Organometallics 1992, *11*, 2157–2162

Addition of Disodium Chalcogenides to 1,5-Bis(trimethylsilyl)penta-1,4-diyn-3-one. Syntheses, Structure, and Reactivity of the Parent Δ-4*H*-Chalcogenapyran-4-ones

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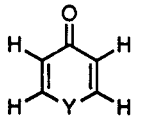
Received November 18, 1991

The addition of sodium hydrosulfide hydrate or disodium chalcogenides to 1,5-bis(trimethylsilyl)-1,4-pentadiyn-3-one (4) gives Δ-4*H*-thiapyran-4-one (1), Δ-4*H*-selenapyran-4-one (2), and Δ-4*H*-tellurapyran-4-one (3) in 72, 35, and 38% isolated yields, respectively. The addition of sodium hydrosulfide hydrate to 1-(trimethylsilyl)-5-phenyl-1,4-pentadiyn-3-one (16) gives 1-phenyl-4*H*-thiapyran-4-one (17) in 44% isolated yield, while the addition of disodium telluride to 16 gives 1-phenyl-4*H*-tellurapyran-4-one (18) in 32% isolated yield. The structures of 1–3 were determined unambiguously by single-crystal X-ray crystallographic analysis. All three molecules were planer although both 2 and 3 have distorted hexagonal rings. The addition of [*p*-(*N*,*N*-dimethylamino)phenyl]magnesium bromide to 2 or 3 gives 1,2-addition exclusively, leading to selenapyrylium and tellurapyrylium dyes 19 and 20, respectively.

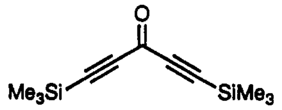
The Δ-4*H*-chalcogenapyran-4-ones are useful building blocks for the construction of chalcogenapyrans, chalcogenapyrylium salts, and chalcogenapyranyl compounds.[1-3] Typically, the 4-position of the chalcogenapyranones are susceptible to nucleophilic attack at carbon or to electrophilic attack at the carbonyl oxygen (Scheme I).

While the thiapyranones have been prepared via a number of synthetic routes,[1] routes to selenapyranones and tellurapyranones have been more limited. Selenapyranones have been prepared by additions of either hydrogen selenide[4a] or disodium selenide[4a] to symmetrical 1,4-pentadiyn-3-ones. Tellurapyranones have been prepared by the addition of disodium telluride to symmetrical[4b] or unsymmetrical[5] 1,4-pentadiyn-3-ones.

The parent Δ-4*H*-chalcogenapyran-4-ones 1–3 have not been prepared by the routes described above. These molecules are of interest as precursors to the rodlike, 2,3,5,6-unsubstituted chalcogenapyrylium dyes and 2,3,5,6-unsubstituted (chalcogenapyranyl)chalcogenapyrans. Furthermore, the parent chalcogenapyranones 1–3 are the simplest structures for comparing theory and experiment in this class of molecules.



1, X = S
2, X = Se
3, X = Te



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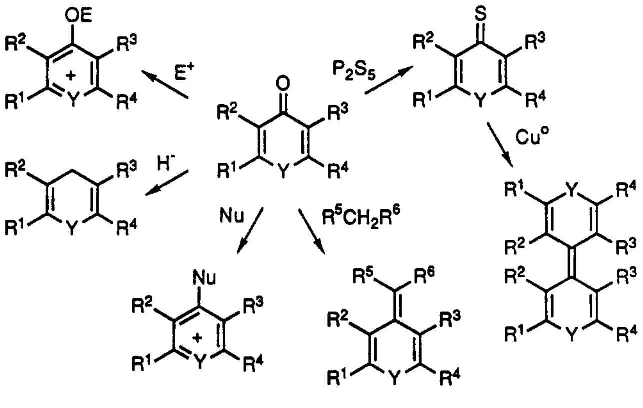
Scheme I



Y = S, Se, Te

We report a facile synthesis of the parent chalcogenapyranones 1–3 from the pentadiynone 4 and the corresponding disodium chalcogenide. The method also works with unsymmetrical diynones with one terminal trimethylsilyl group. X-ray diffraction studies of 1–3 show the molecules to be nearly planar in the solid state.

Results and Discussion

Synthesis of the Parent Chalcogenapyranones. Attempts to prepare the parent chalcogenapyranones 1–3 via the addition of the chalcogenide anions to 1,4-pentadiyn-3-one (5) were unsuccessful. Only trace amounts of

$$(\mathrm{H{-}C{\equiv}C})_2\mathrm{CO}$$

5

the pyranones (<5%) were detected with higher molecular weight oligomeric products predominating. The chalcogenide anions were prepared by either sodium borohydride or lithium triethyl borohydride reduction of the elemental chalcogens. Reaction solvents that were utilized in at-

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(1) Mayer, R.; Broy, W.; Zahradnik, R. *Adv. Heterocycl. Chem.* 1967, *8*, 219–276. Tolmachev, A. I.; Kudinova, M. A. *Khim. Geterotsikl. Soedin.* 1974, 49–52 and references therein. Detty, M. R.; Murray, B. J.; Seidler, M. D. *J. Org. Chem.* 1982, *47*, 1968–1969.

(2) Reynolds, G. A.; Van Allan, J. A. U.S. Patent 3417083, 1972. Williams, J. L. R.; Reynolds, G. A. *J. Appl. Phys.* 1968, *39*, 5327–5332. Wizinger, R.; Angliker, H. J. *Helv. Chim. Acta* 1966, *49*, 2046–2052. Tolmachev, A. I.; Kudinova, M. A. *Khim. Geterotsikl. Soedin.* 1974, 49. Detty, M. R.; Murray, B. J. *J. Org. Chem.* 1982, *47*, 5235–5239. Detty, M. R.; McKelvey, J. M.; Luss, H. R. *Organometallics* 1988, *7*, 1131–1143.

