Preparation of Arylpropiolate Esters from Trichlorocyclopropenium Cation and Elaboration of the Esters to Unsymmetrical 1,4-Pentadiyn-3-ones and Unsymmetrical Tellurapyranones

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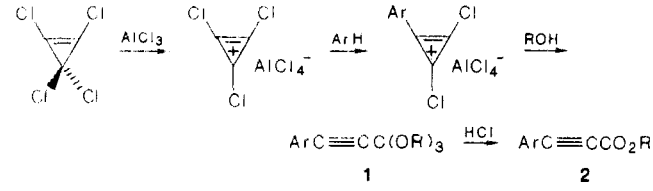
The addition of aromatic compounds including thiophene, naphthalene derivatives, and some benzene derivatives to trichlorocyclopropenium cation gave nearly quantitative yields of 1-aryl-2,3,3-trichlorocyclopropenes. Alcoholysis of the cyclopropene derivatives gave either arylpropiolate esters or arylpropiolate orthoesters (in the presence of added amine base). The arylpropiolates can be converted to unsymmetrical 1,4-pentadiyn-3-ones by two different approaches. The first approach involved reduction of the arylpropiolate esters with diisobutylaluminum hydride to give the corresponding propargyl alcohol. Pyridinium chlorochromate or manganese dioxide oxidation of the alcohol gave the propargyl aldehydes. Addition of a lithium acetylenide gave a 1,4-pentadiyn-3-ol, which could then be oxidized to the 1,4-pentadiyn-3-one with 10% chromic acid or manganese dioxide. The second pathway used a Lewis acid mediated coupling of a propargylic acid chloride with a (trimethylsilyl)acetylene to give the 1,4-pentadiyn-3-ones directly. The coupling of 2-thiophenepropiolic acid chloride gave the product of HCl addition to the expected 1,4-diynone. The regiochemistry of addition was determined to be chloride addition to the thiophene-bearing triple bond on the basis of ^{1}H NMR studies. The diynones were converted to unsymmetrical 2,6-disubstituted tellura-4*H*-pyran-4-ones with disodium telluride anion.

We have been interested in developing synthetic routes to the naturally occurring chromones and flavones as well as analogues incorporating the heavier chalcogen atoms S, Se, and Te for the ring O atom. These compounds are of interest for their potential biological activity in both plants and humans. Flavones and chromones have been found to be active in a number of plant cycles, including growth regulation,[1] indoleacetic acid oxidation,[2] and dormancy inhibition,[3] as well as exhibiting cytokinin-type behavior[4] and stimulating oxygen uptake in plant tissues.[5] The furochromone khellin has lipid-altering capabilities,[6] while styryl chromones have been found to be potent cytotoxic agents for P388 lymphocytic leukemia and HL-60 human promyelocytic cell lines.[7]

Two routes to these compounds are of particular interest to us. The sequential Michael addition of a phenol or an aryl chalcogenide anion to an arylpropiolate followed by an intramolecular acylation to generate the chromone or flavone[8] is one, and the use of an unsymmetrically substituted, monocyclic chalcogenapyranone as a starting template that can be elaborated to benzo analogues by Fischer carbene chemistry[9] is the other.

In the synthetic strategies described above, acetylenic compounds are the required precursors. Propiolic acid

Scheme I



derivatives have been prepared typically by the reaction of a metal acetylenide with carbon dioxide, often at elevated pressure,[10] or by addition of the metal acetylenide to ethyl chloroformate.[11] Chalcogenapyranones are conveniently prepared by the addition of a chalcogenide dianion to a 1,4-pentadiyn-3-one.[12] The preparation of unsymmetrical pyranones would require unsymmetrically substituted 1,4-pentadiyn-3-ones prepared in modest yield by the coupling of Cu(I) acetylenides with propiolic acid chlorides in the presence of alkali-metal salts.[13]

We report a convenient synthesis of arylpropiolates via cyclopropenium chemistry and subsequent conversion of the arylpropiolates to unsymmetrical 1,4-pentadiyn-3-ones by two different routes. The first involves coupling of arylpropiolic acid chlorides with (trimethylsilyl)acetylenes by using Lewis acids; the second involves the addition of metal acetylenides to propargyl aldehydes.

Results and Discussion

Preparation of Arylpropiolate Esters and Orthoesters. 1-Aryl-2,3,3-trihalocyclopropenes have been prepared from tetrahalocyclopropene, aluminum halide, and benzene derivatives.[14] Hydrolysis of 1-aryl-2,3,3-tribromocyclopropenes gave arylpropiolic acids.[14b] We have found that the formation of 1-aryl-2,3,3-trichlorocyclo-

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(9) Heteroaromatic carbene complexes have been prepared and used in the synthesis of khellin analogues as in ref 6a. In this reference, the chromone ring was constructed in the final steps. In our approach, a carbene-bearing chalcogenapyranone would be converted to chromone and flavone analogues.
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Table I. Preparation of Arylpropiolates 2 from Trichlorocyclopropenium Cation and Aromatic Compounds

compd	Ar	R	isol yield, %	mp (solvent) or bp (Torr), °C	addn temp,[a] °C
2a	Ph	Me	94	60–62 (0.01)	0[b]
2b	Ph	$CHMe_2$	90	88 (0.02)	0[b,c]
2c	2,4,6-$Me_3C_6H_2$	Me	95	68–69 (MeOH)	−30[b]
2d	2,4,6-$Me_3C_6H_2$	$CHMe_2$	88	90 (0.005)	−30[b,c]
2e	4-$MeOC_6H_4$	Me	59	43–44 (MeOH)	−78
2f	2,5-$(MeO)_2C_6H_3$	Me	82	74–75 (MeOH)	−78[b]
2g	4-FC_6H_4	Me	72	57–59 (MeOH)	−10
2h	2,5-$F_2C_6H_3$	Me	82		83[d,e]
2i	2-$MeOC_{10}H_6$	Me	79	94–95 (MeOH)	−78
2j	2-thienyl	Me	95	54–55 (MeOH)	−30[b]
2k	2,4-$(MeO)_2C_6H_3$	Me	95	78–80 (MeOH)	−78
2l	4-*t*-BuC_6H_4	Et	90		0
2m	Ph	Et	93	75–76 (0.02)	0[b]
2n	3,4-$(MeO)_2C_6H_3$	Me	95	81–83 (MeOH)	−78[b]

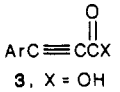
[a] For addition of ArH to $C_3Cl_3^+$. [b] Crude yield was 95–100%. ^1H NMR showed only minor amounts of impurities. [c] Isopropyl esters took longer in the heating phase after $NaHCO_3$ addition than methyl esters. [d] Reaction required heating at reflux for 15 h. Purified by silica gel chromatography eluting with 3/1 (v/v) hexane/dichloromethane. [e] Not acid washed after isolation.

propenes can be extended to include the addition of trichlorocyclopropenium cation to heteroaromatics, naphthalene derivatives, and benzene derivatives that are at least as susceptible as *p*-difluorobenzene to electrophilic attack. Alcoholysis of the corresponding cyclopropene derivatives provides nearly quantitative yields of the corresponding arylpropiolate orthoesters **1**, which are then converted to the arylpropiolate esters **2**, upon treatment with HCl (Scheme I). One reaction path apparently involves alcoholysis of both *gem*-dichlorides, ring opening with stepwise or concerted elimination of chloride, and acid decomposition of the orthoester.

In typical procedures, dichloroethane or dichloromethane solutions (or suspensions) of an aryldichlorocyclopropenium chloroaluminate (prepared in situ from tetrachlorocyclopropene, aluminum chloride, and the appropriate aryl compound) are either washed with ice–water or diluted with an equal volume of tetrahydrofuran (THF) and then stirred with sodium bicarbonate and an excess of the appropriate alcohol until gas evolution ceases. The arylpropiolates are obtained by filtering the reaction mixture, warming the filtrate to complete the ring opening, and washing the filtrate with 1 N HCl to convert any remaining orthoester. The arylpropiolate esters prepared in this manner are summarized in Table I along with their physical properties and the reaction conditions used in their preparation.

