Chalcogenopyranones from Disodium Chalcogenide Additions to 1,4-Pentadiyn-3-ones. The Role of Enol Ethers as Intermediates

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Enol ethers **9** are formed as a mixture of *E*- and *Z*-isomers from the addition of ethanol to 1,4-pentadiyn-3-ones **2** in sodium ethoxide/ethanol. The enol ethers react with disodium chalcogenides to give the corresponding 2,6-disubstituted chalcogenopyranones **1** bearing alkyl, aryl, or heteroaryl substituents in high yield as the only heterocyclic product of reaction. Diynones **2** react with disodium chalcogenides to give mixtures of products in which the chalcogenopyranones **1** are minor components and the dihydrochalcogenophenes **3** are the major products. The addition of hydrogen sulfide to diynone **2b** in ethanol gives a product mixture nearly identical to that observed for the addition of disodium sulfide in sodium ethoxide in ethanol to **2b**. Intermediates for the addition of hydrogen chalcogenides and disodium chalcogenides to both **2** and **9** are described, which lead to the heterocyclic products.

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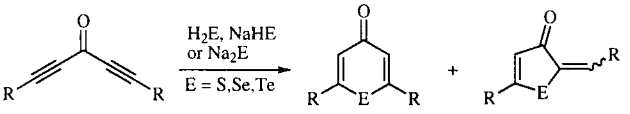
Introduction.

The Δ-4*H*-chalcogenopyran-4-ones **1**, where chalcogen refers to S, Se, or Te atoms, are the building blocks for chalcogenopyrylium dyes and chalcogenopyranyl compounds, both of which have found utility in a variety of applications [1-7]. Although thiopyranones have been prepared *via* many routes [7,9,12,13], routes to selenopyranones [8-11] and telluropyranones [8-12] are few and involve the addition of a hydrogen chalcogenide anion or chalcogenide dianion to 1,4-pentadiyn-3-ones **2**. The syntheses of chalcogenopyranones **1** from 1,4-pentadiyn-3-ones **2** have been complicated by the formation of dihydrochalcogenophenes **3** as illustrated in Scheme 1. While the addition of hydrogen sulfide to 1,5-diphenyl-1,4-pentadiyn-3-one (**2a**) in a bomb at 180° gives thiopyranone **1aS** as the major product [14], hydrolysis of *N*,*N*'-diphenylthiourea or thiourea as sources of hydrogen sulfide in the presence of **2a** gives dihydrothiophene **3aS** as the primary product [15]. Mixtures of both isomers have also been observed for the formal addition of hydrogen selenide or hydrogen telluride to **2a** and 1,5-di-*tert*-butyl-1,4-pentadiyn-3-one (**2b**) [9,11]. The factors influencing the regiochemistry of these addition reactions are not clearly understood.

Scheme 1



2a, R = Ph
2b, R = *tert*-Bu
2c, R = $Me_2NC_6H_4$

1a, R = Ph
1b, R = *tert*-Bu
1c, R = $Me_2NC_6H_4$

3a, R = Ph
3b, R = *tert*-Bu
3c, R = $Me_2NC_6H_4$

The yields of dihydrochalcogenophenes **3** have been reduced by pretreating ethanol solutions of diynones **2** with sodium ethoxide prior to the addition of disodium chalcogenide [9,11,12]. Empirically, the addition of the sodium ethoxide was thought to deprotonate thiol, selenol, or tellurol functionality in the reaction (from sodium hydrogen chalcogenide and hydrogen chalcogenide species as well as organochalcogenol species following addition) promoting nucleophilic addition from the anion. Alternatively, the 1,4-addition of sodium ethoxide to diynones **2** could give either enol ethers or bis enol ethers [16] *in situ*, which may be better substrates for 1,4-addition. Herein, we examine the differences between the formal addition of hydrogen chalcogenides to diynones **2** (with alkyl, aryl and heteroaryl substituents) and to the enol ethers derived from addition of ethanol to diynones **2** under basic conditions. Based on these observations, we describe an improved, general synthesis of symmetrical and unsymmetrical 2,6-disubstituted chalcogenopyranones **1** bearing alkyl, aryl, or heteroaryl substituents.

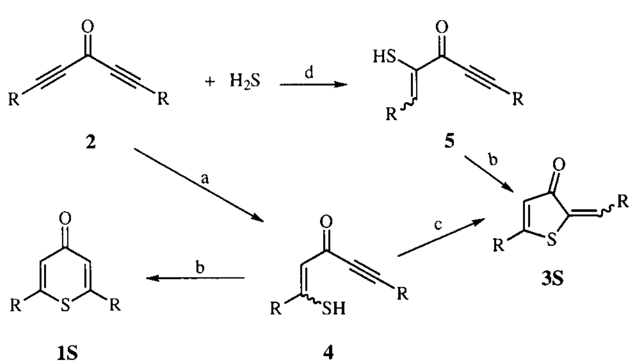
Results and Discussion.

Addition of Hydrogen Chalcogenides to Diynones under Neutral Conditions.

The addition of hydrogen sulfide to an ethanol solution of 2,6-di-*tert*-butyl-1,4-pentadiyn-3-one (**2b**) [11] gave a 40:60 mixture of **1bS** [11] to **3bS** [17]. After partial reaction, diynone **2b** was recovered from the reaction mixture. Furthermore, **2b** was stable in ethanol for several hours at ambient temperature, which suggests that diynone **2b** reacts directly with hydrogen sulfide and not through the formation of enol ethers as intermediates.

Two possible mechanistic paths to compounds **1S** and **3S** from diynones **2** and hydrogen sulfide are shown in Scheme 2. The addition of hydrogen sulfide to diynones **2**

Scheme 2 [a]

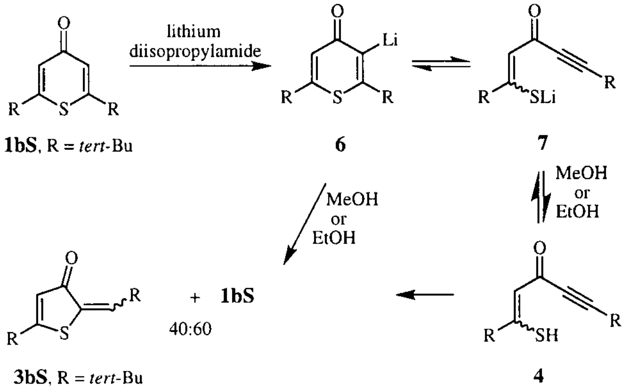


[a] Key: (a) 1,4-addition; (b) *endo*-cyclization *via* 1,4-addition; (c) *exo*-cyclization *via* 4,3-addition; (d) 4,3-addition.

could give either 1,4-addition to produce thioenol **4** (or a tautomer) or 4,3-addition to produce thiol **5** (or its thione tautomer). The 4,3-addition to the triple bond has precedent in the addition of thiophenol or benzene selenol to ethyl phenylpropiolate [18]. *Endo*-cyclization of **4** *via* an intramolecular 1,4-addition would give thiopyranone **1S** while *exo*-cyclization of **4** would give dihydrothiophene **3S**. Dihydrothiophene **3S**, but not thiopyranone **1S**, could also be produced *via endo*-cyclization of thiol **5**.

Intermediate **4** has been prepared indirectly, which allows a more definitive discussion of its chemistry [17]. The lithiation of **1bS** with lithium diisopropylamide and electrophilic capture of the resulting anion(s) gives products derived from either 3-lithio thiopyranone **6** or the ring-opened thiolate **7** (Scheme 3) [17]. The addition of either methanol or, in this study, ethanol to lithiated **1bS** gives a 60:40 mixture of thiopyranone **1bS** to dihydrothiophene **3bS**, which is similar to the 40:60 mixture observed for the addition of hydrogen sulfide to **2b**. The extent to which protonation of anion **6** gave **1bS** directly could not determined. However, the similarity of product mixtures suggests a common intermediate, which could only be **4** as **5** could not be formed from lithiation/protonation of thiopyranone **1bS**.

Scheme 3

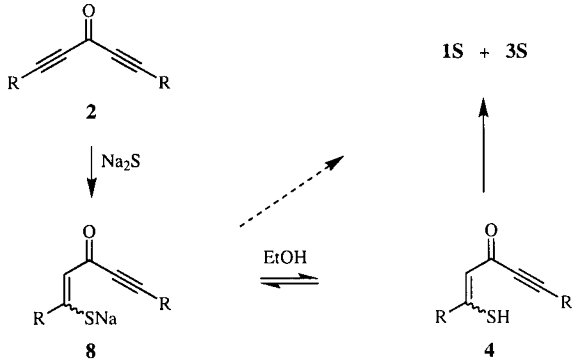


Addition of Disodium Chalcogenides to Diynones.

The addition of diynones **2** to disodium chalcogenides under basic conditions was thought, in part, to promote intramolecular 1,4-addition following initial 1,4-addition of the disodium chalcogenide to **2** [9,11,12]. The added base would deprotonate intermediates such as **4**. The addition of an ethanol solution of **2b** to a solution of disodium sulfide in 0.1 *M* sodium ethoxide/ethanol at ambient temperature gave a 35:65 mixture of **1bS** to **3bS**, which is nearly identical to the 40:60 mixture observed for the addition of hydrogen sulfide under neutral conditions. These data suggest that added base does little to alter the regiochemistry of the addition of disodium chalcogenides to diynones **2**.