(3) Alizon, J.; Gallice, J.; Robert, H.; Delplanque, G.; Weyl, C.; Fabre, C.; Stizelecka, H. *Mol. Cryst. Liq. Cryst.* 1976, *32*, 157. Chen, C. H.; Reynolds, G. A. *J. Org. Chem.* 1980, *45*, 2449–2453. Reynolds, G. A.; Chen, C. H. *J. Org. Chem.* 1979, *44*, 4456–4458. Hunig, S.; Garner, B. J.; Ruider, G.; Schenk, W. *Justus Liebigs Ann. Chem.* 1973, 1036–1042. Detty, M. R.; Murray, B. J. *J. Org. Chem.* 1982, *47*, 1146–1148.

(4) (a) Es-Seddiki, S.; Le Coustumer, G.; Mollier, Y. *Tetrahedron Lett.* 1981, 2771–2772. (b) Detty, M. R.; Hassett, J. W.; Murray, B. J.; Reynolds, G. A. *Tetrahedron* 1985, *45*, 4853–4859.

(5) Detty, M. R.; Geer, S. M.; Wadsworth, D. H. *J. Org. Chem.* 1987, *52*, 3662.

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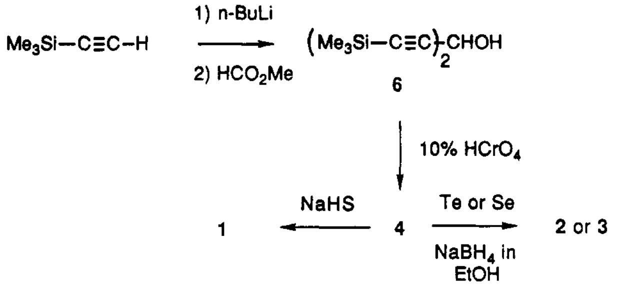
Scheme II



tempts to optimize this reaction included tetrahydrofuran (THF) (with either 4 equiv of ethanol or *tert*-butyl alcohol as a proton source), ethanol, or 0.1 M sodium ethoxide in ethanol.

(Trimethylsilyl)acetylenes have been employed as masked terminal acetylenes in chalcogenide-addition reactions.[6] The diynone 4 was prepared in hope that the trimethylsilyl groups would shield the terminal acetylene carbons from rapid nucleophilic attack from the chalcogenide anions and that stepwise desilylation of 4 with a chalcogenide anion would lead to the chalcogenapyranones 1–3 via intramolecular Michael addition rather than to oligomeric products via intermolecular Michael addition.

The synthesis of 1,5-bis(trimethylsilyl)-1,4-pentadiyn-3-one (4)[7] was achieved in two steps as shown in Scheme II. The addition of *n*-butyllithium to (trimethylsilyl)acetylene at 0 °C in THF generated the (trimethylsilyl)acetylide. The addition of methyl formate to this mixture gave the diynol 6 in 95% isolated yield. The oxidation of the diynol 6 with a 10% chromic acid solution in acetone at 0 °C gave diynone 4 in 87% isolated yield as a low-melting, crystalline solid.

Addition of chalcogenide anions to 4 gave the chalcogenapyranones in much better yield. The thiapyranone 1 was prepared in 72% isolated yield by the addition of a solution of 2.0 equiv of sodium hydrosulfide hydrate (Aldrich)[8] and excess sodium bicarbonate to a solution of 4 in ethanol. When 1.0 equiv of sodium hydrosulfide hydrate was used, thiapyranone 1 was isolated in 40% yield and unreacted 4 was recovered in 30% yield.

Alternatively, the reduction of elemental sulfur with sodium borohydride in 0.1 M sodium ethoxide in ethanol[4b] gave a solution of disodium sulfide. The addition of diynone 4 to this solution gave thiapyranone 1 in 44% isolated yield.

Selenapyranone 2 was prepared in 35% isolated yield via the addition of 2.0 equiv of disodium selenide in 0.1 M sodium ethoxide in ethanol to diynone 4. The disodium selenide was generated via the sodium borohydride reduction of selenium metal in 0.1 M sodium ethoxide in ethanol.[4b] When 1.0 equiv of disodium selenide was used, selenapyranone 2 was isolated in 15% yield and diynone 4 was recovered in 20% yield.

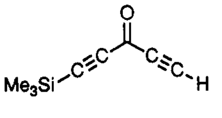
Tellurapyranone 3 was isolated in 38% yield via the addition of 2.0 equiv of disodium telluride in 0.1 M sodium ethoxide in ethanol to diynone 4. The disodium telluride was prepared by the sodium borohydride reduction of tellurium powder in 0.1 M sodium ethoxide in ethanol.[4b] When 1.0 equiv of disodium telluride was used, tellurapyranone 3 was isolated in 21% yield and diynone 4 was recovered in 20% yield.

Table I. Proton and Carbon Chemical Shifts in Chalcogenapyranones 1–3[a]

		δ, ppm				
compd	Y	H_A	H_B	C_1, C_5	C_2, C_4	C_3
1	S	7.47	7.02	137.7	131.7	179.6
2	Se	8.205	7.17	138.8	132.6	181.0
3	Te	8.71	7.31	136.8	129.3	184.7

[a] In $CDCl_3$.

The recovery of unreacted 4 from the reaction mixtures with the chalcogenide anion as limiting reagent suggests that initial desilylation of 4, perhaps to unsymmetrical diynone 7, is the rate-limiting step in these reactions.



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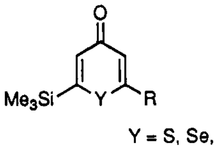

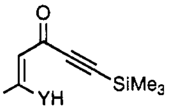

Y = S, Se, Te

8, R = Me3Si
9, R = H

10

Silylated pyranones 8 and 9 were not detected in the product mixtures from the reactions with either chalcogenide anion or diynone 4 as limiting reagent. This suggests that desilylation occurs prior to ring formation.