This procedure provides quick access to arylpropiolates with very few side products. Although the crude reaction mixtures of both **2e** and **2g** contained small amounts (≤10%) of the ortho isomers by ^1H NMR, the para isomers were obtained pure by recrystallization.

Hydrolysis of the aryltrichlorocyclopropenes gave propiolic acids directly, but the product mixtures contained a number of components. The arylpropiolic acids **3** were more conveniently prepared in good overall yield by saponification of the esters **2** with sodium hydroxide in aqueous methanol. The acids **3** were converted to the acid chlorides **4** in quantitative yields with thionyl chloride.



3, X = OH
4, X = Cl

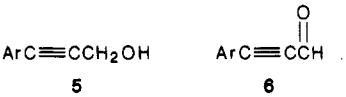
Although the orthoesters **1** are somewhat unstable molecules, they can be isolated from the alcoholysis of the 1-aryl-2,3,3-trichlorocyclopropenes by adding excess tertiary amine base (diisopropylethylamine, triethylamine) to the bicarbonate suspension. Appropriate physical properties for the orthoesters **1** are compiled in Table II.

Table II. Preparation of Arylpropiolate Orthoesters 1 from Trichlorocyclopropenium Cation and Aromatic Compounds

compd	Ar	R	isol yield, %	bp (Torr),[a] °C
1a	Ph	Me	85	85–92 (0.08)
1b	2,4,6-$Me_3C_6H_2$	Me	95	
1c	2,6-$Me_2C_6H_3$	Me	95	115–120 (0.005)

[a] Some decomposition during distillation.

Preparation of Propargyl Aldehydes. While diisobutylaluminum hydride has been used to reduce esters to aldehydes directly,[15] the use of 1 equiv of diisobutylaluminum hydride with methyl phenylpropiolate (**2a**) in THF at −78 °C gave a mixture of the propargyl alcohol and unreacted starting ester. Apparently, the initially formed propargyl aldehyde **6** is much more reactive than propiolate ester **2** toward the reducing agent.



5 **6**

The use of 2 equiv of diisobutylaluminum hydride in THF at −78 °C reduces the propiolates **2a**, **2e**, **2g**, **2h**, and **2j** to the propargyl alcohols **5** in 72–95% isolated yields. (Small amounts (<10%) of allylic alcohols were detected in the crude reaction mixtures by ^1H NMR and mass spectroscopy.) The propargyl alcohols **5** were then oxidized to the propargyl aldehydes **6** with pyridinium chlorochromate (PCC)[16] in dichloromethane at ambient temperature under an inert atmosphere. While overoxidation with PCC was not a problem in the conversion of **5** to **6**, the propargyl aldehydes **6** were sensitive to air oxidation and were prone to decomposition on silica gel. Consequently, the aldehydes were prepared immediately before use and were used without purification.

As an alternative to the use of PCC, MnO_2 with benzene as a solvent, under an inert atmosphere, gave the aldehydes **6** in 85–95% yields.[17] In larger scale reactions, large volumes of solvent were required to remove the propargyl aldehydes from the inorganic solids.

Preparation of Unsymmetrical 1,4-Pentadiyn-3-ones. Two routes were explored to provide unsymmetrical 1,4-pentadiyn-3-ones. Aryl alkynyl ketones[18] and alkyl

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Table III. Comparison of Synthetic Routes to 1,4-Pentadiyn-3-ones

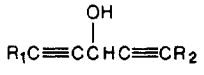
compd	R_1	R_2	method[a]	yield,[b] %	mp (solvent), °C
8a	Ph	Ph	A	36	69–72
			B	42	(pentane)
			C	63	
8b	4-$MeOC_6H_4$	Ph	A	20	115–116.5
			C	45	(MeCN)
8c	4-FC_6H_4	Ph	A	29	75.5–77.5
					(pentane)
8d	2,5-$F_2C_6H_3$	Ph	A	41	72–74
			C	53	(MeCN)
8e	Ph	Me_3Si	A	38	oil
8f	Ph	H	B	42	47–48.5
			C	62	(Et_2O/hexane)
8g	Ph	$(CH_2)_3O$-($SiMe_2$-*t*-Bu)	B	84	oil
8h	Ph	2-thienyl	B	12	oil
9			C	40	57–58.5 (Et_2O)

[a] Method A: acetylenide addition to aldehyde, PCC oxidation of diynol. Method B: same as A, but MnO_2 oxidation of diynol. Method C: $AlCl_3$ coupling of propiolic acid chloride with silylacetylene derivative. [b] Overall isolated yield from arylpropiolate.

alkynyl ketones[19] have been prepared by the Lewis acid promoted coupling of aromatic acid chlorides with (trimethylsilyl)acetylenes. A modification of this approach coupled propiolic acid chlorides with 1-(trimethylsilyl)-acetylenes to give unsymmetrical 1,4-pentadiyn-3-ones.

In cases where Lewis acid induced coupling would be problematic because of acid-sensitive functionality, Chauvelier's original approach to symmetrical pentadiynones[20] can be used to prepare the unsymmetrical derivatives. The addition of a metal acetylenide to a propargyl aldehyde followed by oxidation gives the unsymmetrical diynones.

A. From Propargyl Aldehydes. The addition of metal acetylenides to the arylpropargyl aldehydes **6** gave the diynols **7** in 51–96% yields. Compounds **7a–d** and **7h** were prepared by the addition of a propargyl aldehyde **6** to phenylacetylenide at −78 °C in THF. Diynol **7e** was prepared by adding phenylpropargyl aldehyde to lithium (trimethylsilyl)acetylenide in THF at −78 °C. Diynol **7g** was prepared by the addition of phenylpropargyl aldehyde to a THF solution of 1-lithio-1-pentyn-5-ol dimethyl-*tert*-butylsilyl ether.



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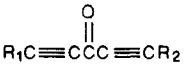

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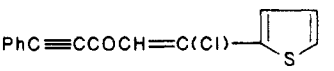
7a: $R_1 = R_2 = Ph$
b: $R_1 = 4\text{-}MeOC_6H_4$, $R_2 = Ph$
c: $R_1 = 4\text{-}FC_6H_4$, $R_2 = Ph$
d: $R_1 = 2,5\text{-}F_2C_6H_3$, $R_2 = Ph$
e: $R_1 = Ph$, $R_2 = Me_3Si$
f: $R_1 = Ph$, $R_2 = H$
g: $R_1 = Ph$, $R_2 = (CH_2)_3O(SiMe_2\text{-}t\text{-}Bu)$
h: $R_1 = Ph$, $R_2 = 2\text{-thienyl}$

The diynols **7** were oxidized to diynones **8** with either PCC or MnO_2. Physical properties of the diynones as well as overall isolated yields from the arylpropiolates **2** are compiled in Table III.

B. From Propiolic Acid Chlorides. The manipulation of the oxidation state of the propiolate esters **2** in the route to diynones described above adds two steps to the reaction sequence and involves the propargyl aldehyde **6**, an air- and acid-sensitive intermediate. The direct conversion of a propiolate derivative to the diynone would circumvent both the use of propargyl aldehyde intermediates and the oxidation of the diynol to the diynone. The Lewis acid mediated coupling of phenylpropiolic acid chloride with phenyl(trimethylsilyl)acetylene in dichloromethane gave 1,5-diphenyl-1,4-pentadiyn-3-one (**8**). Stoichiometric amounts of the Lewis acid gave the best yields.[18b] Aluminum chloride gave better yields of **8a** (35–45%) than either titanium tetrachloride (30%) or zinc chloride (30%). When catalytic amounts of aluminum chloride (5–20 mol %) were used, yields of **8a** approaching only 25% could be isolated even after prolonged reaction time. The physical properties and yields of the diynones prepared by the aluminum chloride method are summarized in Table III.

