

the receiver. It had mp 81–83 °C and was identical in all respects with the material described above.

Diethyl 3-Amino-2-benzoylglutaconate (9). A solution of 74 g (0.33 mol) of diethyl 3-aminoglutaconate and 36 g (0.33 mol) of 2,6-lutidine in 500 mL of THF was stirred at reflux while 47 g (0.33 mol) of benzoyl chloride was added dropwise over a 30-min period. After the mixture was heated overnight the solvent was evaporated and the residue partitioned between ether and H₂O. The ether phase was separated, dried, and evaporated to give an oily residue which was chromatographed on 400 g of Florisil. Elution with 6 L of 4:1 (v/v) pentane–benzene removed the N-benzoylated isomer. Further elution with 4 L of ether removed the C-benzoylated isomer 9. Recrystallization from ethyl acetate–pentane gave 19 g (19% yield) of 9 as white crystals, mp 77 °C. Anal. Calcd for C₁₆H₁₉NO₆: C, 62.94; H, 6.27; N, 4.59. Found: C, 63.04; H, 6.37; N, 4.45.

Oxazine 10 and Pyrone 11. A solution of 6.1 g (0.02 mol) of diester 9 and 4.3 g (0.04 mol) of 2,6-lutidine in 100 mL of dry ether was cooled to 0 °C and combined with 2 mL of phosgene in 20 mL of ether. The reaction was allowed to stand for 15 days under an inert atmosphere. Water was added and the layers were separated. Evaporation of the ether layer gave an oil which was chromatographed on 1 kg of silica gel. The column was eluted with 19:1 (v/v) CCl₄–acetone and 20-mL fractions were collected. Fractions 228 to 252 were combined and evaporated, and the residue was recrystallized from ether–pentane to give 2 g (30% yield) of oxazinone 10 as yellow crystals: mp 97 °C; IR (CHCl₃) 1775, 1735, 1725 cm⁻¹ (CO); ¹H NMR (CDCl₃) δ 1.04 and 1.30 (2 t, *J* = 8 Hz, 6 H, 2 OCH₂CH₃), 4.2 (2 q, *J* = 8 Hz, 4 H, 2 OCH₂CH₃), 5.23 (s, 1 H, vinyl), 7.5 (s, 5 H, C₆H₅), 11.0 (s, 1 H, NH). Anal. Calcd for C₁₇H₁₇NO₆: C, 61.61; H, 5.17; N, 4.23; *m/e* 331.1055 (M⁺). Found: C, 61.40; H, 5.19; N, 4.23; *m/e* 331.1068.

Fractions 276 to 324 were pooled and evaporated, and the residue was recrystallized from ether–pentane to give 1 g (15%

yield) of the pyrone 11 as white crystals: mp 87 °C; IR (CHCl₃) 3400, 3250 (NH₂), 1755–1690 cm⁻¹ (CO's); ¹H NMR (CDCl₃) δ 0.8 (t, *J* = 8 Hz, 3 H, OCH₂CH₃), 1.4 (t, *J* = 7 Hz, 3 H, OCH₂CH₃), 3.95 (q, *J* = 8 Hz, 2 H, OCH₂CH₃), 4.39 (q, *J* = 7 Hz, 2 H, OCH₂CH₃), 7.4–8.2 (m, 5 H, C₆H₅), 9.8 (s, 2 H, NH₂). Anal. Calcd for C₁₇H₁₇NO₆: C, 61.61; H, 5.17; N, 4.23; *m/e* 331.1055 (M⁺). Found: C, 61.32; H, 5.05; N, 4.08; *m/e* 331.1072.