In a species such as 7, nucleophilic attack would be expected to be more rapid at the terminal acetylenic carbon than at the trimethylsilyl-substituted carbon for steric reasons. The addition of a chalcogenide anion to 7 would lead to enyne 10 or a related structure (perhaps a silylated chalcogen atom). Desilylation and cyclization of 10 could proceed via several routes to give chalcogenapyranones 1–3. The cyclization of enynes similar in structure to 10 to chalcogenapyranones has been described.[9]

Spectroscopic Properties. Compounds 1–3 all display AA'BB' patterns in ^1H NMR spectra and three-line spectra in the proton-decoupled ^{13}C NMR spectra. The assignment of chemical shifts for the protons and carbons in these molecules is given in Table I. The assignment of chemical shifts to H_A and H_B was made possible by the observation of ^{77}Se satellite coupling (J_{Se-H_A} = 51 Hz) in the ^1H NMR spectrum of 2 and ^{125}Te satellite coupling (J_{Te-H_A} = 107 Hz) in the ^1H NMR spectrum of 3.

The carbon chemical shifts are similar in all three compounds, although proton chemical shifts are sensitive to the heteroatom. The chemical shift of H_A is found at significantly lower field as the size of the chalcogen atom increases. Interestingly, while the chemical shift of H_A increases by 1.24 ppm from sulfur to tellurium, the chemical shift of H_B changes relatively little from sulfur to tellurium ($\Delta\delta$ = 0.29 ppm).

The carbonyl stretching frequencies in the infrared spectra of 1–3 are quite low. For thiapyranone 1, the carbonyl stretching frequency is found at 1610 cm^{-1}. In selenapyranone 2, the carbonyl stretching frequency is at 1585 cm^{-1}, while in tellurapyranone 3 the carbonyl stretching frequency is lower still (1560 cm^{-1}).

The UV absorption maximum of compounds 1–3 is found at longer wavelengths as the size of the chalcogen atom increases. Thus, λ_{max} increases from 297 nm (ϵ 11000) for 1 to 310 nm (ϵ 16500) for 2 to 344 nm (ϵ 20000) for 3 in dichloromethane.

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[6] De Jong, R. L. P.; Brandsma, L. *J. Chem. Soc., Chem. Commun.* **1983**, 1056–1057. Brandsma, L.; Verkruijsse, H. D. *Syn. Commun.* **1990**, *20*, 2275–2277.

[7] Hauptmann, H. *Tetrahedron* **1976**, *32*, 1293.

[8] We have found that the hydrate typically analyzes as a dihydrate. All manipulations and reactions of this reagent assume the following empirical structure: $NaHS \cdot 2H_2O$.

[9] Detty, M. R.; McGarry, L. W. *J. Org. Chem.* **1988**, *53*, 1203–1207.

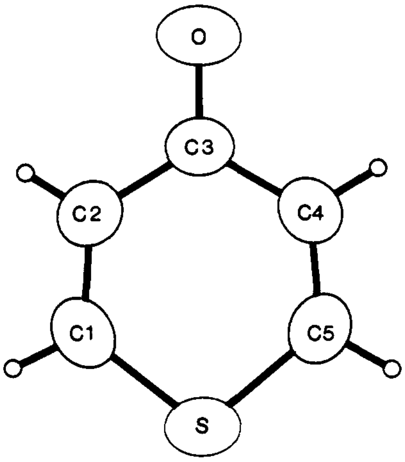

Figure 1. Plot of 1 with thermal ellipsoids at the 50% probability level.

Table II. Crystal Data for 1

formula	SOC_5H_4
M_r	112.15
space group	*Pbca*
cell const	
a, Å	9.557 (1)
b, Å	15.713 (2)
c, Å	19.670 (2)
α, deg	90.0
β	90.0
γ	90.0
V, Å^3	1141.2 (5)
no. of molecules/unit cell (*Z*)	8
D(calc), g cm^{-3}	1.431
abs coeff (*μ*, Mo K*α*), cm^{-1}	4.60
temp, °C	22 (1)
scan technique	ω–2θ
scan rate, deg 2θ min^{-1}	2.4–20
2θ limit, deg	46
no. of unique reflctns measd	730
no. of reflctns used in refinement	508 ($I > \sigma(I)$)
no. of variable parameters	80
cryst dimens, mm	0.05 × 0.23 × 0.23

Table III. Crystal Data for 2

formula	$SeOC_5H_4$
M_r	159.05
space group	*Pbcn*
cell const	
a, Å	5.772 (2)
b, Å	12.024 (2)
c, Å	7.582 (2)
α, deg	90.0
β	90.0
γ	90.0
V, Å^3	526.2 (4)
no. of molecules/unit cell (*Z*)	4
D(calc), g cm^{-3}	2.007
abs coeff (*μ*, Mo K*α*), cm^{-1}	69.25
temp, °C	22 (1)
scan technique	ω–2θ
scan rate, deg 2θ min^{-1}	2.9–20
2θ limit, deg	50
no. of unique reflctns measd	466
no. of reflectns used in refinement	366 ($I > \sigma(I)$)
no. of variable parameters	42
cryst dimens, mm	0.15 × 0.23 × 0.23

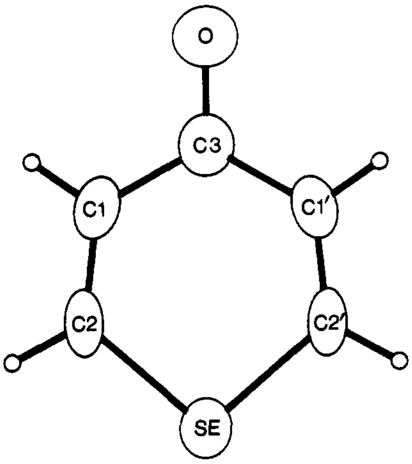

Figure 2. Plot of 2 with thermal ellipsoids at the 50% probability level.