The addition of disodium sulfide to diynones **2** is presumed to involve initial nucleophilic 1,4-addition to give thiolate **8** as shown in Scheme 4. *Endo*-cyclization of **8** in the presence of ethanol as a proton source *via* an intramolecular, nucleophilic 1,4-addition is a likely path to thiopyranone **1S**. However, *exo*-cyclization of **8** *via* a nucleophilic addition to give dihydrothiophenes **3S** appears less likely. Alternatively, protonation of **8** in ethanol would generate intermediate thiol **4**, which could then cyclize to either **1** or **3** as described above. If intramolecular cyclization of **4** were significantly faster than cyclization of **8**, then the chemistry associated with **4** would dominate. In view of the similarities in product mixtures between the hydrogen sulfide and disodium sulfide additions, protonation of **8** to give **4** would seem to be the more likely path involving a common intermediate under both reaction conditions.

Scheme 4



In related systems, formation of five-membered rings from intramolecular addition of chalcogenols to acetylenes appears to be preferred relative to the formation of either four- or six-memberd rings [19]. 2-Alkynylphenylchalcogenols give benzochalcogenophenes *via* an *endo*-cyclization and 2-alkynylphenylchalcogenocarboxylic acids give alkylidene γ-chalcogenolactones *via* an *exo*-cyclization.

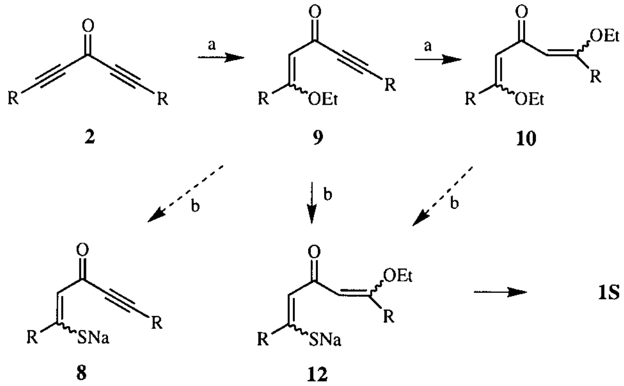
The formation of a mixture of **1** and **3** was a general phenomenon for the addition of diynones **2** to any of the disodium chalcogenides. The addition of diynone **2b** to disodium selenide in 0.1 *M* sodium ethoxide in ethanol gave **1bSe** [11] in 20% isolated yield and **3bSe** [17] in 67% isolated yield while addition of **2b** to disodium telluride in 0.1 *M* sodium ethoxide in ethanol gave **1bTe** [11] in 11% isolated yield and **3bTe** [17] in 57% isolated yield. The addition of a tetrahydrofuran/ethanol solution of **2c** (1) to disodium sulfide in 0.25 *M* sodium ethoxide/ethanol at ambient temperature gave a 4% isolated yield of thiopyranone **1cS** and a 42% isolated yield of dihydrothiophene **3cS**, (2) to disodium selenide gave selenopyranone **1cSe** in 21% isolated yield and dihydroselenophene **3cSe** in 61% isolated yield, and (3) to disodium telluride gave telluropyranone **1cTe** in 20% isolated yield. For the addition of **2c** to disodium telluride, none of the corresponding dihydrotellurophene **3cTe** was isolated.

The low yields of pyranone products from disodium chalcogenide addition to **2c** suggest that *endo*-cyclization of either intermediate **4** or **8** (or Se and Te analogues) is not the major reaction pathway. The preference for *exo*-cyclization with disodium sulfide and disodium selenide additions again would argue that intermediate **4** and its selenium analogue determine the regiochemical fate of reaction.

Generation of Enol Ethers.

In sodium ethoxide in ethanol solution, the diynones **2** are reactive and can add one molecule of ethanol to give enol ethers **9** or two molecules of ethanol to give bis enol ethers **10** (Scheme 5) [16]. If formed, the enol ethers would add disodium chalcogenides to give a new set of acyclic intermediates that could then cyclize to give the observed products.

Scheme 5 [a]

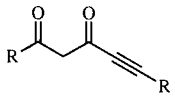


[a] Key: (a) NaOEt/EtOH; (b) Na_2S.

There are several literature examples of enol ether formation from 1,4-pentadiyn-3-ones. The addition of sodium ethoxide/ethanol to **2a** has been reported to give mixtures of enol ethers **9a** and bis enol ethers **10a** [16b] while the addition of sodium ethoxide/ethanol to 2,5-heptadiyn-4-one gives only the bis enol ether after 15 hours at reflux [16a]. We have found that under controlled conditions the addition of sodium ethoxide/ethanol to diynone **2a** gives predominantly enol ethers **9a** (as a mixture of *E*- and *Z*-isomers) while the addition of sodium ethoxide/ethanol to **2b** and to 1,5-di-(4-*N*,*N*-dimethylaminophenyl)-1,4-pentadiyn-3-one (**2c**) gave essentially quantitative conversion to the corresponding mono enol ethers **9a-c** (as mixtures of *E*- and *Z*-isomers), respectively.

Diynone **2a** was stirred for 450 seconds at ambient temperature in 0.07 *M* sodium ethoxide in ethanol. The reaction mixture was poured into water and the products isolated. The proton nmr spectrum of the product mixture showed a complete loss of **2a**, an 80:20 mixture of *E*- and *Z*-enol ethers **9a** (the stereochemistry can not be assigned unambiguously) for 90% of the product mixture, and bis enol ethers **10a** as approximately 10% of the product mixture.

Diynone **2b** was dissolved in 0.25 *M* sodium ethoxide in ethanol at ambient temperature. When **2b** had been consumed (15 minutes), the reaction mixture was poured into water and the products isolated. The proton nmr spectrum of the product mixture showed a complete loss of **2b** and a 58:42 mixture of two enol ethers. If diynone **2b** were stirred for 3 hours at ambient temperature in 0.07 *M* sodium ethoxide in ethanol, an 84:16 mixture of the same *E*- and *Z*-enol ethers **9b** was obtained although the stereochemistry of each component could not be assigned unambiguously. None of the bis enol ether **10b** was detected by proton nmr. Presumably a kinetic mixture of *E*- and *Z*-enol ethers equilibrates to the thermodynamic mixture upon standing in this system. Attempts to separate the **9b** mixture *via* chromatography gave diketone **11b** [17] from hydrolysis of the enol ether.



11b, R = *tert*-Bu
11c, R = 4-$Me_2NC_6H_4$

Diynone **2c** was sparingly soluble in 0.25 *M* sodium ethoxide/ethanol requiring an equal volume of tetrahydrofuran to dissolve the diynone completely (0.05 *M* in **2c**). At 50°, diynone **2c** was consumed after 0.5 hour and an 81:19 mixture of *E*- and *Z*-enol ethers **9c** was obtained. This ratio was unchanged after 3 hours at 50°. Several minor components were observed by proton nmr but accounted for less than 10% of the product mixture and were not investigated further. Although these materials were not separated and characterized, the bis enol ether **10c** was not detected in the mixture by mass spectroscopy under conditions that gave a strong parent ion for the mixture **9c**. Chromatography on silica gel gave diketone **11c** as one product, which was also detected in the crude enol ether mixture.

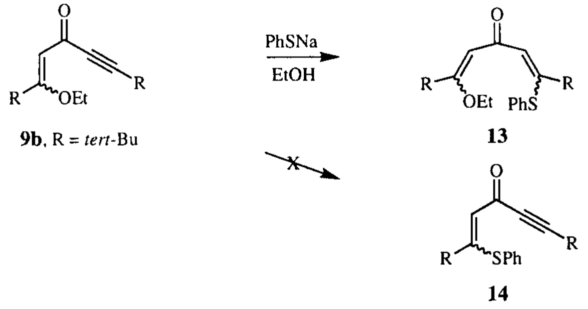
For diynones **2b** and **2c**, formation of the mono enol ethers **9** was much more rapid than the addition of a second ethanol to **9** under the same conditions. Compounds **9** could be isolated as a crude mixture of products, although the enol ethers **9** did not survive chromatographic separation. While we were somewhat surprised by the selectivity for forming mono enol ethers **9**, the literature examples of bis enol ether formation from diynones **2** require more forcing conditions than those used in this study [16].

Addition of Enol Ethers to Disodium Chalcogenides.

The 84:16 enol ether mixture **9b** was redissolved in ethanol and was added to solutions of disodium chalcogenides in 0.25 *M* sodium ethoxide/ethanol at ambient temperature. The proton nmr spectra of the crude reaction mixtures indicated that the chalcogenopyranones **1b** were produced as >95% of the product mixture and none of the dihydrochalcogenophenes **3b** could be detected by proton nmr (assuming a 2% detection limit). Thiopyranone **1bS** [11] was isolated in 84% yield; selenopyranone **1bSe** [11], in 89% yield; and telluropyranone **1bTe** [11], in 85% yield.