5-Carboethoxy-4-ethylidene-3,4-dihydro-6-phenyl-2H-1,3-oxazin-2-one (13). A solution of 9.7 g (0.04 mol) of ethyl 3-amino-2-benzoylpent-2-enoate (12)⁴ and 10.7 g (0.1 mol) of 2,6-lutidine in 200 mL of dry ether was combined at 0 °C with 4.5 g (0.045 mol) of phosgene in 30 mL of ether. The reaction was allowed to stand under an inert atmosphere for 5 days. Water was then added. The ether phase was separated, washed with dilute HCl, and filtered to give a dark oil that crystallized when triturated with MeOH. Recrystallization from ether gave 700 mg (7% yield) of oxazinone 13 as pale yellow crystals: mp 157–159 °C; IR (CHCl₃) 1765, 1750, 1725 cm⁻¹ (CO); ¹H NMR (CDCl₃) δ 1.0 (t, *J* = 6 Hz, 2 H, OCH₂CH₃), 1.7 (d, *J* = 7 Hz, 3 H, =CHCH₃), 4.1 (q, *J* = 6 Hz, 2 H, OCH₂CH₃), 4.8 (q, *J* = 7 Hz, 1 H, =CHCH₃), 7.45 (m, 5 H, C₆H₅), 8.35 (s, 1 H, NH). Anal. Calcd for C₁₅H₁₅NO₄: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.79; H, 5.57; N, 5.11.

Registry No. 1, 21486-64-6; 2, 74947-55-0; 3, 74947-56-1; 4, 74947-57-2; 5, 74947-58-3; 6, 74947-59-4; 7, 74947-60-7; 8, 74947-61-8; 9, 74947-62-9; 10, 74947-63-0; 11, 74947-64-1; 12, 74947-65-2; 13, 74947-66-3; phosgene, 75-44-5; diethyl 3-aminoglutaconate, 54889-50-8; benzene chloride, 98-88-4; ethyl 3-pyrrolidin-1-ylcinnamate, 53256-23-8; 1-nitropropane, 108-03-2; phenyl isocyanate, 103-71-9; 4-carboethoxy-3-ethyl-5-phenylisoxazole, 74947-67-4; ethyl 3-amino-2-benzoylpent-2-enoate, 74947-68-5.

Supplementary Material Available: ¹³C NMR data of oxazines 4, 7, and 8 (1 page). Ordering information is given on any current masthead page.

Regiochemical Control of the Addition of Aryl Selenols and Aryl Thiols to the Triple Bond of Arylpropiolates. Synthesis of Seleno- and Thioflavones and Seleno- and Thioaurones

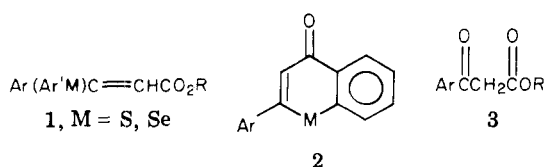
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Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

Received April 29, 1980

Addition of aryl selenols and aryl thiols to arylpropiolates under basic conditions followed by saponification gave exclusively β-substituted cinnamates of predominant *Z* stereochemistry. Neat solutions of aryl selenols or aryl thiols and arylpropiolates after saponification gave α-substituted cinnamates of presumed *Z* stereochemistry. The latter reactions are assumed to be radical additions. Cyclization of the cinnamates with phosphorus pentoxide–methanesulfonic acid gave seleno- and thioflavones and 2-arylidene-3-oxo-2H-benzo[*b*]selenophenes and -thiophenes.

β-(Arylthio)- and β-(arylseleno)cinnamates (1) are useful precursors of the corresponding thio- and selenoflavones (2).¹ Typically, the cinnamates 1 have been prepared by



condensing an appropriate β-keto ester (3) with the cor-

responding aryl thiol or aryl selenol.^{1,2} Although β-keto esters are easily obtained,³ the condensations frequently give poor yields. Similarly, subsequent cyclization of the cinnamates with hot polyphosphoric acid⁴ or with aluminum chloride and the corresponding acid chloride⁵ often

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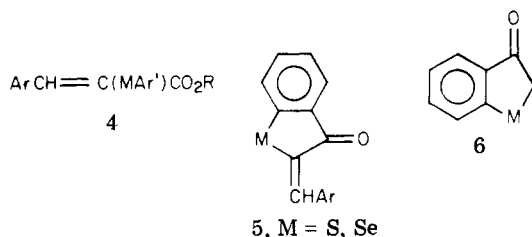
Table I. Michael Additions of Thiols and Selenols to Arylpropiolates. Preparation of $\text{Ar}(\text{Ar}'\text{M})\text{C}=\text{CHCO}_2\text{H}^a$