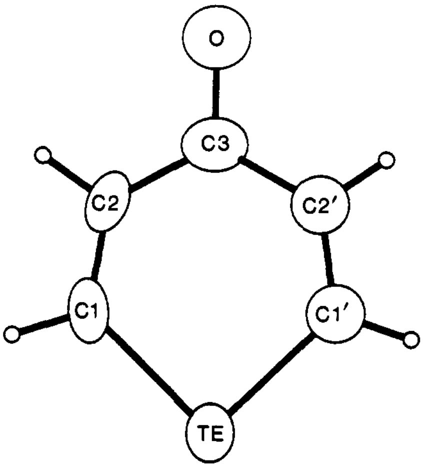

Figure 3. Plot of 3 with thermal ellipsoids at the 50% probability level.

Table IV. Crystal Data for 3

formula	$TeOC_5H_4$
M_r	207.69
space group	*Pbcn*
cell const	
a, Å	5.691 (3)
b, Å	12.419 (6)
c, Å	7.961 (4)
α, deg	90.0
β	90.0
γ	90.0
V, Å^3	562.7 (9)
no. of molecules/unit cell (*Z*)	4
D(calc), g cm^{-3}	2.452
abs coeff (*μ*, Mo K*α*), cm^{-1}	51.70
temp, °C	22 (1)
scan technique	ω–2θ
scan rate, deg 2θ min^{-1}	2.7–20
2θ limit, deg	46
no. of unique reflctns measd	397
no. of reflctns used in refinement	328 ($I > \sigma(I)$)
no. of variable parameters	34
cryst dimens, mm	0.01 × 0.23 × 0.24

The spectroscopic trends observed for **1–3** are similar to those observed for the chalcogenachromones **11–13**[10] and **14**.[11] The changes observed in chemical shifts for H_A and H_B in the ^1H NMR spectra of **11–13** are smaller than those observed for **1–3**. The benzo-fused ring perhaps attenuates the chalcogen atom effect.

X-ray Crystal Structures of 1–3. The structures of **1–3** were determined unambiguously by X-ray crystallographic analyses. Figure 1 shows an ORTEP plot of thiapyranone **1** with atomic labeling; Figure 2 selenapyranone **2**; and Figure 3, tellurapyranone **3**. The thermal ellipsoids

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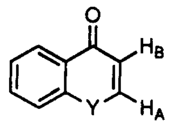
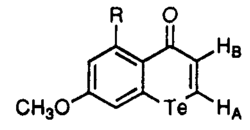
(10) Dereu, N.; Renson, M. *J. Organomet. Chem.* **1981**, *208*, 11–17.
(11) Detty, M. R.; Murray, B. J. *J. Am. Chem. Soc.* **1983**, *105*, 883–890.



11, Y = S
12, Y = Se
13, Y = Te



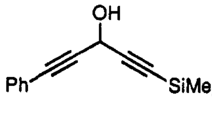
14a, R = H
14b, R = OCH3

were plotted at the 50% probability level, excluding hydrogens. Crystal data for 1–3 are included in Tables II–IV, respectively, and positional and thermal parameters for 1–3 are included in Tables V–VII, respectively. Tables of bond distances and angles and least-squares planes are given in the supplementary material. The selenium and tellurium atoms occupy crystallographic 2-fold axes, and selenapyranone 2 and tellurapyranone 3 are isostructural.

All three molecules are planar with the largest deviation from a least-squares plane occurring in the sulfur analogue 1 (0.014 Å). This is somewhat surprising in the sense that the Te–C bonds (2.05 Å) are much longer than the S–C bonds (1.70 Å), resulting in a greatly distorted hexagonal structure for 3 relative to 1. A boat conformation in 3 would permit the angles about the sp^2-hybridized carbons to be closer to 120°.

The intermolecular contacts between Se⋯Se (3.94 Å) and Te⋯Te (4.11 Å) are about the sum of van der Waals radii (3.80 and 4.12 Å, respectively).[12] However, there is a short intermolecular Te⋯O contact (3.22 Å) which is less than the sum of van der Waals radii (3.58 Å). The corresponding Se⋯O distance is 3.25 Å, which is closer to the sum of van der Waals radii (3.42 Å).

Preparation of 2-Substituted Chalcogenapyranones. The addition of chalcogenide anions to unsymmetrical 1-(trimethylsilyl)-1,4-pentadiyn-3-ones should be a general procedure for the preparation of 2-substituted chalcogenapyranones. The addition of lithium (trimethylsilyl)acetylide to phenylpropargyl aldehyde gave diynol 15 as a yellow oil in 98% isolated yield. oxidation with chromic acid gave diynone 16 in 98% isolated yield. The addition of sodium hydrosulfide hydrate to 16 gave 2-phenyl-4*H*-thiapyran-4-one (17) in 44% isolated yield, and the addition of disodium telluride to 16 gave 2-phenyl-4*H*-tellurapyran-4-one (18) in 32% isolated yield.



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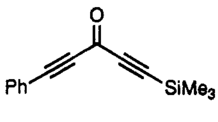

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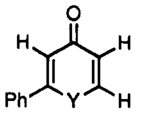


17, Y = S
18, Y = Te

The tellurapyranone 18 has also been prepared by the addition of disodium telluride to 1-phenyl-1,4-pentadiyn-3-one.[5] The yield of 18 was only 12% in this reaction.

Reactions of the Chalcogenapyranones. The addition of organometallic reagents to the parent chalcogenapyranones could proceed via either 1,2- or 1,4-addition. The decreased steric inhibition to 1,4-addition in 1–3 was of concern for subsequent reactions.