The addition of disodium chalcogenides to enol ethers **9** involves initial nucleophilic addition to either the enol ether or the triple bond as summarized in Scheme 5 for the addition of disodium sulfide. The 1,4-addition of disodium sulfide to the enol ether half of **9** would give thiolate **8**, which would then give mixtures of products **1** and **3** as described above. Alternatively, 1,4-addition of disodium sulfide to the triple bond of **9** would give thiolate **12**. *Endo*-cyclization of **12** *via* an intramolecular 1,4-addition/elimination would give thiopyranone **1**. In view of the excellent yields for formation of chalcogenopyranones **1**, initial nucleophilic addition to the triple bond of **9** appears to be the predominant path observed and is fast relative to 1,4-addition to the enol ether of **9**.

Scheme 6



We mimicked the addition of disodium sulfide by adding sodium thiophenoxide to enol ethers **9b** (Scheme 6). The addition product(s) of this reaction cannot close to form a ring. The addition of sodium thiophenoxide to **9b** gave a mixture of four enol ethers **13** in a 74:15:8:3 ratio by proton nmr. One would expect a mixture of *E*- and *Z*-stereoisomers at each double bond in **13** with the 84:16 mixture of enol ether isomers present in **9b** controlling one of the olefinic stereocenters. No **14** containing an acetylene group was observed in this reaction by proton nmr (all products were ethyl enol ethers) or by infrared spectroscopy (no acetylene band). Addition of the chalcogen nucleophile to the triple bond of enol ethers **9** appears to be much faster than addition to the enol ether functionality.

In Situ Generation of Enol Ethers.

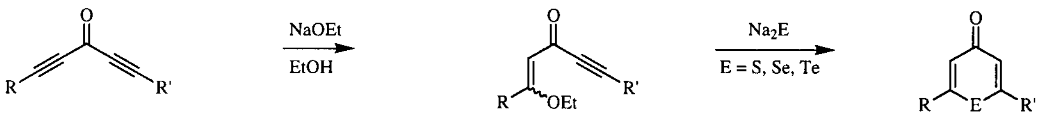
An improved synthesis of chalcogenopyranones **1** from diynones **2** was realized by the initial *in situ* generation of enol ethers **9** followed by addition of the solution of **9** to the disodium chalcogenide as shown in Scheme 7. The formation of enol ethers **9** from diynones **2** in sodium ethoxide/ethanol was easily monitored by thin-layer chromatography on silica gel. Typically, the loss of diynone **2** on the chromatography plate was accompanied by the formation of a single, new spot corresponding to the *E*- and *Z*-enol ethers **9**. When loss of **2** was complete, the enol ether solutions were added immediately to disodium chalcogenide in 0.25 *M* sodium ethoxide in ethanol to give chalcogenopyranones **1**. Yields of chalcogenopyranones **1a-e** were good to excellent (48-89% isolated yields) as summarized in Table 1. None of the chalcogenophenes **3** were detected by proton nmr.

Summary and Conclusions.

The addition of hydrogen chalcogenides or disodium chalcogenides to diynones **2** under protic conditions leads to mixtures of chalcogenopyranones **1** and dihydrochalcogenophenes **3**. The hydrogen chalcogenide additions lead directly to intermediates **4** (or Se and Te analogues, Scheme 2), which can partition between *endo*- and *exo*-cyclization paths. The disodium chalcogenide additions under protic conditions generate thiolate **8** or Se and Te analogues, which are in equilibrium with intermediates **4**. Again, both *endo*- and *exo*-cyclization paths are observed in ratios attributable to intermediates **4**. The cyclizations of intermediates **4** appear to be faster than cyclizations of intermediates **8**.

Diynones **2** are converted to the enol ethers **9** in sodium ethoxide/ethanol solution. Additions of disodium chalcogenides to enol ethers **9** give chalcogenopyranones **1** as the primary product of reaction with none of the isomeric compounds **3** detected by proton nmr. These reactions give initial nucleophilic 1,4-addition to the triple bond to form intermediates **12** (or Se and Te analogues), which

Scheme 7



2a, R, R' = Ph
2b, R, R' = *tert*-Bu
2c, R, R' = 4-$Me_2NC_6H_4$
2d, R, R' = 2-Thienyl
2e, R = Ph, R' = 4-$Me_2NC_6H_4$

9

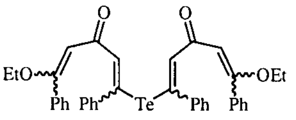
1a, R, R' = Ph
1b, R, R' = *tert*-Bu
1c, R, R' = 4-$Me_2NC_6H_4$
1d, R, R' = 2-Thienyl
1e, R = Ph, R' = 4-$Me_2NC_6H_4$

Table 1

Synthesis of 2,6-Disubstituted 4*H*-Chalcogenopyran-4-ones **1** from Diynones **2** *via* Addition of Enol Ethers **9** to Disodium Chalcogenides

Diynone	Generation of Enol Ether **9**	Disodium Chalcogen	Pyranone	Isolated Yield, %
2a	0.07 *M* NaOEt/EtOH, 450 seconds, 25 °	Na_2S	**1aS**	84
		Na_2Se	**1aSe**	89
		Na_2Te	**1aTe**	86
2b	0.07 *M* NaOEt/EtOH, 3 hours, 25°	Na_2S	**1bS**	84
		Na_2Se	**1bSe**	89
		Na_2Te	**1bTe**	85
2c	0.25 *M* NaOEt/EtOH, 0.5 hour, 50° equal volume of tetrahydrofuran	Na_2S	**1cS**	74
		Na_2Se	**1cSe**	89
		Na_2Te	**1cTe**	76
2d	0.25 *M* NaOEt/EtOH, 0.5 hour, 25°	Na_2S	**1dS**	85
		Na_2Se	**1dSe**	79
		Na_2Te	**1dTe**	48
2e	0.25 *M* NaOEt/EtOH, 0.5 hour, 50° equal volume of tetrahydrofuran	Na_2S	**1eS**	73
		Na_2Se	**1eSe**	68
		Na_2Te	**1eTe**	67

then cyclize to the chalcogenopyranones **1** *via* an intramolecular, nucleophilic 1,4-addition to the enol ether. Telluride **15** has been isolated from the addition of diynone **2a** in sodium ethoxide/ethanol to disodium telluride [9]. A likely route to **15** is formation of enol ethers **9a**, addition of disodium telluride to **9a** to give the Te analogue of intermediate **12**, followed by competing intermolecular 1,4-addition of intermediate **12** to the triple bond of a second enol ether **9a**. Kinetically, the bimolecular addition of the chalcogenide anion to an acetylenic ketone is similar to the intramolecular addition of the chalcogenide anion to the keto enol ether in this system although one might expect the intramolecular process to be faster. At the concentrations employed in this study, no products related to **15** were observed.



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The *in situ* generation of enol ethers **9** from diynones **2** followed by addition of the enol ethers to solutions of disodium chalcogenides represents an improved, general synthesis of both symmetrical and unsymmetrical 2,6-disubstituted chalcogenopyranones **1** bearing alkyl, aryl, and heteroaryl substituents. Since enol ethers **9** can be prepared from diynones **2** under non-forcing conditions with little formation of the bis enol ethers **10**, the conversion of **2** to **9** can be monitored to completion to optimize the yields of chalcogenopyranone products.

EXPERIMENTAL

General Methods.

Solvents and reagents were used as received from Aldrich Chemical Co. Concentrations *in vacuo* were performed on a Büchi rotary evaporator. The nmr spectra were recorded at 30.0° on a Varian Gemini-300, Inova 400, or Inova 500 instrument with residual solvent signal as internal standard: deuteriochloroform (δ: 7.26 for proton, δ: 77.0 for carbon). Infrared spectra were recorded on a Perkin-Elmer FT-IR instrument.

Elemental analyses were conducted by Atlantic Microanalytical, Inc. Diynone **2a** was prepared according to reference 9. Diynone **2b** was prepared according to reference 11. The disodium chalcogenides were prepared according to reference 11 except that the sodium ethoxide/ethanol mixtures were heated at reflux during reduction of S, Se, and Te and were then cooled to ambient temperature.

Preparation of 1,5-Di-(4-*N*,*N*-dimethylaminophenyl)-1,4-pentadiyn-3-one (**2c**).

Diynone **2c** was prepared by the addition of the lithium acetylide of 4-*N*,*N*-dimethylaminophenylethyne (**16**) [20,21] to methyl formate to give 1,5-di-(4-*N*,*N*-dimethylaminophenyl)-1,4-pentadiyn-3-ol (**17**). Oxidation of **17** gave **2c**.

4-Bromo-*N*,*N*-dimethylaniline (19.35 g, 0.0967 mole), trimethylsilylacetylene (19.9 g, 0.193 mole), copper(I) iodide (0.202 g, 1.06 mmoles), and triphenylphosphine (0.51 g, 1.93 mmoles) were dissolved in piperidine (400 ml). Bis(triphenylphosphine)palladium(II) chloride (0.204 g, 0.290 mmoles) was added and the resulting mixture was heated at reflux for 8 hours. The reaction mixture was concentrated *in vacuo* and saturated sodium bicarbonate (200 ml) was added. The product was extracted with hexane (3 x 100 ml). The combined hexane extracts were washed with water and brine, were dried over magnesium sulfate, and concentrated. The 2-(4-*N*,*N*-dimethylaminophenyl)trimethylsilylethyne [21] was isolated *via* chromatography on silica gel eluting with hexanes to give 18.9 g (90%) of product as a yellow solid, mp 82-84°: ^{1}H nmr (deuteriochloroform): δ 7.34 (d, 2H, J = 8 Hz), 6.60 (d, 2H, J = 8 Hz), 2.97 (s, 6H), 0.25 (s, 9H); ir (carbon tetrachloride): 2962, 2146 cm^{-1}.