The product obtained from coupling 2-thienylpropiolic acid chloride (Ar = 2-thienyl) with phenyl(trimethylsilyl)acetylene was shown to have *m/e* 272 ($C_{15}H_9ClOS$) by mass spectral analysis and the same molecular formula by elemental analysis. This molecular formula corresponds to the HCl addition product of the expected diynone **8h**. ^1H NMR analysis of the crystalline product suggested that HCl had added in a Michael fashion to one triple bond (olefinic singlet at δ 6.90, which integrated for one proton). The anti-Michael addition product would give an olefinic singlet at lower field.[2a] The thiophene-bearing triple bond was determined to be the site of HCl addition to give **9** by



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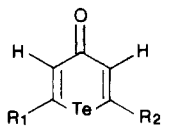
a ^1H–^1H nuclear Overhauser enhancement (NOE) difference experiment. Irradiation of the proton attached to C_2 of the thiophene ring enhanced the signal of the olefinic proton, while irradiation of the phenyl ortho protons gave no enhancement of the olefinic proton. The stereochemistry around the double bond cannot be assigned unambiguously.

The addition of HCl apparently occurred during the coupling reaction, since the ^1H NMR spectrum of **9** (Ar = 2-thienyl) showed very little (<5%) evidence for HCl addition prior to the addition of $AlCl_3$.

The overall yields in Table III suggest that the Lewis acid mediated couplings of arylpropiolic acid chlorides with silylacetylenes are useful reactions for the preparation of 1,4-pentadiyn-3-ones (**8**), furnishing higher overall yields and requiring one less step than the route involving the intermediacy of propargyl aldehydes.

When the propargyl aldehyde is commercially available or when acid-sensitive functionality is present, the addition of a metal acetylenide to the aldehyde followed by oxidation offers a good alternative route to the diynones **8**. The stability of the propargyl aldehyde can be a troublesome factor in this route, however.

Preparation of Tellura-4*H*-pyran-4-ones. The unsymmetrical diynones **8** and the HCl adduct **9** were useful starting materials for the preparation of unsymmetrical monocyclic tellura-4*H*-pyran-4-ones **10**. Symmetrical



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tellura-4*H*-pyran-4-ones ($R_1 = R_2$ = Me, *t*-Bu, Ph) have been prepared by the addition of disodium telluride to the corresponding diynones, which have been treated with dilute ethanolic sodium ethoxide to add one molecule of

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(20) Chauvelier, J. *Ann. Chim. (Paris)* **1948**, *12*, 410.

Table IV. Preparation of Unsymmetrical Tellura-4*H*-pyran-4-ones from Diynones 8 and Enynone 9

compd	R_1	R_2	isol yield, %	mp (solvent), °C
10a	Ph	4-$MeOC_6H_4$	38	127.5–129 (MeCN)
10b	Ph	4-FC_6H_4	53	134–136 (MeCN)
10c	Ph	2,5-$F_2C_6H_4$	58	oil
10d	Ph	H	12	121.5–123 (MeOH)
10e	Ph	$(CH_2)_3O(SiMe_2$-*t*-Bu)	31	oil
10f	Ph	$(CH_2)_3OH$		81.5–84.5 (MeCN)[a]
10g	Ph	2-thienyl	30	119–120.5 (MeCN)

[a] Prepared by $Bu_4N^+BF_4^-$ removal of silyl group from **10e**.

ethanol across a triple bond.[12] This procedure was extended to include the preparation of tellurapyranones **10** compiled in Table IV. The diynone was first treated with 0.1 M sodium ethoxide in ethanol and then added to a solution of disodium telluride in 1 M sodium ethoxide in ethanol. The low yield (12%) for the preparation of **10** perhaps reflects the reactivity of **8** toward the ethoxide. This procedure should be applicable as well to preparation of unsymmetrical thia- and selenapyranones.

The HCl adduct **9**, which is similar to the expected product of ethanol addition across diynone **8h** by having a leaving group located in the β-position, gave **10g** in 30% yield upon addition of an ethanol solution of **9** to dilithium telluride (prepared by the addition of lithium triethylborohydride to Te metal in THF).

Summary and Conclusions

Arylpropiolates **2** can be produced in high yield from alcoholysis of 1-aryl-2,3,3-trichlorocyclopropenes that are prepared by electrophilic attack of trichlorocyclopropenium cation on aromatic substrates. The propiolates serve as starting materials for the preparation of benzo[*b*]chalcogenapyranones and 1,4-pentadiyn-3-ones.

Unsymmetrical 1,4-pentadiyn-3-ones **8** have been prepared from arylpropiolates **2** by two routes. The conversion of the propiolate esters to the acid chlorides allows the direct formation of diynones **8** via the Lewis acid catalyzed coupling of the acid chloride with 1-(trimethylsilyl)acetylenes. Although this method fails with acid-sensitive molecules, an alternative approach utilizes the propargyl aldehydes produced by reduction of the propiolate esters **2** to the alkynols **5** with diisobutylaluminum hydride followed by oxidation to the aldehyde **6** with PCC or MnO_2. The addition of a metal acetylenide to the propargyl aldehydes **6** gives 1,4-pentadiyn-3-ols, which can be oxidized to diynones **8**.

The diynones **8** serve as precursors to unsymmetrically substituted tellurapyranones **10**. The diynone approach has been the only method thus far described for the preparation of monocyclic tellurapyranones. The facile routes to unsymmetrical diynones described here make the diynone approach to tellurapyranones much more versatile.

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are corrected. ^1H NMR spectra were recorded on a Varian EM 390 or a GE NMR QE-300 instrument. Infrared spectra were recorded on a Beckman IR 4250 instrument. UV–visible spectra were recorded on a Cary 17 spectrophotometer. Solvents (Kodak Laboratory Chemicals) were dried over 3A molecular sieves before use. Microanalyses were obtained with a Perkin-Elmer C, H, and N analyzer. Tellurium analyses were obtained by atomic absorption spectroscopy with ±1% accuracy.

Preparation of Arylpropiolates 2. A. To anhydrous aluminum chloride (1.4 g, 10 mmol) in 30 mL of dichloromethane or dichloroethane was added tetrachlorocyclopropene (1.8 g, 10 mmol). The resulting suspension was cooled (see Table I for details and exceptions). The aromatic compound (10 mmol) in 10 mL of dichloromethane or dichloroethane was added dropwise. The resulting solution was allowed to warm to ambient temperature, heated briefly to 50 °C to drive off HCl, and then cooled to 0 °C. After the solution was shaken vigorously with ice–water, the organic layer was dried over $MgSO_4$. The organic phase was stirred 0.5 h with 10 g of solid $NaHCO_3$ and 10 mL of the appropriate alcohol. The reaction mixture was filtered, washed with 1 N HCl to decompose any unreacted orthoester, washed with dilute $NaHCO_3$ solution, and concentrated. Products were obtained in 95–100% yields with 95% or above purity by ^1H NMR. Distillation or recrystallization from the reacting alcohol provided analytical samples.

B. Instead of the ice–water wash of method A, the reaction mixture was treated with 10 mL of THF prior to the $NaHCO_3$/alcohol treatment. The remainder of the procedure was the same as method A. This variation gave less pure products.

With anisole as the added aromatic species, the reaction mixture was maintained below −70 °C during the addition of anisole and for 2 h after the addition was complete in order to minimize the formation of the ortho isomer. With *p*-difluorobenzene as the added aromatic compound, the reaction mixture was heated at reflux for 15 h to complete electrophilic attack by the trichlorocyclopropenium cation. All propiolate esters **2** gave parent ions by field desorption mass spectroscopy.