The addition of [*p*-(*N*,*N*-dimethylamino)phenyl]magnesium bromide to 2 and 3 gave dyes 19 and 20 in 68 and 71% isolated yields, respectively, following recrystallization. Products of 1,4-addition were not detected in the crude crystalline materials. The dyes had absorption maxima at 591 nm for 19 (ε 89 000) and at 628 nm for 20 (ε 80 000) in dichloromethane.

Table V. Positional Parameters and Their Estimated Standard Deviations for 1[a]

atom	*x*	*y*	*z*	*B*, Å^2
S	0.3523 (1)	0.1473 (1)	0.01021 (8)	5.20 (2)
O	0.4249 (3)	0.0542 (3)	−0.3623 (2)	5.73 (7)
C1	0.4651 (4)	0.2237 (4)	−0.0853 (4)	4.77 (9)
C2	0.4811 (4)	0.1890 (4)	−0.1976 (3)	4.59 (9)
C3	0.4042 (4)	0.0810 (4)	−0.2572 (4)	3.92 (7)
C4	0.3014 (4)	0.0070 (4)	−0.1908 (4)	4.53 (9)
C5	0.2729 (4)	0.0280 (4)	−0.0783 (4)	4.89 (9)
H1	0.515 (4)	0.291 (4)	−0.055 (3)	6.0 (9)*
H2	0.541 (3)	0.232 (4)	−0.240 (4)	6.3 (9)*
H4	0.255 (4)	−0.062 (4)	−0.229 (3)	6.3 (9)*
H5	0.204 (3)	−0.018 (4)	−0.038 (3)	6 (1)*

[a] Atoms with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table VI. Positional Parameters and Their Estimated Standard Deviations for 2[a]

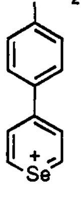
atom	*x*	*y*	*z*	*B*, Å^2
Se	0.000	0.04403 (6)	0.250	4.20 (1)
O	0.000	0.4204 (4)	0.250	4.6 (1)
C1	0.2118 (8)	0.1453 (4)	0.1611 (6)	3.43 (9)
C2	0.1889 (8)	0.2562 (4)	0.1697 (7)	3.28 (9)
C3	0.000	0.3171 (6)	0.250	3.2 (1)
H1	0.34 (1)	0.107 (4)	0.118 (7)	6 (1)*
H2	0.30 (1)	0.301 (4)	0.125 (7)	6 (1)*

[a] Atoms with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

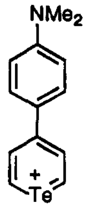
Table VII. Positional Parameters and Their Estimated Standard Deviations for 3[a]

atom	*x*	*y*	*z*	*B*, Å^2
Te	0.000	0.0416 (1)	0.250	4.29 (2)
O	0.000	0.421 (1)	0.250	5.0 (3)
C1	0.221 (2)	0.157 (1)	0.156 (1)	3.5 (3)
C2	0.190 (2)	0.262 (1)	0.169 (2)	3.5 (3)
C3	0.000	0.319 (1)	0.250	3.5 (3)
H1	0.357	0.133	0.098	4.5*
H2	0.307	0.306	0.118	4.5*

[a] Hydrogens with an asterisk were allowed to ride on the parent carbons. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.



19



20

Summary and Conclusions

We have described a simple preparation of both the parent chalcogenapyranones and 2-substituted derivatives via the desilylation of silylated 1,4-diyn-3-ones with chalcogenide anions. This procedure gives much better yields than the direct addition of chalcogenide anions to 1,4-diyn-3-ones bearing one or two terminal acetylenes.

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[12] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

X-ray crystallographic analyses of the chalcogenapyranones **1–3** show the molecules to be nearly planar. Derivatives of these compounds, such as the chalcogenapyrylium dyes **19** and **20**, should be rodlike in shape and show allow closer intermolecular approach than the 2,6-substituted analogues. The properties of molecules derived from the chalcogenapyranones **1–3** are under investigation.

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a General Electric QE-300 spectrophotometer. UV–visible spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Infrared spectra were recorded on a Beckman IR 4250 instrument. Mass spectra were recorded on a Du Pont 21-491 instrument equipped for field desorption. Microanalyses were performed on a Perkin-Elmer 240 C, H, and N analyzer. Tetrahydrofuran (THF) was purchased from Aldrich as anhydrous and was handled via syringe techniques. Butyllithium, (trimethylsilyl)acetylene, phenylacetylene, and sodium hydrosulfide hydrate were used as received from Aldrich.

Preparation of 1,5-Bis(trimethylsilyl)-1,4-pentadiyn-3-ol (6). (Trimethylsilyl)acetylene (29.4 g, 0.300 mol) was dissolved in 100 mL of anhydrous THF under argon and was cooled to 0 °C. *n*-Butyllithium (100 mL of a 2.5 M solution in hexanes, 0.25 mol) was added dropwise via a pressure-equalizing addition funnel. The resulting solution was stirred 1 h at 0 °C. Methyl formate (9.0 g, 0.15 mol) in 20 mL of anhydrous THF was added dropwise. The resulting mixture was stirred an additional hour at 0 °C. The reaction mixture was poured into 500 mL of 10% ammonium chloride solution. The products were extracted with ether (3 × 250 mL). The combined ether extracts were washed with brine, dried over sodium sulfate, and concentrated in vacuo. The residue was purified via chromatography on 300 g of silica gel eluted with ether to give 26.5 g (95%) of the diynol as a pale yellow oil that was used without further purification. ^{1}H NMR (CDCl$_3$) δ 5.075 (br s, 1 H), 3.65 (br s, 1 H), 0.16 (s, 18 H); IR (film, NaCl) 3350, 2945, 2886, 2163, 1403, 1244, 1050, 1020, 915, 830, 753, 693, 642 cm^{-1}; EIMS, *m/z* 223 (M − H), 207 (M − OH), 97 (Me$_3$SiC$_2$), 73 (Me$_3$Si).

