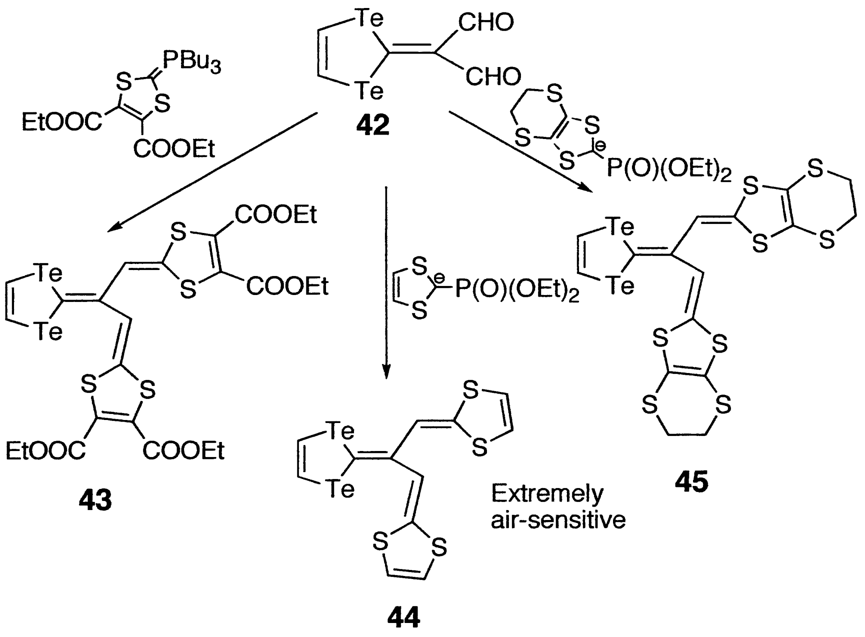
Dialdehyde **42** undergoes Wittig and Wittig-Horner reactions with the appropriate phosphorances to give the first examples of radialene-type tetrathiofulvene (TTF) derivatives **43–45** (Scheme 17).[20]

Protonation of trimethylsilylethynyl tellurolate at −20° using trifluoroacetic acid (TFA)/tBuOH generated the ditelluretane **46** which was reacted with DMF/$POCl_3$ to give the E and Z dialdehydes **47** and **48**, as a difficultly separable mixture (**Scheme 18**). Separation was achieved on a very small scale and the E-isomer **48** gave crystals suitable for X-ray (Figure 1).

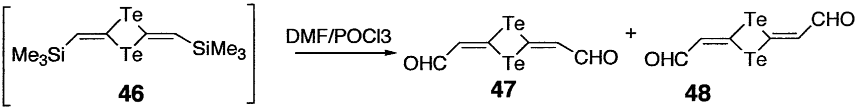
The mixture of dialdehydes **47** and **48** was used in the subsequent Wittig reactions with diester dithiolephosphorane and phosphonate to



SCHEME 16



SCHEME 17



SCHEME 18

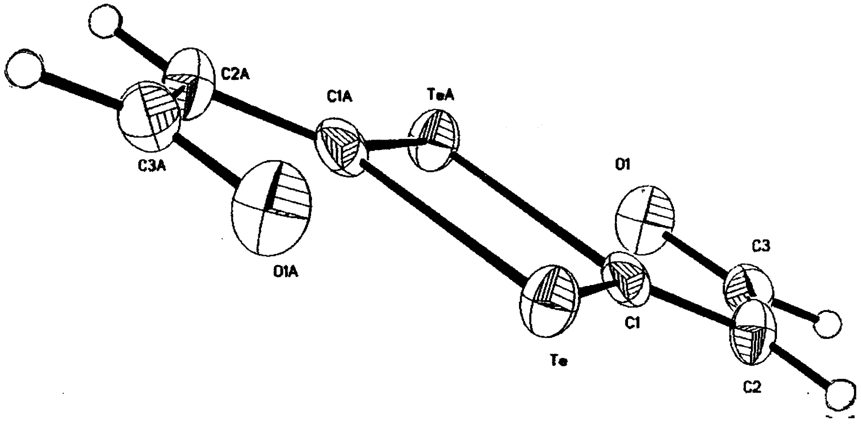


FIGURE 1 Molecular structure of **48**.