2-(4-*N*,*N*-Dimethylaminophenyl)trimethylsilylethyne (47.8 g, 0.219 mole) was dissolved in a mixture of 100 ml of tetrahydrofuran and 15 ml of water. A 1.0 *M* solution of tetrabutylammonium fluoride in tetrahydrofuran (226 ml, 0.226 mole) was added dropwise at 0° and the reaction was stirred for 1 hour at 0°. The reaction mixture was concentrated and water (200 ml) was added. The products were extracted with hexane (6 x 75 ml). The combined hexane extracts were dried over magnesium sulfate and concentrated. The product was purified *via* chromatography on silica gel eluted with hexane to give 26.0 g (82%) of **16** [20,21] as a yellow-orange solid, mp 33-35°: ^{1}H nmr (deuteriochloroform): δ 7.36 (d, 2H, J = 8 Hz), 6.61 (d, 2H, J = 8 Hz), 2.96 (s, 6H), 2.91 (s, 1H); ^{13}C nmr (deuteriochloroform): δ 150.5, 133.2, 111.8, 108.9, 84.9, 74.7, 40.1; ir (carbon tetrachloride): 3262, 2923, 2224 cm^{-1}.

A 2.5 *M* solution of *n*-butyllithium in hexanes (28.4 ml, 0.071 mole) was added dropwise to a solution of **16** (10.3 g, 0.071 mole) in 300 ml of anhydrous tetrahydrofuran at -78°. After addition was complete, the reaction was stirred for 20 minutes at -78°. Methyl formate (2.13 g, 0.0355 mole) in 5 ml of anhydrous tetrahydrofuran was added dropwise at -78°. After addition was complete, the reaction was warmed to ambient temperature over a 20 minute period. Saturated sodium bicarbonate (40 ml) was slowly added followed by an additional 200 ml of water. The product was extracted with dichloromethane (6 x 50 ml). The combined organic extracts were washed with brine, dried over magnesium sulfate, and concentrated. The crude product was recrystallized from hexanes to give 6.41 g (57%) of 1,5-bis(4-*N*,*N*-dimethylaminophenyl)-1,4-pentadiyn-3-ol (**17**) as a tan solid, mp 126-128°: ^{1}H nmr (deuteriochloroform): δ 7.32 (AA'BB', 4H, J ("doublet") = 8 Hz), 6.61 (AA'BB', 4H, J ("doublet") = 8 Hz), 5.53 (s, 1H), 2.95 (s, 12H), 2.31 (s, 1H); ^{13}C nmr (deuteriochloroform): δ 150.3, 133.0, 111.6, 108.8, 85.4, 84.4, 53.5, 40.1; ir (carbon tetrachloride): 3262, 2923, 2224 cm^{-1}; ms: (EI), m/z 318 (M$^+$, base peak).

Anal. Calcd. for $C_{21}H_{22}N_2O$: C, 79.21; H, 6.96; N, 8.80. Found: C, 79.18; H, 7.01; N, 8.69.

Manganese dioxide (12.8 g, 0.147 mole) was added to a solution of **17** (11.8 g, 0.0368 mole) in 100 ml of anhydrous dichloromethane. The resulting mixture was stirred at ambient temperature for 2 hours at which point an additional 6.4 g (0.074 mole) of manganese dioxide was added. The reaction mixture was stirred 72 hours and was then filtered through a pad of Celite. The filter cake was washed with dichloromethane (5 x 75 ml). The combined organic filtrates were concentrated. The residue was purified *via* chromatography on silica gel eluted with dichloromethane followed by recrystallization from ethyl acetate-hexanes to give 9.36 g (81%) of **2c** as a red solid, mp 143-145°; ^{1}H nmr (deuteriochloroform): δ 7.54 (AA'BB', 4H, J ("doublet") = 8 Hz), 6.65 (AA'BB', 4H, J ("doublet") = 8 Hz), 3.03 (s, 12H); ^{13}C nmr (deuteriochloroform): δ 156.4, 147.4, 130.9, 107.1, 100.9, 90.7, 86.7, 35.6; ir (potassium bromide): 2904, 2145, 1598 cm^{-1}; ms: (positive FAB), m/z 317 (MH$^+$, base peak).

Anal. Calcd. for $C_{21}H_{20}N_2O$: C, 79.72; H, 6.33; N, 8.85. Found: C, 79.63; H, 6.39; N, 8.77.

Preparation of 1,5-Di-(2-thienyl)-1,4-pentadiyn-3-one (**2d**).

Diynone **2d** was prepared by the addition of the lithium acetylide of 2-ethynylthiophene (**18**) to methyl formate to give 1,5-di-(2-thienyl)-1,4-pentadiyn-3-ol (**19**). Oxidation of **19** gave **2d**.

2-Bromothiophene (25.7 g, 0.122 mole), trimethylsilylacetylene (25.8 g, 0.268 mole), copper(II) iodide (0.364 g, 1.92 mmoles), and triphenylphosphine (1.54 g, 5.88 mmoles) were dissolved in triethylamine (400 ml). Bis(triphenylphosphine)palladium(II) chloride (0.504 g, 0.720 mmole) was added and the resulting mixture was heated at reflux for 5 hours. Water (400 ml) was added and the product was extracted with hexanes (3 x 200 ml). The combined hexane extracts were washed with water and brine, were dried over magnesium sulfate, and concentrated. The 2-(trimethylsilylethynyl)thiophene was isolated *via* chromatography on silica gel eluting with hexanes to give 38.0 g (89%) of 2-(trimethylsilylethynyl)thiophene, which was used without further purification: ^{1}H nmr (deuteriochloroform): δ 7.21 (d, 2H), 6.93 (t, 1H), 0.25 (s, 1H); ^{13}C nmr (deuteriochloroform): δ 132.5, 127.2, 126.8, 123.3, 98.6, 97.6, 0.09; ir (carbon tetrachloride): 2962, 2146 cm^{-1}.

2-(Trimethylsilylethynyl)thiophene (37.0 g, 0.205 mole) was dissolved in a mixture of 50 ml of tetrahydrofuran and 10 ml of water. A 1.0 *M* solution of tetrabutylammonium fluoride in tetrahydrofuran (226 ml, 0.226 mole) was added dropwise and the reaction was stirred for 4 hours at ambient temperature. Water (200 ml) was added. The products were extracted with hexane (5 x 100 ml). The combined hexane extracts were dried over magnesium sulfate and concentrated. The product was distilled to give 18.8 g (85%) of 2-ethynylthiophene (**18**) as a colorless oil, bp 60-61° at 20 torr (lit bp [22], 54-60° at 20 torr): ^{1}H nmr (deuteriochloroform): δ 7.28 (m, 2H), 6.96 (m, 1H), 3.33 (s, 1H); ^{13}C nmr (deuteriochloroform): δ 133.1, 127.6, 126.9, 122.1, 81.4, 77.1; ir (CCl_4) 3306, 2975, 2108 cm^{-1}.

A 1.0 *M* solution of ethyl magnesium bromide in tetrahydrofuran (43.0 ml, 0.043 mole) was added dropwise to a solution of **18** (4.65 g, 0.043 mole) in 15 ml of anhydrous tetrahydrofuran at 0°. After addition was complete, the reaction was stirred for 20 minutes at 0°. Methyl formate (1.29 g, 0.0215 mole) in 5 ml of anhydrous tetrahydrofuran was added dropwise at 0°. After addition was complete, the reaction was warmed to ambient temperature over a 20 minute period. A 1 *N* solution of hydrochloric acid (50 ml) was added and the product was extracted with dichloromethane (3 x 30 ml). The combined organic extracts were washed with brine, dried over magnesium sulfate, and concentrated. The product was purified *via* chromatography on silica gel eluted with 1:1 dichloromethane/hexanes to give 4.88 g (93%) of 1,5-bis(2-thienyl)-1,4-pentadiyn-3-ol as a colorless oil: ^{1}H nmr (deuteriochloroform): δ 7.29 (m, 4H), 6.96 (m, 4H), 5.60 (s, 1H), 2.50 (s, 1H); ^{13}C nmr (deuteriochloroform): δ 133.0, 127.9, 127.0, 121.9, 89.8, 78.1, 53.2; ir (carbon tetrachloride): 3597, 2190 cm^{-1}; ms: (EI), m/z 244 (M$^+$, base peak).

1,5-Bis(2-thienyl)-1,4-pentadiyn-3-ol (4.36 g, 17.8 mmoles) was dissolved in 30 ml of acetone and the resulting solution was cooled to 0°. A 10% chromic acid solution (100 ml) was added dropwise at 0° and the resulting mixture was stirred for 1 hour after addition was complete. The product was extracted with dichloromethane (3 x 100 ml). The combined organic extracts were washed with brine, were dried over magnesium sulfate, and concentrated. Diynone **2d** was purified *via* chromatography on silica gel eluted with 1:1 dichloromethane/hexanes to give 3.59 g (83%) of the diynone **2d** as a yellow solid, mp 82-84°; ^{1}H nmr (deuteriochloroform): δ 7.55 (m, 4H), 7.10 (m, 2H); ^{13}C nmr (deuteriochloroform): δ 159.5, 137.5, 132.7, 127.9, 119.3, 93.9, 86.1; ir (carbon tetrachloride): 2189, 1612 cm^{-1}; ms: (ES), m/z 242 (M$^+$, base peak).