Chromic Acid Oxidation of 6. Preparation of 1,5-Bis(trimethylsilyl)-1,4-pentadiyn-3-one (4). A 10% chromic acid solution was prepared by the addition of sodium dichromate nonahydrate (20.0 g, 0.0670 mol) to a stirred slurry of 30 g of sulfuric acid and 220 g of ice. The resulting solution was stirred 1 h at ambient temperature. The diynol **6** (26.5 g, 0.118 mol) was dissolved in 200 mL of acetone and was cooled to 0 °C. The chromic acid solution was added dropwise with stirring. After addition was complete, the reaction mixture was stirred 2 h at ambient temperature. The reaction mixture was poured into 500 mL of water. The products were extracted with ether (3 × 200 mL). The combined ether extracts were washed with brine, dried over sodium sulfate, and concentrated. The residue was recrystallized from hexanes to give 23.0 g (87%) of **4** as a white crystalline solid, mp 48.5–51 °C: ^{1}H NMR (CDCl$_3$) δ 0.27 (s, 18 H); IR (KBr) 2960, 2155, 1622, 1251, 1160, 840, 760, 727 cm^{-1}; FDMS, *m/z* 207 (M − CH$_3$), 222 (M, C$_{11}$H$_{18}$OSi$_2$). Anal. Calcd for C$_{11}$H$_{18}$OSi$_2$: C, 59.40; H, 8.10. Found: C, 59.70; H, 7.81.

Preparation of Δ-4*H*-Thiapyran-4-one (1). Diynone **4** (2.22 g, 10.0 mmol) was dissolved in 25 mL of ethanol. To this solution was added a solution of sodium hydrosulfide hydrate (1.84 g, 20.0 mmol) in 25 mL of saturated sodium bicarbonate and 25 mL of water. The resulting solution turned a deep yellow-orange in color. The reaction mixture was stirred 1 h at ambient temperature and was then diluted with 50 mL of water. The products were extracted with dichloromethane (3 × 50 mL). The combined organic extracts were washed with brine, dried over sodium sulfate, and concentrated. The residue was recrystallized from toluene to give 0.808 g (72%) of **1** as a pale yellow solid, mp 108–110 °C (lit.[13] mp 110.0–110.2 °C): IR (KBr) 3050, 1610, 1580, 1516, 1390, 1163, 1125, 845, 710 cm^{-1}; EIMS, *m/z* 112 (C$_5$H$_4$OS); UV $\lambda_{\max}$ (CH$_2$Cl$_2$) 297 (sh, ϵ 11 000), 289 (ϵ 16 000), 282 nm (sh, ϵ 15 000).

Preparation of Δ-4*H*-Selenapyran-4-one (2). Sodium borohydride (0.52 g, 15 mmol) was added to a slurry of selenium shot (0.79 g, 10 mmol) in 10 mL of 0.25 M sodium ethoxide in ethanol. The resulting mixture was heated at reflux for approximately 1.5 h (until the selenium shot was consumed and the initial purple color faded). The diynone **4** (1.11 g, 5.0 mmol) was dissolved in 10 mL of ethanol. This solution was then added to the disodium selenide. The resulting mixture was stirred 1 h at ambient temperature and was then diluted with 100 mL of water. The products were extracted with dichloromethane (3 × 50 mL). The combined extracts were washed with brine, dried over sodium sulfate, and concentrated. The residue was recrystallized from toluene to give 0.279 g (35%) of selenapyranone **2** as a yellow, crystalline solid, mp 114.0–115.5 °C: IR (KBr) 3045, 1585, 1548, 1373, 1158, 846, 616 cm^{-1}; FDMS, *m/z* 160 (C$_5$H$_4$O^{77}Se); UV $\lambda_{\max}$ (CH$_2$Cl$_2$) 310 (sh, ϵ 16 500), 302 (ϵ 17 000), 275 nm (sh, ϵ 3500). Anal. Calcd for C$_5$H$_4$OSe: C, 37.76; H, 2.54. Found: C, 37.69; H, 2.58.

Preparation of Δ-4*H*-Tellurapyran-4-one (3). Sodium borohydride (0.285 g, 7.5 mmol) was added to a slurry of tellurium powder (0.76 g, 6.0 mmol) in 10 mL of 0.25 M sodium ethoxide in ethanol. The resulting mixture was heated at reflux for approximately 1.5 h (until the tellurium powder was consumed and the initial purple color faded). The diynone **4** (1.11 g, 5.0 mmol) was dissolved in 10 mL of ethanol. This solution was then added to the disodium telluride. The resulting mixture was stirred 1 h at ambient temperature and was then diluted with 100 mL of water. The products were extracted with dichloromethane (3 × 50 mL). The combined extracts were washed with brine, dried over sodium sulfate, and concentrated. The residue was purified via chromatography on silica gel eluted with 25% ethyl acetate in dichloromethane. The product fractions were recrystallized from toluene to give 0.196 g (38%) of tellurapyranone **3** as a tan, crystalline solid, mp 114.0–115 °C: IR (KBr) 3025, 1560, 1516, 1360, 1321, 1154, 860, 843 cm^{-1}; FDMS, *m/z* 210 (C$_5$H$_4$O^{130}Te); UV $\lambda_{\max}$ (CH$_2$Cl$_2$) 344 (ϵ 20 000), 275 nm (sh, ϵ 3400). Anal. Calcd for C$_5$H$_4$OTe: C, 28.92; H, 1.94. Found: C, 28.91; H, 1.92.