2a: ^1H NMR ($CDCl_3$) δ 7.53 (m, 2 H), 7.40 (m, 3 H), 3.77 (s, 3 H).

2b: ^1H NMR ($CDCl_3$) δ 7.53 (m, 2 H), 7.37 (m, 3 H), 5.07 (sept, 1 H, J = 6 Hz), 1.27 (d, 6 H, J = 6 Hz).

2c: ^1H NMR ($CDCl_3$) δ 6.80 (s, 2 H), 3.80 (s, 3 H), 2.40 (s, 6 H), 2.23 (s, 3 H); IR (KBr) 2205, 1705, 1605 cm^{-1}. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.2; H, 7.0. Found: C, 7.4; H, 7.0.

2d: ^1H NMR ($CDCl_3$) δ 6.80 (s, 2 H), 5.10 (sept, 1 H, J = 6 Hz), 2.40 (s, 6 H), 2.23 (s, 3 H), 1.30 (d, 6 H, J = 6 Hz); IR (KBr) 2200, 1703, 1610 cm^{-1}.

2e: ^1H NMR ($CDCl_3$) δ 7.50 (d, 2 H, J = 7.5 Hz), 6.85 (d, 2 H, J = 7.5 Hz), 3.85 (s, 6 H); IR (KBr) 2320, 2190, 2160, 1710, 1605 cm^{-1}. Anal. Calcd for $C_{11}H_{10}O_3$: C, 69.5; H, 5.3. Found: C, 69.2; H, 5.3.

2f: ^1H NMR ($CDCl_3$) δ 6.84 (s, 1 H), 6.70 (m, 2 H), 3.67 (s, 3 H), 3.65 (s, 3 H), 3.57 (s, 3 H); IR (KBr) 2220, 1710 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.4; H, 5.5. Found: C, 65.6; H, 5.4.

2g: ^1H NMR ($CDCl_3$) δ 7.55 (dd, 2 H, J = 5.5, 9 Hz), 7.03 (t, 2 H, J = 9 Hz), 3.82 (s, 3 H); IR (KBr) 2230, 1710, 1601 cm^{-1}. Anal. Calcd for $C_{10}H_7FO_2$: C, 67.4; H, 4.0. Found: C, 67.1; H, 3.9.

2h: ^1H NMR ($CDCl_3$) δ 7.15 (m, 3 H), 3.83 (s, 3 H); IR (film) 2240, 1720 cm^{-1}. Anal. Calcd for $C_{10}H_6F_2O_2$: C, 61.2; H, 3.1. Found: C, 61.1; H, 3.1.

2i: ^1H NMR ($CDCl_3$) δ 8.25 (d, 1 H, J = 8 Hz), 7.57 (m, 4 H), 7.20 (d, 1 H, J = 9 Hz), 4.0 (s, 3 H), 3.85 ns, 3 H); IR (KBr) 2215, 1725 cm^{-1}. Anal. Calcd for $C_{15}H_{12}O_3$: C, 75.0; H, 5.0. Found: C, 75.0; H, 5.2.

2j: ^1H NMR ($CDCl_3$) δ 7.43 (m, 2 H), 6.98 (m, 1 H), 3.80 (s, 3 H); IR 2200, 1705 cm^{-1}. Anal. Calcd for $C_8H_6O_2S$: C, 57.8; H, 3.6. Found: C, 57.6; H, 3.6.

2k: ^1H NMR ($CDCl_3$) δ 7.07 (d, 1 H, J = 3 Hz), 6.99 (dd, 1 H, J = 3.9 Hz), 6.86 (d, 1 H, J = 9 Hz), 3.87 (s, 3 H), 3.86 (s, 3 H), 3.78 (s, 3 H); IR (KBr) 2240, 1720 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.4; H, 5.6. Found: C, 65.4; H, 5.5.

2l: ^1H NMR ($CDCl_3$) δ 7.40 (m, 4 H), 4.23 (q, 2 H, J = 7 Hz), 1.33 (t, 3 H, J = 7 Hz), 1.32 (s, 9 H); IR (KBr) 2220, 1720 cm^{-1}.

2n: ^1H NMR ($CDCl_3$) δ 7.26 (d, 1 H, J = 8.2 Hz), 7.09 (s, 1 H), 6.87 (d, 1 H, J = 8.2 Hz), 3.93 (s, 3 H), 3.90 (s, 3 H), 3.86 (s, 3 H); IR (KBr) 2201, 1705 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.4; H, 5.5. Found: C, 65.3; H, 5.5.

Preparation of Arylpropiolate Orthoesters 1. The procedure described for the preparation of the propiolate esters **2** was followed except that 3 equiv of triethylamine or diisopropylethylamine was added along with the solid $NaHCO_3$ just prior to the addition of the alcohol.

1a: ^1H NMR ($CDCl_3$) δ 7.50 (m, 2 H), 7.33 (m, 3 H), 3.43 (s, 9 H); IR (film) 2250 cm^{-1}.

1b: ^1H NMR ($CDCl_3$) δ 6.80 (s, 2 H), 3.45 (s, 9 H), 2.37 (s, 6 H), 2.22 (s, 3 H). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.5; H, 8.1. Found: C, 72.7; H, 8.3.

1c: ^{1}H NMR ($CDCl_3$) δ 7.25 (s, 1 H), 7.03 (m, 2 H), 3.47 (s, 9 H), 2.40 (s, 3 H), 2.27 (s, 3 H); IR (film) 2250 cm^{-1}.

General Procedure for the Preparation of Arylpropiolic Acids 3. Preparation of Phenylpropiolic Acid (3a). To a solution of ethyl phenylpropiolate (2.64 g, 15.1 mmol) in 120 mL of ethanol was added slowly with stirring an aqueous sodium hydroxide solution (70 mL, 0.24 N). After 1.5 h, the reaction mixture was diluted with water (100 mL) and was washed with dichloromethane (2 × 50 mL). The aqueous phase was acidified with 10% HCl and was extracted with dichloromethane (3 × 75 mL). The combined extracts were dried over Na_2SO_4 and concentrated. Recrystallization of the solid residue from CH_3CN gave 1.85 g (84%) of **3a** as white needles: mp 137–139 °C; ^{1}H NMR ($CDCl_3$) δ 10.21 (s, br, 1 H), 7.50 (m, 5 H); IR (KBr) 3440 (br), 2340, 2300, 1675 cm^{-1} (br, s); FDMS, *m/e* 146 ($C_9H_6O_2$). Anal. Calcd for $C_9H_6O_2$: C, 74.0; H, 4.1. Found: C, 73.8; H, 4.2.

2-Thienylpropiolic acid: 72%; mp 135–136 °C (CH_3CN); ^{1}H NMR ($CDCl_3$) δ 8.20 (br, s, 1 H), 7.5 (m, 2 H), 7.07 (m, 1 H); IR (KBr) 3450 (br), 2300, 1670 cm^{-1} (br, s); FDMS, *m/e* 152 ($C_7H_4O_2S$). Anal. Calcd for $C_7H_4O_2S$: C, 55.3; H, 2.6. Found: C, 55.4; H, 2.6.