Anal. Calcd. for $C_{13}H_6OS_2$: C, 64.43; H, 2.50. Found: C, 64.21; H, 2.50.

Preparation of 1-Phenyl-5-(4-*N*,*N*-dimethylaminophenyl)-1,4-pentadiyn-3-one (**2e**).

A 2.5 *M* solution of *n*-butyllithium in hexanes (28.4 ml, 0.071 mole) was added dropwise to a solution of **16** (10.3 g, 0.071 mole) in 300 ml of anhydrous tetrahydrofuran at -78°. After addition was complete, the reaction was stirred for 20 minutes at -78°. Phenylpropargyl aldehyde (9.10 g, 0.070 mole) in 50 ml of anhydrous tetrahydrofuran was added dropwise at -78°. After addition was complete, the reaction was warmed to ambient temperature over a 20 minute period. Saturated sodium bicarbonate (40 ml) was slowly added followed by an additional 200 ml of water. The product was extracted with dichloromethane (4 x 100 ml). The combined organic extracts were washed with brine, dried over magnesium sulfate, and concentrated. The crude product was purified *via* chromatography on silica gel eluted with dichloromethane to give 22.0 g (80%) of 1-phenyl-5-(4-*N*,*N*-dimethylaminophenyl)-1,4-pentadiyn-3-ol (**19**) as a yellow oil: ^{1}H nmr (deuteriochloroform): δ 7.50 (m, 2H), 7.34 (m, 7H), 6.62 (AA'BB', 2H, J ("doublet") = 8 Hz), 5.57 (d, 1H, J = 7 Hz), 2.98 (s, 6H), 2.32 (d, 1H, J = 7 Hz); ^{13}C nmr (deuteriochloroform): δ 150.4, 133.0, 131.9, 128.7, 128.3, 122.1, 111.7, 108.5, 86.5, 85.9, 84.1, 83.9, 53.3, 40.1; ir (carbon tetrachloride): 3262, 2923, 2224 cm^{-1}; ms: (positive FAB), m/z 276 (M$^+$, base peak).

Anal. Calcd. for $C_{19}H_{17}NO$: C, 82.29; H, 6.22; N, 5.09. Found: C, 82.66; H, 6.14; N, 5.11.

Manganese dioxide (12.8 g, 0.147 mole) was added to a solution of **19** (11.0 g, 0.040 mole) in 100 ml of anhydrous dichloromethane. The resulting mixture was stirred at ambient temperature for 2 hours at which point an additional 6.4 g (0.074 mole) of manganese dioxide was added. The reaction mixture was stirred 72 hours and was then filtered through a pad of Celite. The filter cake was washed with dichloromethane (5 x 75 ml). The combined organic filtrates were concentrated. The residue was purified *via* chromatography on silica gel eluted with dichloromethane followed by recrystallization from ethyl acetate-hexanes to give 9.36 g (81%) of **2e** as a red solid, mp 123-125°; ^{1}H nmr (deuteriochloroform): δ 7.63 (m, 2H), 7.53 (AA'BB', 2H, J ("doublet") = 8 Hz), 7.42 (m, 3H), 6.63 (AA'BB', 2H, J ("doublet") = 8 Hz), 3.03 (s, 6H); ^{13}C nmr (deuteriochloroform): δ 160.7, 152.1, 135.6, 133.1, 130.8, 128.6, 119.9, 111.5, 104.6, 97.1, 91.4, 90.1, 89.5, 39.9; ir (potassium bromide): 2145, 1598 cm^{-1}; ms: (positive FAB), m/z 274 (MH$^+$, base peak).

Anal. Calcd. for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.13. Found: C, 83.31; H, 5.46; N, 5.10.

Addition of Hydrogen Sulfide to 1,5-Di-*tert*-butyl-1,4-pentadiyn-3-one (**2b**).

Diynone **2b** (0.38 g, 2.0 mmoles) was dissolved in 40 ml of ethanol. A stream of hydrogen sulfide was introduced *via* a gas dispersion tube and the progress of reaction was monitored by thin-layer chromatography on silica gel (5% ethyl acetate-dichloromethane). When the diynone **2b** had been consumed (≈ 1 hour), the reaction mixture was poured into 200 ml of water and the products were extracted with dichloromethane (3 x 50 ml). The combined organic extracts were washed with brine, dried over sodium sulfate, and concentrated. The ^{1}H nmr spectrum of the crude reaction mixture showed a 40:60 mixture of thiopyranone **1bS** [11] to dihydrothiophene **3bS** [17]. Chromatography on silica gel eluted with 5% ethyl acetate-dichloromethane gave 0.13 g (30%) of **1bS** and 0.24 g (55%) of **3bS**.

Repetition of the reaction, but with workup after approximately 50% reaction, gave 0.15 g (40%) of unreacted **2b**, 0.048 g (11%) of **1bS**, and 0.088 g (20%) of **3bS** following chromatography on silica gel as before.

4*H*-2,6-Di-*tert*-butylthiopyran-4-one (**1bS**) [11].

This compound had mp 96-98°; ^{1}H nmr (deuteriochloroform): δ 6.88 (s, 2H), 1.33 (s, 18H).

2-*tert*-Butyl-5-(*tert*-butylmethylidene)-4-oxo-4,5-dihydrothiophene (**3bS**) [17].

This compound had ^{1}H nmr (deuteriochloroform): δ 7.03 (s, 1H), 6.13 (s, 1H), 1.31 (s, 9H), 1.24 (s, 9H).

Addition of Diynone **2b** to Disodium Sulfide.

An ethanol solution of **2b** (0.38 g, 2.0 mmoles in 10 ml) was added to disodium sulfide, prepared from the addition of sodium borohydride(0.080 g, 2.2 mmoles) to elemental sulfur (0.070 g, 2.2 mmoles) in 20 ml of 0.1 *M* sodium ethoxide in ethanol. The reaction mixture was stirred at ambient temperature for 15 minutes and was then poured into 150 ml of water. The products were extracted with dichloromethane (3 x 50 ml) and the combined organic extracts were washed with brine, dried over magnesium sulfate, and concentrated. The ^{1}H nmr spectrum of the crude reaction mixture showed a 35:65 mixture of **1bS** to **3bS**.

Addition of Diynone **2b** to Disodium Selenide.

An ethanol solution of **2b** (0.38 g, 2.0 mmoles in 10 ml) was added to disodium selenide, prepared from the addition of sodium borohydride (0.080 g, 2.2 mmoles) to elemental selenium (0.174 g, 2.2 mmoles) in 20 ml of 0.1 *M* sodium ethoxide in ethanol. The reaction mixture was stirred at ambient temperature for 15 minutes with workup as described above for the addition of **2b** to disodium sulfide. The residue was purified *via* chromatography on silica gel eluted with 10% ethyl acetate-dichloromethane to give **1bSe** in 20% isolated yield (0.12 g) and **3bSe** in 67% isolated yield (0.44 g).

4*H*-2,6-Di-*tert*-butylselenopyran-4-one (**1bSe**) [11].

This compound had mp 98-102°; ^{1}H nmr (deuteriochloroform): δ 6.96 (s, 2H), 1.36 (s, 18H).

2-*tert*-Butyl-5-(*tert*-butylmethylidene)-4-oxo-4,5-dihydroselenophene (**3bSe**) [17].

This compound had ^{1}H nmr (deuteriochloroform): δ 7.26 (s, 1H), 6.41 (s, 1H), 1.32 (s, 9H), 1.22 (s, 9H).

Addition of Diynone **2b** to Disodium Telluride.

An ethanol solution of **2b** (0.38 g, 2.0 mmoles in 10 ml) was added to disodium telluride, prepared from the addition of sodium borohydride (0.080 g, 2.2 mmoles) to elemental tellurium (0.28 g, 2.2 mmoles) in 20 ml of 0.1 *M* sodium ethoxide in ethanol. The reaction mixture was stirred at ambient temperature for 15 minutes with workup as described above for the addition of **2b** to disodium sulfide. The residue was purified *via* chromatography on silica gel eluted with 10% ethyl acetate-dichloromethane to give **1bTe** in 11% (0.077 g) isolated yield and **3bTe** in 57% isolated yield (0.40 g).

4*H*-2,6-Di-*tert*-butyltelluropyran-4-one (**1bTe**) [11].

This compound had mp 83.5-84°; ^{1}H nmr (deuteriochloroform): δ 7.02 (s, 2H), 1.33 (s, 18H).

2-*tert*-Butyl-5-(*tert*-butylmethylidene)-4-oxo-4,5-dihydrotellurophene (**3bTe**) [17].

This compound had ^{1}H nmr (deuteriochloroform): δ 7.55 (s, 1H), 6.75 (s, 1H), 1.28 (s, 9H), 1.17 (s, 9H).

General Procedure for Addition of Diynone **2c** to Disodium Chalcogenides.