Preparation of 1-(Trimethylsilyl)-5-phenyl-1,4-pentadiyn-3-ol (15). (Trimethylsilyl)acetylene (3.9 g, 40 mmol) in 20 mL of anhydrous THF was added dropwise to a 1.6 M in hexanes solution of *n*-butyllithium (20 mL, 32 mmol) cooled to 0 °C under an argon atmosphere. The resulting solution was stirred 0.5 h at 0 °C. Phenylpropargyl aldehyde (3.30 g, 25.4 mmol) in 20 mL of THF was added dropwise at 0 °C. The resulting solution was stirred 3 h at ambient temperature and was then diluted with 125 mL of 5% HCl. The products were extracted with ether (3 × 60 mL). The combined ether extracts were washed with brine, dried over sodium sulfate, and concentrated to give 5.65 g (98%) of the diynol **15** as a yellow oil which was used without further purification: ^{1}H NMR (CDCl$_3$) δ 7.46 (m, 2 H), 7.33 (m, 3 H), 5.35 (s, 1 H), 2.61 (br s, 1 H), 0.21 (s, 9 H); IR (film, NaCl) 3300 (br), 2955, 2228, 2170, 1488, 1247, 1030, 909, 830, 753, 687 cm^{-1}.

Preparation of 1-(Trimethylsilyl)-5-phenyl-1,4-pentadiyn-3-one (16). Diynol **15** (5.60 g, 0.0246 mol) in 50 mL of acetone was cooled to 0 °C. To this solution was added 40 mL (0.34 mol) of a 10% chromic acid solution. The resulting mixture was stirred 1 h at 0 °C and was then poured into 150 mL of water. The products were extracted with ether (3 × 100 mL). The combined ether extracts were washed with brine, dried over sodium sulfate, and concentrated. The residue was purified via chromatography on silica gel eluted with ether to give 5.45 g (98%) of diynone **16** as a yellow oil: ^{1}H NMR (CDCl$_3$) δ 7.63 (d, 2 H, J = 7.3 Hz), 7.49 (t, 1 H, J = 7.2 Hz), 7.40 (t, 2 H, J = 7.5 Hz), 0.29 (s, 9 H); IR (film, NaCl) 2945, 2190, 2130, 1615, 1482, 1436, 1271, 1245, 1120, 870, 739 cm^{-1}; FDMS, *m/z* 226 (C$_{14}$H$_{14}$OSi). Anal. Calcd for C$_{14}$H$_{14}$OSi: C, 74.29; H, 6.23. Found: C, 74.28; H, 6.13.

Preparation of 2-Phenyl-4*H*-thiapyran-4-one (17). Diynone **16** (4.52 g, 0.0200 mol) was dissolved in 75 mL of 2-propanol. Sodium hydrosulfide hydrate (3.68 g, 0.0400 mol) was dissolved in 50 mL of saturated sodium bicarbonate solution and 25 mL of water. The aqueous solution was added to the 2-propanol solution, and the resulting mixture was stirred for 3 h at ambient temperature. The reaction mixture was poured into 300 mL of water. The products were extracted with dichloromethane (3 ×

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[13] Rolla, M.; Sanesi, M.; Traverso, G. *Ann. Chim.* (*Rome*) **1952**, *42*, 673–680.

150 mL). The combined organic extracts were washed with brine (2 × 100 mL), dried over magnesium sulfate, and concentrated. The residue was purified via chromatography on silica gel (20% ethyl acetate in dichloromethane) to give 1.64 g (44%) of the thiapyranone 17, mp 90–92.5 °C (lit.[5] mp 92–92.5 °C): ^{1}H NMR ($CDCl_3$) δ 7.80 (d, 1 H, J = 10.3 Hz), 7.58 (m, 2 H), 7.51 (m, 3 H), 7.22 (d, 1 H, J = 1.3 Hz), 7.07 (d × d, 1 H, J = 1.3, 10.3 Hz); IR (KBr) 1608 (s), 1160, 880, 796, 751, 728, 690 cm^{-1}; FDMS, m/z 188 ($C_{11}H_8OS$).

Preparation of 2-Phenyl-4*H*-tellurapyran-4-one (18). Sodium borohydride (0.285 g, 7.5 mmol) was added to a slurry of tellurium powder (0.76 g, 6.0 mmol) in 10 mL of 0.25 M sodium ethoxide in ethanol. The resulting mixture was heated at reflux for approximately 1.5 h (until the tellurium powder was consumed and the initial purple color faded). The diynone 4 (0.68 g, 3.0 mmol) was dissolved in 10 mL of ethanol. This solution was then added to the disodium telluride. The resulting mixture was stirred 1 h at ambient temperature and was then diluted with 100 mL of water. The products were extracted with dichloromethane (3 × 50 mL). The combined extracts were washed with brine, dried over sodium sulfate, and concentrated. The residue was purified via chromatography on silica gel eluted with 25% ethyl acetate in dichloromethane. The product fractions were recrystallized from toluene to give 0.273 g (32%) of tellurapyranone 18 as a tan, crystalline solid, mp 121.5–123 °C (lit.[5] mp 121.5–123 °C): ^{1}H NMR ($CDCl_3$) δ 8.70 (d, 1 H, J = 11.4 Hz), 7.45 (br s, 5 H), 7.35 (d × d, 1 H, J = 1.0, 11.4 Hz), 7.27 (d, 1 H, J = 1.0 Hz); IR (KBr) 3050, 1560, 1530, 1480, 1440 cm^{-1}; FDMS, m/z 286 ($C_{11}H_8O^{130}Te$).