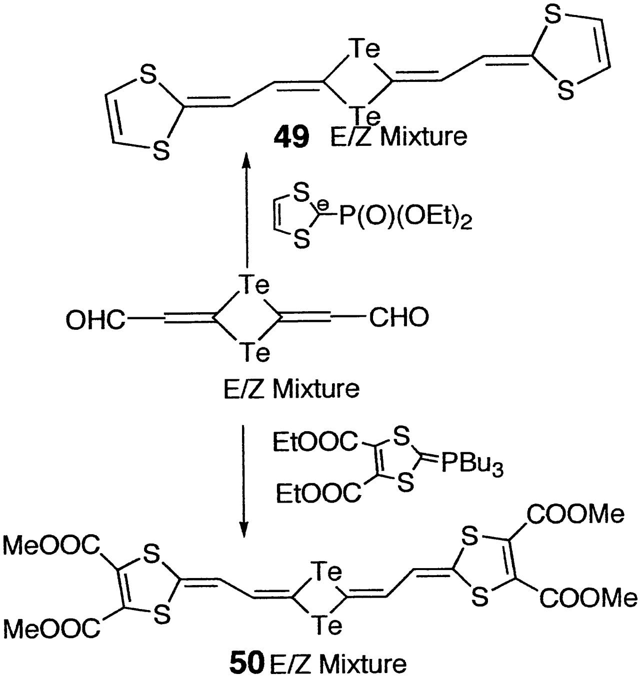
give the first examples of TTF vinylogs **49** and **50** separated by a 1,3-ditelluretane moiety (Scheme 19). The vinylog **49** was extremely sensitive to ambient conditions. Therefore, the cyclic voltametry (CV) was done on the more stable **50**. In contrast to the known TTF analog(s) separated by N-Me-pyrrole, thiophene etc. vinylog **50** shows at least four peaks in its CV, only two of which appear to be reversible. In short, the CV is very complex and requires the attention of a electrochemist. It has already been documented that the 1,3-ditelluronium ion has a propensity to rearrange to the 1,2-isomer. It is possible that similar rearrangements to other as yet unidentified species may be occurring.[21]

It can be said in conclusion, these selenium and tellurium heterocycles hold a lot of interesting chemistry to be uncovered.

EXPERIMENTAL

Reaction of Selenophthalic Anhydride (10) with Triethylphosphite

A suspension of selenophthalic anhydride[22] (**10**, 0.30 g, 1.42 mmol) in 4 mL of triethyl phosphite was stirred at reflux for 3 h. The mixture was cooled to room temperature and the resulting precipitate was filtered, washed with cooled methanol and dried. Thin Layer Chromatogrophy (TLC) test indicated the disappearence of the starting material and the formation of two new products. The two products were separated by column chromatography using initially methylene chloride:hexane (1:1) for the isolation of **11** (130 mg) and then methylene chloride for the isolation of **12** (60 mg).



SCHEME 19

Dimer 11

mp 238°C. ^{1}H NMR ($CDCl_3$) δ: 7.64 (t, J = 7.2 Hz, 2H), 7.82 (t, J = 7.5 Hz, 2H), 8.02 (d, J = 7.5 Hz, 2H), 8.29 (d, J = 7.5 Hz, 2H). MS m/e (relative intensity): 391 (13), 328 (17), 284 (13), 248 (37), 232 (100), 204 (60). Anal. Calcd. For $C_{16}H_8O_2Se_2$: C, 49.26; H, 2.07. Found: C, 48.99, H, 2.07.

Trimer 12

mp 265°C ^{1}H NMR ($CDCl_3$) δ: 7.49 (t, J = 7.92 Hz, 2H), 7.65 (t, J = 3.6 Hz, 2H), 7.73 (m, 2H), 7.89 (d, J = 7.2, 2H), 8.04 (d, 7.2, 2H), 8.80 (d, J = 8.4 Hz, 2H).