General Procedure for the Preparation of 3-Arylpropargyl Alcohols. Preparation of 3-(2,5-Difluorophenyl)propargyl Alcohol (5a). To a solution of methyl (2,5-difluorophenyl)propiolate (1.20 g, 6.12 mmol) in 15 mL of dry THF cooled to −78 °C under a nitrogen atmosphere was added dropwise via syringe a 1 M solution of diisobutylaluminum hydride in hexane (12.3 mL, 12.3 mmol). The resulting mixture was warmed to ambient temperature, and 1.5 mL of saturated NH_4Cl solution was added to the reaction mixture, forming a gel. The gel was broken up with 3 mL of 10% HCl. The reaction mixture was diluted with ether (35 mL), washed with 10% HCl (2 × 50 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated. The residue was purified by gradient elution chromatography on silica gel with 1/1 (v/v) hexane/dichloromethane to dichloromethane to give 0.86 g (84% of **5a** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.00 (m, 3 H), 4.50 (s, 2 H), 2.70 (br s, 1 H); IR (film) 3340 (br), 2240 cm^{-1}; FDMS, *m/e* 168 ($C_9H_6F_2$). Anal. Calcd for $C_9H_6F_2O$: C, 64.3; H, 3.6. Found: C, 63.9; H, 3.9.

3-(4-Fluorophenyl)propargyl alcohol (5b): 72%; oil; ^{1}H NMR ($CDCl_3$) δ 7.37 (dd, 2 H, *J* = 5, 9 Hz), 6.91 (t, 2 H, *J* = 9 Hz), 4.50 (br s, 2 H), 3.79 (br s, 1 H); IR (film) 3340 (br), 2240 cm^{-1}; FDMS, *m/e* 150 (C_9H_7FO). Anal. Calcd for C_9H_7FO: C, 71.2; H, 4.8. Found: C, 71.1; H, 4.8. The alcohol was heat and air sensitive.

3-(4-Methoxyphenyl)propargyl alcohol (5c): 95%; mp 62.5–64.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.38 (d, 2 H, *J* = 9 Hz), 6.80 (d, 2 H, *J* = 9 Hz), 4.46 (s, 2 H), 3.78 ns, 3 H), 2.33 (br s, 1 H); IR (KBr) 3260, 2240 cm^{-1}; FDMS, *m/e* 162 ($C_{10}H_{10}O_2$). Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.1; H, 6.2. Found: C, 73.7; H, 6.1.

3-(2-Thienyl)propargyl alcohol (5d): 76%; oil; ^{1}H NMR ($CDCl_3$) δ 7.13 (m, 2 H), 6.87 (m, 1 H), 4.45 (s, 2 H), 3.32 (br s, 1 H); IR (film) 3340, 3100, 2920, 2860, 2310 cm^{-1}; FDMS, *m/e* 138 (C_7H_6OS). Anal. Calcd for C_7H_6OS: C, 60.1; H, 4.4. Found: C, 60.0; H, 4.4.

General Procedure for Preparation of Arylpropargyl Aldehydes. Preparation of (2,5-Difluorophenyl)propargyl Aldehyde (6a). Pyridinium chlorochromate (1.89 g, 8.80 mmol) was added to a slurry of **5a** (0.74 g, 4.40 mmol), dry Celite (2.2 g), and dichloromethane (25 mL). The resulting mixture was stirred at ambient temperature for 1.5 h and was then diluted with 100 mL of ether. The resulting mixture was filtered through a pad of silica gel and concentrated to give **6a** as a yellow oil: 0.54 g, 74% yield; ^{1}H NMR ($CDCl_3$) δ 9.43 (s, 1 H), 7.19 (m, 3 H); IR (film) 2200, 1665 cm^{-1}; FDMS, *m/e* 166 ($C_9H_4F_2O$). Anal. calcd for $C_9H_4F_2O$: C, 65.1; H, 2.4. Found: C, 64.9; H, 2.8.

(4-Fluorophenyl)propargyl aldehyde (6b): 55%; oil; ^{1}H NMR ($CDCl_3$) δ 9.38 (s, 1 H), 7.57 (dd, 2 H, *J* = 5, 9 Hz), 7.03 (t, 2 H, *J* = 9 Hz); IR (film) 2185, 1655 cm^{-1}; FDMS, *m/e* 148 (C_9H_5FO). Anal. Calcd for C_9H_5FO: C, 73.0; H, 3.4. Found: C, 72.6; H, 3.6. The aldehyde was air sensitive.

(4-Methoxyphenyl)propargyl aldehyde (6c): 51.5%; mp 47–48.5 °C; ^{1}H NMR ($CDCl_3$) δ 9.28 (s, 1 H), 7.42 (d, 2 H, *J* = 9 Hz), 6.80 (d, 2 H, *J* = 9 Hz), 3.78 (s, 3 H); IR (KBr) 2180, 1650 cm^{-1}; FDMS, *m/e* 160 ($C_{10}H_8O_2$). Anal. Calcd for $C_{10}H_8O_2$: C, 75.0; H, 5.0. Found: C, 74.7; H, 4.9.

General Procedure for the Preparation of 1,4-Pentadiyn-3-ols. Preparation of 1-(2,5-Difluorophenyl)-5-phenyl-1,4-pentadiyn-3-ol (7d). To a solution of phenylacetylene (0.30 g, 2.47 mmol) in 10 mL of dry THF cooled to −78 °C, under a nitrogen atmosphere, was added dropwise via syringe a 2.5 M solution of *n*-butyllithium in hexane (1.0 mL, 2.5 mmol). The reaction mixture was stirred for 15 min at −78 °C and was then warmed to ambient temperature. A solution of the aldehyde **6d** in 10 mL of THF (2.5 mmol) was added over 15 min. The reaction mixture was quenched with saturated NH_4Cl solution (15 mL) and was diluted with ether (50 mL). The organic phase was washed with brine (30 mL), dried over Na_2SO_4, and concentrated. The residue was purified by gradient elution chromatography on silica gel with 1/1 (v/v) hexane–dichloromethane to dichloromethane to give 0.53 g (80%) of **7d** as a yellow solid: mp 74.5–76.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.25 (m, 8 H), 5.60 (d, 1 H, *J* = 7 Hz), 2.53 (d, 1 H, *J* = 7 Hz); IR (KBr) 3265 (br), 2230 cm^{-1}; FDMS, *m/e* 268 ($C_{17}H_{10}F_2O$). Anal. calcd for $C_{17}H_{10}F_2O$: C, 76.1; H, 3.8. Found: C, 76.1; H, 3.9.

1-(4-Methoxyphenyl)-5-phenyl-1,4-pentadiyn-3-ol (7b): 51%; mp 40–45 °C; ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 7 H), 6.80 (d, 2 H, *J* = 9 Hz), 5.51 (s, 1 H), 3.80 (s, 3 H), 2.44 (br s, 1 H); IR (KBr) 3320 (br), 2315 cm^{-1}; FDMS, *m/e* 262 ($C_{18}H_{14}O_2$). Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.4; H, 5.4. Found: C, 82.1; H, 5.6.

1-(4-Fluorophenyl)-5-phenyl-1,4-pentadiyn-3-ol (7c): 96% mp 91.5–93 °C; ^{1}H NMR ($CDCl_3$) δ 7.42 (m, 7 H); 7.00 (t, 2 H, *J* = 9 Hz), 5.57 (d, 1 H, *J* = 7 Hz), 2.48 (d, 1 H, *J* = 7 Hz); IR (KBr) 3330 (br), 2240 cm^{-1}; FDMS, *m/e* 250 ($C_{17}H_{11}FO$). Anal. Calcd for $C_{17}H_{11}FO \cdot H_2O$: C, 76.1; H, 4.9. Found: C, 75.7; H, 4.5.

1-(Trimethylsilyl)-5-phenyl-1,4-pentadiyn-3-ol (7e): 86%; oil; ^{1}H NMR ($CDCl_3$) δ 7.3 (m, 5 H), 5.27 (d, 1 H, *J* = 6 Hz), 2.42 (d, 1 H, *J* = 6 Hz), 0.20 (s, 9 H); IR (film) 3330, 2205, 2160 cm^{-1}; FDMS, *m/e* 228 ($C_{14}H_{16}OSi$). Anal. Calcd for $C_{14}H_{16}OSi$: C, 73.6; H, 7.1. Found: C, 73.2; H, 7.3.