Diynone **2c** (1.00 g, 3.16 mmoles) was dissolved in 15 ml of tetrahydrofuran and 15 ml of ethanol. The resulting solution was poured into a solution of disodium chalcogenide, prepared from 3.79 mg-atoms of sulfur (0.121 g), selenium, (0.300 g), or telluride (0.484 g) and 0.122 g (3.79 mmoles) of sodium borohydride in 40 ml of degassed 0.25 *M* sodium ethoxide in ethanol under an argon atmosphere. The reaction mixture was stirred for 15 minutes at ambient temperature and was then poured into 200 ml of water. The products were extracted with dichloromethane (4 x 50 ml) and the combined organic extracts were washed with brine, dried over magnesium sulfate, and concentrated. The residue was purified by chromatography on silica gel eluted with 20% ethyl acetate-dichloromethane to give chalcogenopyranones **1c** (R_f = 0.15-0.25) and dihydrochalcogenophenes **3c** (R_f = 0.6-0.75). The products were recrystallized from acetonitrile.

4*H*-2,6-Di-4-(*N*,*N*-dimethylaminophenyl)thiopyran-4-one (**1cS**).

The yield was 0.133 g (12%), mp 205° dec; ^{1}H nmr (deuteriochloroform): δ 7.56 (AA'BB', 4H, J ("doublet") = 9 Hz), 7.11 (s, 2H), 6.73 (AA'BB', 4H, J ("doublet") = 9 Hz), 3.02 (s, 12H); ^{13}C nmr (deuteriochloroform): δ 178.6, 148.8, 147.5, 123.3, 119.1, 118.8, 107.6, 35.7; ir (potassium bromide): 1607, 1583 cm^{-1}; uv (dichloromethane): λ_{max} 383 nm (log ε 4.49); ms: (ES), m/z 351 (MH$^+$, base peak).

Anal. Calcd. for $C_{21}H_{22}N_2OS$: C, 71.96; H, 6.33; N, 7.99. Found: C, 72.13; H, 6.36; N, 7.91.

2-(4-*N*,*N*-Dimethylaminophenyl)-5-[(4-*N*,*N*-dimethylaminophenyl)methylidene]-4-oxo-4,5-dihydrothiophene (**3cS**).

The yield was 0.465 g (42%), mp, 256-258°; ^{1}H nmr (deuteriochloroform): δ 7.77 (s, 1H), 7.67 (AA'BB', 2H, J ("doublet") = 9 Hz), 7.66 (AA'BB', 2H, J ("doublet") = 9 Hz), 6.76 (AA'BB', 2H, J ("doublet") = 9 Hz), 6.72 (AA'BB', 2H, J ("doublet") = 9 Hz), 6.62 (s, 1H), 3.07 (s, 6H), 3.06 (s, 6H); ^{13}C nmr (deuteriochloroform): δ 191.8, 166.3, 153.3, 152.0, 134.6, 133.7, 128.9, 127.0, 122.7, 120.5, 115.1, 112.6, 40.82, 40.80; ir (potassium bromide): 1603 cm^{-1}; ms: (ES), m/z 351 (MH$^+$, base peak).

Anal. Calcd. for $C_{21}H_{22}N_2OS$: C, 71.96; H, 6.33; N, 7.99. Found: C, 72.13; H, 6.36; N, 7.91.

4*H*-2,6-Di-4-(*N*,*N*-dimethylaminophenyl)selenopyran-4-one (**1cSe**).

The yield was 0.263 g (21%), mp 215° dec; ^{1}H nmr (deuteriochloroform): δ 7.53 (AA'BB', 4H, J ("doublet") = 9 Hz), 7.19 (s, 2H), 6.75 (AA'BB', 4H, J ("doublet") = 9 Hz), 3.03 (s, 12H); ^{13}C nmr (deuteriochloroform): δ 180.7, 150.9, 147.4, 123.3, 120.5, 120.3, 107.7, 35.7; ir (potassium bromide): 1602, 1516 cm^{-1}; uv (dichloromethane): λ_{max} 396 nm (log ε 4.51); ms: (ES), m/z 399 (MH$^+$, base peak, ^{80}Se isotope).

Anal. Calcd. for $C_{21}H_{22}N_2OSe$: C, 63.47; H, 5.58; N, 7.05. Found: C, 63.68; H, 5.66; N, 7.00.

2-(4-*N*,*N*-Dimethylaminophenyl)-5-[(4-*N*,*N*-dimethylaminophenyl)methylidene]-4-oxo-4,5-dihydroselenophene (**3cSe**).

The yield was 0.77 g (61%), mp >260°; ^{1}H nmr (deuteriochloroform): δ 7.99 (s, 1H), 7.55 (AA'BB', 2H, J ("doublet") = 9 Hz), 7.51 (AA'BB', 2H, J ("doublet") = 9 Hz), 6.87 (s, 1H), 6.73 (AA'BB', 2H, J ("doublet") = 9 Hz), 6.68 (AA'BB', 2H, J ("doublet") = 9 Hz), 3.05 (s, 6H), 3.04 (s, 6H); ^{13}C nmr (deuteriochloroform): δ 189.6, 160.6, 148.1, 147.0, 131.9, 128.0, 124.2, 121.2, 118.0, 117.0, 112.9, 107.5, 107.1, 35.6 (overlapping peaks); ir (potassium bromide): 1617 cm^{-1}; ms: (ES), m/z 399 (MH$^+$, base peak, ^{80}Se isotope).

Anal. Calcd. for $C_{21}H_{22}N_2OSe$: C, 63.47; H, 5.58; N, 7.05. Found: C, 63.58; H, 5.76; N, 7.01.

4*H*-2,6-Di-4-(*N*,*N*-dimethylaminophenyl)telluropyran-4-one (**1cTe**).

The yield was 0.281 g (20%), mp 260° dec; ^{1}H nmr (dichloromethane-d_2): δ 7.46 (AA'BB', 4H, J ("doublet") = 8 Hz), 7.17 (s, 2H), 6.74 (AA'BB', 4H, J ("doublet") = 8 Hz), 3.01 (s, 12H); ^{13}C nmr (dichloromethane-d_2): δ 189.9, 153.9, 149.3, 130.6, 129.8, 129.7, 114.1, 41.9; ir (potassium bromide): 1604, 1595 cm^{-1}; uv (dichloromethane): λ_{max} 411 nm (log ε 4.54); ms: (ES), m/z 449 (MH$^+$, base peak, ^{130}Te isotope).

Anal. Calcd. for $C_{21}H_{22}N_2OTe$: C, 56.30; H, 4.95; N, 6.25. Found: C, 56.63; H, 5.01; N, 6.20.

Preparation of Enol Ethers **9a**.

Diynone **2a** (0.23 g, 1.00 mmole) was dissolved in 20 ml of 0.07 *M* sodium ethoxide in ethanol. The resulting solution was allowed to stand at ambient temperature for 450 seconds. The reaction mixture was poured into 60 ml of water. The products were extracted with dichloromethane (3 x 15 ml) and the combined organic extracts were washed with water (until neutral *p*H), dried over sodium sulfate, and concentrated. The ^{1}H nmr spectrum of the crude reaction mixture was indicative of a 80:20 mixture of two enol ethers **9a** [16b].

The major enol ether **9a** had ^{1}H nmr (deuteriochloroform): δ 7.10-7.60 (arom, m, 10H), 5.81 (s, 1H), 4.09 (q, 2H, J = 7 Hz), 1.27 (t, 3H, J = 7 Hz.

Minor enol ether **9a** had ^{1}H nmr (deuteriochloroform): δ 7.10-7.60 (arom, m, 10H), 5.84 (s, 1H), 3.75 (q, 2H, J = 7 Hz), 1.34 (t, 3H, J = 7 Hz), 1.25 (s, 9H), 1.24 (s, 9H).

The mixture had ms: (EI), m/z 276 (M$^+$); ir (film on sodium chloride): 2001, 1641 cm^{-1}.

Preparation of Enol Ethers **9b**.

Diynone **2b** (0.10 g, 0.50 mmole) was dissolved in 10 ml of 0.25 *M* sodium ethoxide in ethanol. The resulting solution was allowed to stand at ambient temperature and the disappearance of **2b** was monitored by thin-layer chromatography on silica gel eluted with dichloromethane. After 15 minutes, loss of **2b** was complete and the reaction mixture was poured into 30 ml of water. The products were extracted with dichloromethane (3 x 15 ml) and the combined organic extracts were washed with water (until neutral *p*H), dried over sodium sulfate, and concentrated. The ^{1}H nmr spectrum of the crude reaction mixture was indicative of a 58:42 mixture of two enol ethers **9b**. The reaction was repeated in 0.07 *M* sodium ethoxide in ethanol and the reaction mixture was allowed to stand 3 hours at ambient temperature. Workup as before gave an 84:16 mixture of the same two enol ethers **9b**.

The major enol ether **9b** had ^{1}H nmr (deuteriochloroform): δ 5.56 (s, 1H), 4.09 (q, 2H, J = 7 Hz), 1.27 (t, 3H, J = 7 Hz), 1.26 (s, 9H), 1.12 (s, 9H); ir (film on sodium chloride): 2201, 1641 cm^{-1}.

For minor enol ether **9b** had ^{1}H nmr (deuteriochloroform): δ 5.38 (s, 1H), 3.82 (q, 2H, J = 7 Hz), 1.34 (t, 3H, J = 7 Hz), 1.25 (s, 9H), 1.24 (s, 9H); ir (film on sodium chloride): 2215, 1641 cm^{-1}.