MS m/e (relative intensity): 569 (20), 329 (10.82), 300 (20), 271 (15), 284 (100), 220 (23). Anal. Calcd. For $C_{24}H_{12}O_2Se_3$: C, 50.64; H, 2.12. Found: C, 50.18, H, 2.51.

Thionation of 11

A solution of compound 11 (0.2 g, 0.5 mmol) and Lawesson's reagent[23] (0.62 g, 1.53 mmol) in 5 mL of xylene was heated under reflux for

3 h. The precipitate was suspended in ethanol and the suspension was boiled for 15 min. The product (**12**) was filterd and recrystalized from xylene. Yield 0.13 g, (60%). mp > 300°C. MS m/e (relative intensity): 424 (20), 35 (10.82), 318 (20), 291 (15), 214 (100), 220 (23). Anal. Calcd. For $C_{16}H_8S_2Se_2$: C, 46.85; H, 2.22, S, 15.16. Found: C, 47.47, H, 2.22, 15.67.

Reaction of Selenophthalic Anhydride (10) with Benzaldehyde

A solution of selenophthalic anhydride (**10**, 0.5 g, 2.3 mmol), benzaldehyde (0.30 g, 2.8 mmol) and 2 mL of triethyl phosphite in 7 mL of *o*-xylene was refluxed for 5 h. After this time, about 2/3 of the solvent was distilled off. A precipitate which formed upon cooling to room temperature, was filtered and washed with hexane and dried. The precipitate was dissolved in a minimal amount of methylene chloride and the solution was passed through short column of silica gel using methylene chloride: hexane 1:3. Evaporation of the solvent and further recrystallization from acetonitrile gave colorless microcrystals of **20**. Yield 0.22 g (33%): mp 92°C. ^{1}H NMR ($CDCl_3$) δ: 6.40 (s, 1H), 7.29 (m, 1H), 7.39 (m, 2H), 7.54 (m, 1H), 7.72 (m, 2H), 7.83 (d, 2H), 7.91 (d, 1H). MS m/e (relative intensity): 286 (60), 254 (20), 207 (100), 196 (34). Anal. Calcd. For $C_{15}H_{10}OSe$: C, 63.17; H, 3.53. Found: C, 62.98, H, 3.50.

2-(1,1-Diformylmethylene)-1,3-telluraselenole (40)

Trimethylsilylethynyl tellurolate was generated from trimethylsilyl acetylene (1·40 g, 0·014 mole) and n-BuLi (5·6 mL, 2·5 M) in anhydrous THF containing tetramethyl ethylene diamine (TMEDA) (1·85 g) followed by the addition of well-ground tellurium metal in one portion. Trimethylsilylethynyl selenolate was generated in a separate flask in THF solution (125 mL), using TMSacetylene (1·40 g), n-Buli (5·6 mL), TMEDA (1·85 g) and selenium metal (1·1 g). The 2 mixtures were stirred until the metals dissolved (9–10 hrs). They were combined and treated with t-butanol (5 mL), added dropwise within 15 min. After 4–5 h, the solvent was removed under reduced pressure. The dark brown residue was dissolved in DMF (12 mL) and treated with the Vilsmeier reagent prepared from DMF (5 mL) and $POCl_3$ (10·0 g) at O° with stirring. After 8–9 h, the mixture was poured into ice water. Extraction with CH_2Cl_2 followed by standard work-up yielded the dialdehyde **40** in 5% yield after chromatography on SiO_2 using hexane-5% EtOAc. Orange crystals, mp 168–170·4°C (decomp). ^{1}HNMR ($CDCl_3$) δ 10.06(S, 1H), 9.9 (S, 1H), 9.50 (d, 1H, J = 8.5 Hz), 9.20 (d, 1H, J = 8.5 Hz). ^{13}C NMR ($CDCl_3$) δ 185.45, 184.63, 143.94, 141.14, 135.10. MS m/z (relative intensity) 318 (M^+ 75), 316 (85), 288 (100), 260 (50), 208 (70), 155 (43), 130 (84).

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