1-Phenyl-8-[(dimethyl-*tert*-butylsilyl)oxy]-1,4-octadiyn-3-ol (7g): 97%; oil; ^{1}H NMR ($CDCl_3$) δ 7.56 (m, 5 H), 5.53 (t, 1 H, *J* = 2 Hz), 3.93 (t, 2 H, *J* = 6 Hz), 3.17 (br s, 1 H), 2.58 (dt, 2 H, *J* = 2, 6 Hz), 1.90 (m, 2 H), 1.15 (s, 9 H), 0.33 (s, 6 H); IR (film) 3340, 2280, 2220 cm^{-1}; FDMS, *m/e* 271 (M− C_4H_9).

Diynols **7f** and **7h** were prepared as described above but were oxidized directly to the diynones **8** with MnO_2 without characterization.

General Procedure for the Chromic Acid Oxidation of Diynols 5 to Diynones 8. Preparation of 1-(2,5-Difluorophenyl)-5-phenyl-1,4-pentadiyn-3-ol (8d). To a solution of **5a** (0.50 g, 1.86 mmol) in 4 mL of acetone cooled to 5 °C was added a 10% chromic acid solution[7] (3.85 mL). The reaction mixture was warmed to ambient temperature, where stirring was continued for 0.5 h. The reaction mixture was diluted with water (25 mL) and was extracted with dichloromethane (3 × 30 mL). The combined organic extracts were washed with brine (3 × 30 mL) and saturated $NaHCO_3$ (30 mL), dried over Na_2SO_4, and concentrated. The residue was purified by gradient elution chromatography on silica gel with 3/1 (v/v) hexane/dichloromethane to 1/3 (v/v) hexane/dichloromethane to give 0.38 g (76%) of **8d** as a yellow crystalline solid: ^{1}H NMR ($CDCl_3$) δ 7.38 (m, 8 H); IR (KBr) 2300, 1625, 1610, 1595 cm^{-1}; FDMS, *m/e* 266 ($C_{17}H_8F_2O$). Anal. Calcd for $C_{17}H_8F_2O$: C, 76.7; H, 3.0. Found: C, 76.8; H, 3.1.

1-(4-Methoxyphenyl)-5-phenyl-1,4-pentadiyn-3-one (8b): 80%; ^{1}H NMR ($CDCl_3$) δ 7.50 (m, 7 H), 6.88 (d, 2 H, *J* = 9 Hz), 3.82 (s, 3 H); IR (KBr) 2220, 2170, 1610, 1595 cm^{-1}; FDMS, *m/e* 260 ($C_{18}H_{12}O_2$). Anal. Calcd for $C_{18}H_{12}O_2$: C, 83.1; H, 4.6. Found: C, 82.7; H, 4.7.

1-(4-Fluorophenyl)-5-phenyl-1,4-pentadiyn-3-one (8c): 72%; ^{1}H NMR ($CDCl_3$) δ 7.56 (m, 7 H), 7.09 (t, 2 H, *J* = 9 Hz); IR (KBr) 2215, 2175, 1620, 1600 cm^{-1}; FDMS, *m/e* 248 ($C_{17}H_9FO$). Anal. Calcd for $C_{17}H_9FO$: C, 82.2; H, 3.7. Found: C, 81.8; H, 3.8.

1-(Trimethylsilyl)-5-phenyl-1,4-pentadiyn-3-one (8e): 62%; ^{1}H NMR ($CDCl_3$) δ 7.60 (m, 2 H), 7.42 (m, 3 H), 0.30 (s, 9 H); IR (film) 2200, 2160, 1625 cm^{-1}; FDMS, *m/e* 226 ($C_{14}H_{14}OSi$). Anal. Calcd for $C_{14}H_{14}OSi$: C, 74.3; H, 6.2. Found: C, 73.9; H, 6.1.

General Procedure for Manganese Dioxide Oxidation of Diynols 7 to Diynones 8. Preparation of 8-[(Dimethyl-

tert-butylsilyl)oxy]-1-phenyl-1,4-octadiyn-3-one (8g). Diynol **7g** (4.50 g, 13.7 mmol) was dissolved in 50 mL of benzene. Manganese dioxide (30.0 g, 34 mmol) was added in two portions (the second 1.5 h after the first). The resulting mixture was stirred at ambient temperature for 3 h. The reaction mixture was filtered through a pad of Celite. The filter cake was washed with dichloromethane (3 × 50 mL). The combined filtrates were concentrated to give 4.30 g (96%) of **8g** as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.73 (m, 2 H), 7.45 (m, 3 H), 3.83 (t, 2 H, J = 6 Hz), 2.65 (t, 2 H, J = 6.5 Hz), 1.92 (m, 2 H), 1.03 (s, 9 H), 0.20 (s, 6 H); IR (film) 2960, 2940, 2865, 2230, 2215, 1630 cm^{-1}; FDMS, m/e 269 (M − C_4H_9).

1-Phenyl-1,4-pentadiyn-3-one (8f): 47% from **2a**; ^{1}H NMR ($CDCl_3$) δ 7.52 (m, 5 H), 3.40 (s, 1 H); IR (KBr) 3250, 2200, 2090, 1625, 1600 cm^{-1}; FDMS, m/e 154 ($C_{11}H_6O$). Anal. Calcd for $C_{11}H_6O$: C, 85.7; H, 3.9. Found: C, 85.2; H, 4.0.

General Procedure for the Preparation of Diynones 8 via Aluminum Chloride Mediated Coupling of Arylpropiolic Acid Chlorides with (Trimethylsilyl)acetylenes. Preparation of 5-Phenyl-1,4-pentadiyn-3-one (5f). Phenylpropiolic acid (2.0 g, 13.7 mmol) was stirred in 10 mL of thionyl chloride for 16 h under a nitrogen atmosphere. The reaction mixture was concentrated to give the acid chloride, which was immediately used in the coupling reaction. To an aluminum chloride (1.74 g, 13.0 mmol) suspension in dichloromethane (35 mL) cooled to −78 °C under a nitrogen atmosphere was added over a 30-min period a solution of phenylpropargylic acid chloride (1.95 g, 11.8 mmol) and (trimethylsilyl)acetylene (2.50 mL, 17.8 mmol) in 25 mL of dichloromethane. The reaction mixture was stirred at −78 °C for 1 h, warmed to −10 °C, and poured over ice (75 g) in a separatory funnel. The separatory funnel was shaken vigorously until the organic phase lightened in color. Water (75 mL) was added, and the solution was warmed to ambient temperature. The aqueous layer was extracted with dichloromethane (3 × 50 mL). The combined organic extracts were dired over Na_2SO_4, filtered through a 5-cm plug of silica gel eluted with dichloromethane, and concentrated. Recrystallization from ligroin gave 1.42 g (78%) of **8f**.

Preparation of 5-Chloro-1-phenyl-5-(2-thienyl)pent-4-en-1-yn-3-one (9). 2-Thienylpropiolic acid (5.0 g, 33 mmol), (trimethylsilyl)phenylacetylene (5.7 g, 33 mmol), and aluminum chloride (4.82 g, 36 mmol) were treated as described above for the preparation of **8f**. The reaction mixture was stirred for 16 h at −78 °C before workup. The residue was recrystallized from ethyl ether to give 4.88 g (54%) of **9** as a tan solid: ^{1}H NMR ($CDCl_3$) δ 7.46 (m, 7 H), 7.04 (m, 1 H), 6.90 (s, 1 H); IR (KBr) 3100 (w), 2220, 2190, 1600 (s), 1595 (s), 1580 cm^{-1}; FDMS, m/e 272 ($C_{15}H_9ClOS$). Anal. Calcd for $C_{15}H_9ClOS$: C, 66.1; H, 3.3. Found: C, 66.1; H, 3.1.