The mixture **9b** had ms: (ES), m/z 237 (MH$^+$, base peak).

Anal. Calcd. for $C_{15}H_{24}O_2$: C, 76.19; H, 10.23. Found: C, 76.52; H, 10.44.

General Procedure for the Addition of Enol Ethers **9b** to Disodium Chalcogenides.

The isolated enol ethers **9b** (0.090 g, 0.40 mmole) obtained above after 3 hours were redissolved in 5 ml of ethanol. The resulting solution was then added to disodium chalcogenide, prepared from the addition of sodium borohydride (0.040 g, 1.1 mmoles) to sulfur (0.017 g, 0.50 mg-atom), selenium (0.040 g, 0.50 mg-atom), or tellurium (0.064 g, 0.50 mg-atom) in 7 ml of 0.25 *M* sodium ethoxide in ethanol. After 30 minutes, the reaction mixture was poured into 50 ml of water. The products were extracted with dichloromethane (3 x 20 ml) and the combined organic extracts were washed with water (until neutral *p*H), dried over sodium sulfate, and concentrated. The ^{1}H nmr spectrum of the crude reaction mixtures were indicative of >95% thiopyranone **1bS**, selenopyranone **1bSe**, or telluropyranone **1bTe**. The chalcogenopyranones were purified by recrystallization from ethanol to give 0.070 g (84%) of **1bS**, 0.121 g (89%) of **1bSe**, and 0.136 g (85%) of **1bTe**.

Preparation of Enol Ethers **9c**.

Diynone **2c** (0.316 g, 1.00 mmole) was dissolved in 20 ml of tetrahydrofuran and 20 ml of 0.25 *M* sodium ethoxide in ethanol. The resulting solution was allowed to stand at 50° and the disappearance of **2c** was monitored by thin-layer chromatography on silica gel eluted with dichloromethane. After 0.5 hour at 50°, loss of **2c** was complete and the reaction mixture was poured into 100 ml of water. The products were extracted with dichloromethane (3 x 15 ml) and the combined organic extracts were washed with brine, dried over magnesium sulfate, and concentrated. The ^{1}H nmr spectrum of the crude reaction mixture was indicative of a 81:19 mixture of two enol ethers **9c**. The reaction was repeated and the reaction mixture was allowed to stand 3 hours at 50°. Workup as before gave an 81:19 mixture of the same two enol ethers **9c**.

The major enol ether **9c** had ^{1}H nmr (deuteriochloroform): δ 7.53 (AA'BB', 2H, J ("doublet") = 9 Hz), 6.97 (AA'BB', 2H, J ("doublet") = 9 Hz), 6.68 (AA'BB', 2H, J ("doublet") = 9 Hz), 6.45 (AA'BB', 2H, J ("doublet") = 9 Hz), 5.69 (s, 1H), 4.05 (q, 2H, J = 7 Hz); 2.97 (s, 6H), 2.96 (s, 6H), 1.43 (t, 3H, J = 7 Hz).

The minor enol ether **9c** had ^{1}H nmr (deuteriochloroform): δ 7.53 (AA'BB', 4H, J ("doublet") = 9 Hz), 6.66 (AA'BB', 2H, J ("doublet") = 9 Hz), 6.64 (AA'BB', 2H, J ("doublet") = 9 Hz), 6.02 (s, 1H), 4.22 (q, 2H, J = 7 Hz); 3.02 (s, 6H), 3.00 (s, 6H), 1.22 (t, 3H, J = 7 Hz).

The mixture **9c** had ir (potassium bromide): 2170, 1603 cm^{-1}; ms: (EI), m/z 362.2019 (M$^+$, Calcd. for $C_{23}H_{26}N_2O_2$: 362.1994).

Diketone **11c** had ^{1}H nmr (deuteriochloroform, enol form): δ 7.84 (AA'BB', 2H, J ("doublet") = 9 Hz), 7.48 (AA'BB', 2H, J ("doublet") = 9 Hz), 6.67 (AA'BB', 2H, J ("doublet") = 9 Hz), 6.63 (AA'BB', 2H, J ("doublet") = 9 Hz), 6.38 (s, 1H), 3.07 (s, 6H), 3.02 (s, 6H); (keto form): δ 7.54 (AA'BB', 4H, J ("doublet") = 9 Hz), 6.97 (AA'BB', 2H, J ("doublet") = 9 Hz), 6.47 (AA'BB', 2H, J ("doublet") = 9 Hz), 5.70 (s, 2H), 2.967 (s, 6H), 2.963 (s, 6H); ir (potassium bromide): 2171, 1607 cm^{-1}; ms: (EI), m/z 334.1736 (M$^+$, Calcd. for $C_{21}H_{22}N_2O_2$: 334.1711).

Addition of Sodium Thiophenoxide to Enol Ethers **9b**.

Thiophenol (0.11 g, 1.0 mmole) was dissolved in 7 ml of 0.07 *M* sodium ethoxide in ethanol. The resulting solution was added to the enol ether mixture **9b** generated *in situ* from 0.19 g (1.0 mmole) of **2b** in 7 ml of 0.07 *M* sodium ethoxide in ethanol for 3 hours. The reaction mixture was allowed to stand 15 hours at ambient temperature and was then poured into 50 ml of water. The products were extracted with dichloromethane (4 x 20 ml) and the combined organic extracts were washed with water (until neutral *p*H), dried over sodium sulfate, and concentrated. The ^{1}H nmr spectral analysis of the crude reaction mixture showed a mixture of four enol ethers **13** in a 74:15:8:3 ratio. Although the aromatic protons (5 protons between δ 7.00-7.70) and the methyl groups (δ 0.99-1.01) were not clearly resolved, the two olefinic protons, the protons of the two *tert*-butyl groups, and the methylene protons of the ethyl group were resolved for each isomer.

The major isomer had ^{1}H nmr (deuteriochloroform): δ 6.47 (s, 1H), 5.93 (s, 1H), 3.23 (q, 2H, J = 7 Hz), 1.28 (s, 9H), 1.04 (s, 9H), 0.99 (t, 3H, J = 7 Hz).

The "15%" isomer had ^{1}H nmr (deuteriochloroform): δ 5.56 (s, 1H), 5.21 (s, 1H), 3.98 (q, 2H, J = 7 Hz), 1.41 (s, 9H), 1.01 (s, 9H).

The "8%" isomer had ^{1}H nmr (deuteriochloroform): δ 6.51 (s, 1H), 5.64 (s, 1H), 3.64 (q, 2H, J = 7 Hz), 1.25 (s, 9H), 1.03 (s, 9H).

The minor isomer had ^{1}H nmr (deuteriochloroform): δ 5.59 (s, 1H), 5.08 (s, 1H), 4.07 (q, 2H, J = 7 Hz), 1.37 (s, 9H), 1.23 (s, 9H).

The mixture of enol ethers **13** had ir (film, sodium chloride): 1641 cm^{-1}; ms: (positive FAB), m/z 347 (MH$^+$, base peak).

General Procedure for Addition of Enol Ethers **9a** (Generated *In Situ*) to Disodium Chalcogenides.

Diynone **2a** (0.46 g, 2.0 mmoles) was dissolved in 20 ml of 0.07 *M* sodium ethoxide in ethanol. After 450 seconds, the reaction mixture was added to disodium chalcogenides, prepared from the addition of sodium borohydride (0.080 g, 2.2 mmoles) to 2.2 mg-atoms of sulfur (0.070 g), selenium (0.174 g), or tellurium (0.28 g). After 15 minutes, the reaction mixture was poured into 200 ml of water. The products were extracted with dichloromethane (3 x 30 ml) and the combined organic extracts were washed with brine, dried over magnesium sulfate, and concentrated. The ^{1}H nmr spectrum of the crude reaction mixture was indicative of >95% chalcogenopyranones **1a**, which were purified by recrystallization from acetonitrile.

4*H*-2,6-Diphenylthiopyran-4-one (**1aS**) [11].

The yield was 0.443 g (84%), mp 125-128°; ^{1}H nmr (deuteriochloroform): δ 7.64 (m, 4H), 7.50 (m, 6H), 7.23 (s, 2H).

4*H*-2,6-Diphenylselenopyran-4-one (**1aSe**) [11].

The yield was 0.554 g (89%), mp 147-148°; ^{1}H nmr (deuteriochloroform): δ 7.50 (m, 10H), 7.27 (s, 2H).

4H-2,6-Diphenyltelluropyran-4-one (**1aTe**) [11].

The yield was 0.443 g (84%), mp 127-129°; ^{1}H nmr (deuteriochloroform): δ 7.47 (m, 10H), 7.35 (s, 2H).

General Procedure for Addition of Enol Ethers **9b** (Generated *In Situ*) to Disodium Chalcogenides.

Diynone **2b** (0.38 g, 2.0 mmoles) was dissolved in 20 ml of 0.07 *M* sodium ethoxide in ethanol. After 3 hours, the reaction mixture was added to disodiumchalcogenides, prepared from the addition of sodium borohydride (0.080 g, 2.2 mmoles) to 2.2 mg-atoms of sulfur (0.070 g), selenium (0.174 g), or tellurium (0.28 g). After 15 minutes, the reaction mixture was poured into 200 ml of water. The products were extracted with dichloromethane (3 x 30 ml) and the combined organic extracts were washed with brine, dried over magnesium sulfate, and concentrated. The ^{1}H nmr spectrum of the crude reaction mixture was indicative of >95% chalcogenopyranones **1b**. The thiopyranone was purified by recrystallization from ethanol to give 0.376 g (84%) of thiopyranone **1bS**, 0.48 g (89%) of selenopyranone **1bSe**, and 0.544 g (85%) of telluropyranone **1bTe**.