Preparation of 4-(*p*-(*N*,*N*-Dimethylamino)phenyl)selenapyrylium Hexafluorophosphate (19). A mixture of *p*-bromo-*N*,*N*-dimethylaniline (1.20 g, 6.00 mmol) and magnesium turnings (0.144 g, 6.0 mg-atom) in 10 mL of anhydrous THF was heated at reflux for 1.5 h under argon. The reaction mixture was cooled to ambient temperature, and selenapyranone 2 (0.477 g, 3.00 mmol) in 5 mL of anhydrous THF was added dropwise via syringe. The reaction mixture was heated at reflux for 1 h and was then poured into 50 mL of cold, 10% HPF_6. The purple solid was collected by filtration, washed with water (4 × 10 mL) and ether (4 × 10 mL), and dried. The solid was recrystallized from acetonitrile and an equal volume of ether to give 0.83 g (68%) of 19 as a purple-black solid, mp 205.5–208 °C (dec): ^{1}H NMR (CD_2Cl_2) δ 9.48 (d, 2 H, J = 10.6 Hz), 8.61 (d, 2 H, J = 10.6 Hz), 8.07 (AA′BB′, 2 H), 6.94 (AA′BB′, 2 H), 3.24 (s, 6 H); UV λ_{max} (CH_2Cl_2) 591 nm (ϵ 89000). Anal. Calcd for $C_{13}H_{14}NSe\cdot PF_6$: C, 38.25; H, 3.46; N, 3.43. Found: C, 38.47; H, 3.48; N, 3.60.

Preparation of 4-(*p*-(*N*,*N*-Dimethylamino)phenyl)tellurapyrylium Hexafluorophosphate (20). A mixture of *p*-bromo-*N*,*N*-dimethylaniline (0.60 g, 3.0 mmol) and magneisum turnings (0.12 g, 5.0 mg-atom) in 10 mL of anhydrous THF was heated at reflux for 1.5 h under argon. The reaction mixture was cooled to ambient temperature, and tellurapyranone 3 (0.312 g, 1.50 mmol) in 5 mL of anhydrous THF was added dropwise via syringe. The reaction mixture was heated at reflux for 1 h and was then poured into 50 mL of cold, 10% HPF_6. The purple solid was collected by filtration, washed with water (4 × 10 mL) and ether (4 × 10 mL), and dried. The solid was recrystallized from acetonitrile and an equal volume of ether to give 0.486 g (71%) of 20 as a purple-black solid, mp 220–221 °C (dec): ^{1}H NMR (CD_2Cl_2) δ 10.60 (d, 2 H, J = 11.6 Hz), 8.80 (d, 2 H, J = 11.6 Hz), 8.08 (AA′BB′, 2 H), 6.93 (AA′BB′, 2 H), 3.24 (s, 6 H); UV λ_{max} (CH_2Cl_2) 628 nm (ϵ 80000). Anal. Calcd for $C_{13}H_{14}NTe\cdot PF_6$: C, 34.18; H, 3.09; N, 3.07. Found: C, 34.64; H, 3.22; N, 3.17.

Crystal Data Collection. All data were collected on an Enraf-Nonius CAD4 diffractometer.[14] Crystals of thiapyranone 1 and selenapyranone 2 were mounted in glass capillaries to prevent sublimation. Unit cell parameters obtained by least-squares refinement of the setting angles for 25 computer-centered reflections are given in Tables II–IV along with other pertinent information.

Each reflection was scanned from $2\theta(\text{Mo K}\alpha_1) - \Delta°$ to $2\theta(\text{Mo K}\alpha_2) + \Delta°$, where Δ = 0.75, 0.90, and 0.85 for 1, 2, and 3, respectively. The scan width was extended 25% at each end to measure background intensities. As a check on experimental stability, the intensities of three reflections were remeasured every hour. No significant change in these intensities was noted.

The net intensities were calculated according to $I = ASK(C - RB)$, and the standard deviations were $\sigma^2(I) = (ASK)^2(C + 2RB)$ and $\sigma(F_o) = [I + \sigma(I)/\text{Lp}]^{1/2} - F_o$, where A is the attenuator factor, S is the scale, C is the total integrated peak count, $(\text{Lp})^{-1}$ is the Lorentz polarization correction, and $F_o = (I/\text{Lp})^{1/2}$ is the observed structure factor. Empirical absorption corrections were applied to the data for 2 and 3 using the program DIFABS.[15]

Structure Solution and Refinement. The structures were solved by direct methods using MULTAN 81.[16] Refinement was by the full-matrix least-squares method. Hydrogen atoms were included in the refinement but, for the tellurium analogue 3, were only allowed to ride on the parent carbon atoms. The function minimized was $\sum w(|F_o| - K|F_c|)^2$, where $w^{-1} = \sigma^2(F_o) + (0.02F_o)^2 + q$, where q = 0.1, 0.5, and 0.7 for 1, 2, and 3, respectively. Scattering factors and anomalous dispersion corrections were from ref 17. The agreement indices are $R = \sum||F_o| - K|F_c||/\sum|F_o|$ and $R_w = (\sum(|F_o| - K|F_c|)^2/\sum wF_o^2)^{1/2}$.

In the final stages, anisotropic thermal parameters were applied and refinement converged to give R = 0.038, R_w = 0.043, and K = 0.5642 (7) for 1; R = 0.033, R_w = 0.039, and K = 1.070 (2) for 2; and R = 0.048, R_w = 0.054, and K = 0.4187 (6) for 3. The final difference electron density maps contained residual electron densities between −0.18 and +0.19 e/A^3 for 1, −0.58 and +0.41 e/A^3 for 2, and −0.84 and +1.18 e/A^3 for 3. For 3, the largest positive peak is at a center of symmetry between two tellurium atoms, and the next four positive peaks are found near tellurium.

Supplementary Material Available: Tables of bond distances, bond angles, refined temperature factors, and least-squares planes, for C_5H_4OTe, C_5H_4OSe, and C_5H_4OS (6 pages). Ordering information is given on any current masthead page.

OM910712L

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(14) Programs used in this study were from: *MolEN, An Interactive Structure Solution Procedure*; Enraf-Nonius: Delft, The Netherlands, 1990.

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(16) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declerq, J. P.; Woolfson, M. M. *MULTAN80, A system of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*; University of York: York, England, 1980.

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