General Procedure for the Preparation of 2-Substituted 6-Phenyltellura-4*H*-pyran-4-ones from Unsymmetrical 1,4-Pentadiyn-3-ones. Preparation of 2-(*p*-Fluorophenyl)-6-phenyltellura-4*H*-pyran-4-one (10b). A 1 M solution of lithium triethylborohydride in hexane (2.5 mL, 2.5 mmol) was added to tellurium shot (0.14 g, 1.1 mmol) under nitrogen. The mixture was heated at reflux for 2 h until a suspended white solid in a clear solution was obtained. To a solution of **8c** in ethanol (2.5 mL) was added dropwise a 1 M solution of sodium ethoxide in ethanol (0.5 mL). The resulting solution was stirred until TLC analysis on silica gel eluted with dichloromethane showed complete addition of ethanol (R_f for **8c**, 0.9; R_f for ethanol addition product, 0.65). To the dilithium telluride solution was added 1 M sodium ethoxide in ethanol (2.5 mL). The resulting mixture was cooled to −5 °C and the diynone–ethanol adduction solution was then added. The resulting mixture was stirred for 0.5 h at −5 °C and was then heated to reflux for 0.5 h. The reaction mixture was diluted with water (100 mL), and the products were extracted with dichloromethane (4 × 25 mL). The combined organic extracts were filtered through a pad of Celite to remove tellurium and then washed sequentially with water and brine, dried over Na_2SO_4, and concentrated. The residue was purified by gradient elution chromatography on silica gel with 1% ethyl acetate/dichloromethane to 10% ethyl acetate/dichloromethane. The product was recrystallized from acetonitrile to give 0.20 g (53%) of **10b** as yellow needles: ^{1}H NMR ($CDCl_3$) δ 7.47 (m, 7 H), 7.36 (s, 1 H), 7.31 (s, 1 H), 7.17 (t, 2 H, J = 9 Hz); IR (KBr) 3050 nw), 1595 (s), 1570, 1500 cm^{-1}; FDMS, m/e 380 ($C_{17}H_{11}FO^{130}Te$). Anal. Calcd for $C_{17}H_{11}FOTe$: C, 54.0; H, 2.9. Found: C, 54.0; H, 3.0.

2-(4-Methoxyphenyl)-6-phenyltellura-4*H*-pyran-4-one (10a): ^{1}H NMR ($CDCl_3$) δ 7.47 (m, 7 H), 7.34 (s, 1 H), 7.32 (s, 1 H), 6.98 (d, 2 H, J = 8.3 Hz), 3.90 (s, 3 H); IR (KBr) 2950 (w), 1585, 1570, 1550, 1505, 1490 cm^{-1}; FDMS, m/e 392 ($C_{18}H_{14}O_2{}^{130}Te$). Anal. Calcd for $C_{18}H_{14}O_2Te$: C, 55.4; H, 2.5. Found: C, 55.6; H, 3.5.

2-(2,5-Difluorophenyl)-6-phenyltellura-4*H*-pyran-4-one (10c): ^{1}H NMR ($CDCl_3$) δ 7.48 (s, 5 H), 7.34 (s, 1 H), 7.27 (s, 1 H), 7.31 (m, 3 H); IR (film) 3060, 1590 (s), 1490 cm^{-1}; FDMS, m/e 398 ($C_{17}H_{10}F_2O^{130}Te$). Anal. Calcd for $C_{17}H_{10}F_2OTe$: C, 51.6; H, 2.5. Found: C, 51.4; H, 2.3.

2-[3-[(Dimethyl-*tert*-butylsilyl)oxy]propyl]-6-phenyltellura-4*H*-pyran-4-one (10e): ^{1}H NMR ($CDCl_3$) δ 7.37 (s, 5 H), 7.00 (s, 1 H), 6.83 (br s, 1 H, signal sharpens when triplet at δ 2.67 is decoupled), 3.68 (t, 2 H, J = 5.8 Hz), 2.67 (br t, 2 H, J = 7.5 Hz, signal sharpens when singlet at δ 6.83 is decoupled), 1.88 (m, 2 H); IR (film) 2945, 2860, 1600 cm^{-1}; FDMS, m/e 401 (M − C_4H_9).

Preparation of 2-(3-Hydroxypropyl)-6-phenyltellura-4*H*-pyran-4-one (10f). Tellurapyranone **10e** (0.46 g, 1.0 mmol) was dissolved in 5 mL of 1 M tetra-*n*-butylammonium tetrafluoroborate in THF. The resulting solution was stirred at ambient temperature for 15 h. The reaction mixture was poured into 50 mL of water. The products were extracted with 1/1 (v/v) ether/ethyl acetate (3 × 25 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by chromatography on silica gel eluted with 30% ethyl acetate/dichloromethane. Recrystallization of the residue from 1/1 (v/v) acetonitrile/CCl_4 gave 0.14 g (42%) of **10f**: ^{1}H NMR ($CDCl_3$) δ 7.75 (s, 1 H), 7.40 (s, 5 H), 3.72 (t, 2 H, J = 5.8 Hz), 2.71 (t, 2 H, J = 7.5 Hz), 1.98 (m, 2 H), 1.60 (br s, 1 H); FDMS, m/e 344 ($C_{14}H_{14}O_2{}^{130}Te$). Anal. Calcd for $C_{14}H_{14}O_2Te$: C, 49.2; H, 4.1. Found: C, 49.2; H, 4.1.

Preparation of 2-Phenyltellura-4*H*-pyran-4-one (10d). Sodium borohydride (1.0 g, 2.6 mmol) was added in several portions over a 1-h period to tellurium powder (1.30 g, 10.2 mmol) in 50 mL of ethanol. After addition was complete, the reaction mixture was heated to reflux for 10 min and then cooled to ambient temperature. A 1 M solution of sodium ethoxide in ethanol (20 mL) was added. 1-Phenyl-1,4-pentadiynone (**8f**; 1.60 g, 10.4 mmol) in 20 mL of ethanol was added. The reaction mixture was poured into water (500 mL), and the products were extracted with dichloromethane (3 × 100 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel and eluted with 20% ethyl acetate/dichloromethane to give 0.36 g (12%) of **10d**: ^{1}H NMR ($CDCl_3$) δ 8.70 (d, 1 H, J = 11.4 Hz), 7.45 (s, 5 H), 7.35 (dd, 1 H, J = 1.0, 11.4 Hz), 7.27 (d, 1 H, J = 1.0 Hz); IR (KBr) 3050 nw), 1560 (s), 1530, 1480, 1440 cm^{-1}; FDMS, m/e 286 ($C_{11}H_8O^{130}Te$).

Preparation of 2-(2-Thienyl)-6-phenyltellura-4*H*-pyran-4-one (10g). A 1 M solution of lithium triethylborohydride in THF (8.1 mL, 8.1 mmol) was added to tellurium shot (0.41 g, 3.22 mmol) under a nitrogen atmosphere. The resulting mixture was heated at reflux for 2 h until a suspended white solid in a clear solution was obtained. The solution was cooled to −10 °C and 8 mL of absolute ethanol was added. Ynene **9** in 10 mL of THF was added, and the resulting mixture was stirred at −10 °C for 15 min and then heated at reflux for 1 h. The reaction mixture was concentrated, and the residue was triturated with 200 mL of dichloromethane. The organic solution was filtered through a pad of Celite and then through a pad of silica gel and concentrated. The residue was purified by chromatography on silica gel and eluted with 10% ethyl acetate/dichloromethane. The product was recrystallized from acetonitrile to give 0.32 g (30%) of **10g**: ^{1}H NMR ($CDCl_3$) δ 7.36 (s, 5 H), 7.23 (s, 1 H), 7.17 (s, 1 H), 7.16 (m, 3 H); IR (KBr) 3390 (w), 3380, 1590 (s), 1570, 1545, 1490, 1445, 1415 cm^{-1}; FDMS, m/e 368 ($C_{15}H_{10}OS^{130}Te$). Anal. Calcd for $C_{15}H_{10}OSTe$: C, 49.2; H, 2.8. Found: C, 49.0; H, 2.9.