General Procedure for the Addition of Enol Ethers **9c** (Generated *In Situ*) to Disodium Chalcogenides.

Enol ethers **9c** were prepared as described above from diynone **2c** (1.00 g, 3.16 mmoles) and the 0.25 *M* sodium ethoxide in ethanol/tetrahydrofuran solution was added to disodium chalcogenides, prepared from 3.79 mg-atoms of sulfur (0.121 g), selenium (0.300 g), or tellurium (0.484 g) and 0.122 g (3.79 mmoles) of sodium borohydride in 40 ml of degassed 0.25 *M* sodium ethoxide in ethanol under an argon atmosphere. The reaction mixture was stirred for 15 minutes at ambient temperature and was then poured into 200 ml of water. The products were extracted with dichloromethane (4 x 50 ml) and the combined organic extracts were washed with brine, dried over magnesium sulfate, and concentrated. The residue was purified by chromatography on silica gel eluted with 20% ethyl acetate-dichloromethane to give chalcogenopyranones **1c**. The products were recrystallized from acetonitrile to give 0.818 g (74%) of **1cS**, 1.12 g (89%) of **1cSe**, and 1.07 g (76%) of **1cTe**.

General Procedure for Addition of Enol Ethers **9d** (Generated *In Situ*) to Disodium Chalcogenides.

Diynone **2d** (0.38 g, 2.0 mmoles) was dissolved in 20 ml of 0.25 *M* sodium ethoxide in ethanol. After 0.5 hour, the reaction mixture was added to disodium chalcogenides, prepared from the addition of sodium borohydride (0.080 g, 2.2 mmoles) to 2.2 mg-atoms of sulfur (0.070 g), selenium (0.174 g), or tellurium (0.28 g) in 20 ml of 0.25 *M* sodium ethoxide in ethanol. After 0.5 hour, the reaction mixture was poured into 200 ml of water. The products were extracted with dichloromethane (3 x 30 ml) and the combined organic extracts were washed with brine, dried over magnesium sulfate, and concentrated. The ^{1}H nmr spectrum of the crude reaction mixture was indicative of >95% chalcogenopyranones **1d**. The thiopyranone was purified by recrystallization from ethanol to give 0.408 g (74%) of thiopyranone **1dS**, 0.562 g (87%) of selenopyranone **1dSe**, and 0.558 g (75%) of selenopyranone **1dTe**.

4*H*-2,6-Di-(2-thienyl)thiopyran-4-one (**1dS**).

This compound had mp 148-149°; ^{1}H nmr (deuteriochloroform): δ 7.53 (m, 4H), 7.17 (m, 2H), 7.17 (s, 2H); ^{13}C nmr (dichloromethane-d$_2$): δ 182.7, 145.6, 138.9, 129.7, 129.3, 127.9, 125.7; ir (potassium bromide): 1598 cm^{-1}; uv (dichloromethane): λ_{max} 331 nm (log ε 4.31); ms: (ES), m/z 276 (M$^+$, base peak).

Anal. Calcd. for $C_{13}H_8OS_3$: C, 56.49; H, 2.92. Found: C, 56.51; H, 2.86.

4*H*-2,6-Di-(2-thienyl)selenopyran-4-one (**1dSe**).

This compound had mp 153-154°; ^{1}H nmr (dichloromethane-d$_2$): δ 7.51 (d, 2H), 7.45 (d, 2H), 7.27 (s, 2H), 7.17 (t, 2H); ^{13}C nmr (dichloromethane-d$_2$): δ 184.0, 145.6, 139.9, 129.1, 128.6, 127.2, 126.0; ir (potassium bromide): 1598 cm^{-1}; uv (dichloromethane): λ_{max} 341 nm (log ε 4.38); ms: (ES), m/z 324 (M$^+$, base peak, ^{80}Se isotope).

Anal. Calcd. for $C_{13}H_8OS_2Se$: C, 48.30; H, 2.49. Found: C, 48.13; H, 2.55.

4*H*-2,6-Di-(2-thienyl)telluropyran-4-one (**1dTe**).

This compound had mp 165-167°; ^{1}H nmr (dichloromethane-d$_2$): δ 7.51 (d, 2H), 7.35 (d, 2H), 7.23 (s, 2H), 7.13 (t, 2H); ^{13}C nmr (dichloromethane-d$_2$): δ 188.9, 145.5, 137.7, 132.4, 130.4, 130.2, 129.2; ir (potassium bromide): 1604, 1595 cm^{-1}; uv (dichloromethane): λ_{max} 359 nm (log ε 4.21); ms: (AP), m/z 375 (MH$^+$, base peak, ^{130}Te isotope).

Anal. Calcd. for $C_{13}H_8OS_2Te$: C, 41.98; H, 2.17. Found: C, 42.92; H, 2.22.

General Procedure for the Addition of Enol Ethers **9e** (Generated *In Situ*) to Disodium Chalcogenides.

Diynone **2e** (0.273 g, 1.00 mmole) was dissolved in 20 ml of tetrahydrofuran and 20 ml of 0.25 *M* sodium ethoxide in ethanol.

The resulting solution was allowed to stand at 50° and the disappearance of **2e** was monitored by thin-layer chromatography on silica gel eluted with dichloromethane. After 0.5 hour, the resulting solution was added to disodium chalcogenides, prepared from 1.1 mg-atoms of sulfur (0.035 g), selenium (0.087 g), or tellurium (0.141 g) and 0.042 g (1.1 mmoles) of sodium borohydride in 10 ml of degassed 0.25 *M* sodium ethoxide in ethanol under an argon atmosphere. The reaction mixture was stirred for 15 minutes at ambient temperature and was then poured into 100 ml of water. The products were extracted with dichloromethane (3 x 15 ml) and the combined organic extracts were washed with brine, dried over magnesium sulfate, and concentrated. The residue was purified by chromatography on silica gel eluted with 20% ethyl acetate-dichloromethane to give chalcogenopyranones **1c**. The products were recrystallized from acetonitrile to give 0.224 g (73%) of **1eS**, 0.241 g (68%) of **1eSe**, and 0.245 g (67%) of **1eTe**.

4*H*-2-Phenyl-6-(4-*N*,*N*-dimethylaminophenyl)thiopyran-4-one (**1eS**).

This compound had mp 154-155°; ^{1}H nmr (deuteriochloroform): δ 7.50-7.66 (m, 7H), 7.18 (s, 2H), 6.74 (AA'BB', 2H, J ("doublet") = 8 Hz), 3.04 (s, 6H; ^{13}C nmr (deuteriochloroform): δ 182.6, 153.7, 152.5, 151.9, 136.3, 130.4, 129.2, 127.6, 126.8, 126.7, 123.5, 122.6, 111.9, 40.0; ir (potassium bromide): 3448, 3006, 1615 cm^{-1}; ms: (positive FAB), m/z 308 (MH^{+}, base peak).

Anal. Calcd. for $C_{19}H_{17}NOS$: C, 74.23; H, 5.57; N, 4.56. Found: C, 74.13; H, 5.56; N, 4.55.

4*H*-2-Phenyl-6-(4-*N*,*N*-dimethylaminophenyl)selenopyran-4-one (**1eSe**).

This compound had mp 155-156°; ^{1}H nmr (deuteriochloroform): δ 7.48-7.59 (m, 7H), 7.23 (s, 2H), 6.72 (AA'BB', 2H, J ("doublet") = 8 Hz), 3.03 (s, 6H; ^{13}C nmr (deuteriochloroform): δ 184.8, 156.2, 154.7, 152.0, 138.0, 130.4, 129.3, 128.0, 127.8, 126.8, 124.6, 124.5, 112.1, 40.1; ir (potassium bromide): 3421, 2895, 1596 cm^{-1}; ms: (positive FAB), m/z 356 (MH^{+}, base peak, ^{80}Se isotope).

Anal. Calcd. for $C_{19}H_{17}NOSe$: C, 64.41; H, 4.84; N, 3.95. Found: C, 64.53; H, 4.87; N, 3.96.

4*H*-2-Phenyl-6-(4-*N*,*N*-dimethylaminophenyl)telluropyran-4-one (**1eTe**).

This compound had mp 130-131°; ^{1}H nmr (deuteriochloroform): δ 7.43-7.51 (m, 7H), 7.41 (s, 2H), 6.71 (AA'BB', 2H, J ("doublet") = 8 Hz), 3.02 (s, 6H; ^{13}C nmr (deuteriochloroform): δ 188.3, 151.9, 150.1, 148.0, 141.1, 132.7, 130.0, 129.4, 128.7, 127.7, 126.8, 112.1, 40.1; ir (potassium bromide): 3448, 2895, 1586 cm^{-1}; ms: (positive FAB), m/z 406 (MH^{+}, base peak, ^{130}Te isotope).

Anal. Calcd. for $C_{19}H_{17}NOTe$: C, 56.63; H, 4.25; N, 3.48. Found: C, 56.73; H, 4.16; N, 3.55.

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