Registry No. **1a**, 108932-57-6; **1b**, 109034-19-7; **1c**, 109034-20-0; **2a**, 4891-38-7; **2b**, 74714-06-0; **2c**, 109034-21-1; **2d**, 109034-22-2;

2e, 7515-17-5; 2f, 71797-96-1; 2g, 42122-44-1; 2h, 109034-23-3; 2i, 109034-24-4; 2j, 6824-26-6; 2k, 109034-25-5; 2l, 109034-26-6; 2m, 2216-94-6; 2n, 62497-24-9; 3a, 637-44-5; 3b, 4843-44-1; 4a, 7299-58-3; 4b, 109034-48-2; 4c, 109034-49-3; 4d, 21985-04-6; 5a, 109034-27-7; 5b, 80151-28-6; 5c, 37614-59-8; 5d, 1194-13-4; 6a, 109034-28-8; 6b, 74929-23-0; 6c, 90696-21-2; 7a, 15814-32-1; 7b, 109034-29-9; 7c, 109034-30-2; 7d, 109034-31-3; 7e, 109034-32-4; 7f, 62679-57-6; 7g, 109034-33-5; 7h, 109034-50-6; 8a, 15814-30-9; 8b, 109034-34-6; 8c, 109034-35-7; 8d, 109034-36-8; 8e, 109034-37-9; 8f, 54668-28-9; 8g, 109034-38-0; 8h, 109034-39-1; 9, 109034-40-4; 10a, 109034-41-5; 10b, 109034-42-6; 10c, 109034-43-7; 10d, 109034-44-8; 10e, 109034-45-9; 10f, 109034-46-0; 10g, 109034-47-1; 2,4,6-$Me_3C_6H_3$, 108-67-8; PhH, 71-43-2; 2,6-$Me_2C_6H_4$, 108-38-3; 4-$MeOC_6H_5$, 100-66-3; 2,5-$(MeO)_2C_6H_4$, 150-78-7; 4-F-C_6H_5, 462-06-6; 2,5-$F_2C_6H_4$, 540-36-3; 2-$MeOC_{10}H_7$, 93-04-9; 2,4-$(MeO)_2C_6H_4$, 151-10-0; 4-*t*-BuC_6H_5, 98-06-6; 3,4-$(MeO)_2C_6H_4$, 91-16-7; PhC≡CHO, 2579-22-8; $Me_3SiC{\equiv}CLi$, 54655-07-1; *t*-$BuMe_2SiO(CH_2)_3C{\equiv}CLi$, 61600-82-6; PhC≡CH, 536-74-3; $Me_3SiC{\equiv}CH$, 1066-54-2; $Me_3SiC{\equiv}CPH$, 2170-06-1; thiophene, 110-02-1; tetrachlorocyclopropane, 6262-42-6.

Synthesis of New Cyclic Sulfur Ylides 9-Alkyl-10-cyano-9-thiaphenanthrenes and Their Novel Addition Reactions with Acetylenic Electrophiles

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Novel cyclic sulfur ylides 9-alkyl-10-cyano-9-thiaphenanthrenes **5** were synthesized in good yield by proton abstraction from the corresponding 10*H*-9-thiaphenanthrenium salts **4** with triethylamine in ethanol. 10-Cyano-9-methyl-9-thiaphenanthrene (**5a**) was treated with dimethyl or diethyl acetylenedicarboxylate in benzene to afford three 1:1 adducts, novel spiro compounds **7a,b**, dibenzothiocin derivatives **8a,b**, and benzothiocinium ylide derivatives **9a,b**. On the contrary, treatment of 9-ethylthiaphenanthrene derivative **5b** with the above acetylenic compounds afforded dibenzothiepin derivatives **16a,b** as major products together with dibenzothiocinium ylide derivatives **17a,b**. 10-Cyano-10-methyl-10*H*-9-thiaphenanthren-9-ium 9-methanide (D), generated from 10-cyano-9,10-dimethyl-10*H*-9-thiaphenanthrenium salt **10** by deprotonation with sodium hydride, rearranged to afford the two isomeric spiro compounds **11** and **12**. On heating at 200 °C, the spiro compounds **7a,b** underwent 1,5-sigmatropic rearrangement to afford dibenzothionin derivatives **14a,b** in high yield. On the other hand, pyrolysis of the spiro compounds **11** and **12** under similar conditions caused 1,3-rearrangement to give dibenzothiepin derivative **15**. Reaction of **5a** with methyl propiolate afforded 1:2 adduct **18**. Mechanisms for the above reactions are also discussed.

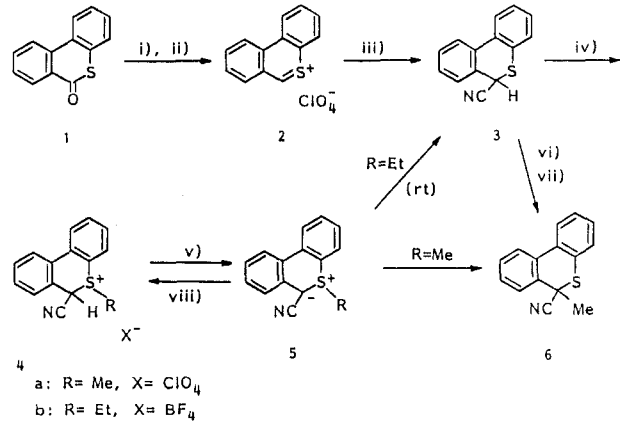
In conjunction with our interest in the chemistry of cyclic sulfur ylides, we have already reported the synthesis and reactions of 1- or 2-thianaphthalene derivatives[1] and 10-thiaanthracene derivatives,[2] in which ylide bond forms part of a cyclic conjugated ring system containing six π-electrons. In the reactions with various kinds of electrophiles, especially, unusual addition reactions occurred to provide a number of novel sulfur-containing heterocyclic compounds. This prompted us to investigate the synthesis and reactions with electrophiles of other new types of stable cyclic sulfur ylides.

We report here the synthesis and the novel addition reactions with acetylenic electrophiles of new cyclic sulfur ylides, 9-alkyl-10-cyano-9-thiaphenanthrenes **5**, which are considered to have the skeletons of both 1- and 2-thianaphthalenes. Addition products were quite unique compared with those observed from 1- or 2-thianaphthalenes.

Results and Discussion

Synthesis and Thermal Stability of 9-Alkyl-10-cyano-9-thiaphenanthrenes. The four-step synthesis of the title compounds was performed as shown in Scheme I.

Scheme I[a]



[a] Reagents: (i) $LiAlH_4$, ether; (ii) 70% $HClO_4$; (iii) NaCN, ClC-H_2CH_2Cl; (iv) RI, AgX, CH_2Cl_2; (v) Et_3N, EtOH; (vi) NaH, THF; (vii) MeI; (viii) HX.

I. 9-Thiaphenanthrenylium perchlorate (**2**) was already synthesized by Lüttringhaus et al. in 1961.[3] However, their method requires five steps, and the yield in the Pschorr cyclization step is poor. Therefore, we investigated the improvement of the steps number and the yield. 3,4-Benzothiocoumarin (**1**) was easily synthesized by

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(2) Hori, M.; Kataoka, T.; Shimizu, H.; Ohno, S. *J. Org. Chem.* **1980**, *45*, 2468.

(3) Lüttringhaus, A.; Kolb, A. *Z. Naturforsch., B. Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1961**, *16B*, 762.

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