compd	Ar	Ar'	M	% yield ^b	mp, °C	¹ H NMR ^c	Z/E ratio
7	C ₆ H ₅	C ₆ H ₅	Se	81	171-175	6.30	
8	4-CH ₃ OC ₆ H ₄	C ₆ H ₅	Se	96	169-169.5	6.30	
9	2,5-(CH ₃) ₂ C ₆ H ₃	C ₆ H ₅	Se	40	175-178	6.39	
10	2,5-(CH ₃ O) ₂ C ₆ H ₃	C ₆ H ₅	Se	68	167-171	6.45	
11	2-CH ₃ OC ₆ H ₄	C ₆ H ₅	Se	55	183-185	6.36	
12	C ₆ H ₅	C ₆ H ₅	S	86	138-144	6.20, 5.35	5/1
13	4-CH ₃ OC ₆ H ₄	C ₆ H ₅	S	81	135-138	6.10, 5.35	5/1
14	2,5-(CH ₃ O) ₂ C ₆ H ₃	C ₆ H ₅	S	84	141-144	5.90, 5.50	4/1
15	2-CH ₃ OC ₆ H ₄	C ₆ H ₅	S	78	200-203	6.00	
16	C ₆ H ₅	1-C ₁₀ H ₇	S	80	179-190	6.05, 5.35	7/1
17	4-CH ₃ OC ₆ H ₄	1-C ₁₀ H ₇	S	75	171-176	6.10	
18	2,5-(CH ₃) ₂ C ₆ H ₃	1-C ₁₀ H ₇	S	76	221-222	5.90	
19	2,5-(CH ₃ O) ₂ C ₆ H ₃	1-C ₁₀ H ₇	S	48	149-161	6.00, 5.20	>10/1
20	2-CH ₃ OC ₆ H ₄	1-C ₁₀ H ₇	S	69	216-217	5.95	

^a Suitable analytical data ($\pm 0.4\%$ for C, H, and S or Se) were obtained for all compounds except 12, which gave the following data. Calcd for C₁₅H₁₁O₂S: C, 70.3; H, 4.7; S, 12.5. Found: C, 69.7; H, 4.5; S, 12.9. ^b Isolated yield. ^c In δ units with respect to Me₄Si, CDCl₃ solvent; chemical shift of olefinic proton α to the carboxyl.

gives poor yields of the cyclized product.

The isomeric α -(arythio)- and α -(arylseleno)cinnamates (4) remain either unknown or unrecognized in the litera-



ture. Cyclization of compounds of this type has not been investigated, but one would expect formation of the corresponding 2-arylidene-3-oxo-2-*H*-benzo[*b*]thiophenes and -selenophenes (hereafter referred to as thio- and selenoaurone dyes) (5).⁶ These compounds have been prepared by condensing aromatic aldehydes with 2,3-dihydro-3-oxobenzo[*b*]thiophene or -selenophene (6)⁶ or, in many steps, from (*o*-acetylphenyl)selenocyanides.⁷

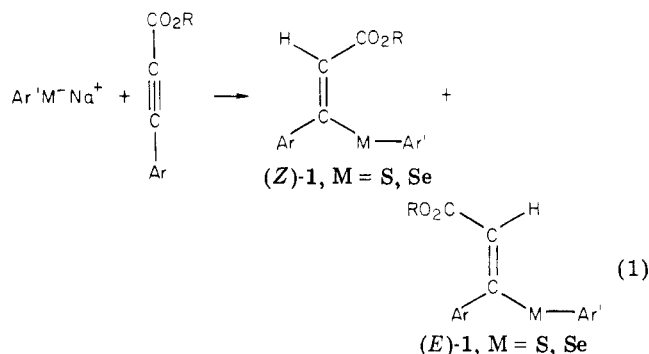
Appropriate regiochemical control of the addition of the elements of an aryl thiol or aryl selenol across the triple bond of an arylpropiolate would give both β -substituted cinnamates 1 and α -substituted cinnamates 4. We have found that the regiochemistry of addition of these elements can be controlled by promoting either free-radical or ionic addition. Thus, although aromatic thiols or selenols added exclusively in the β position of arylpropiolates in methanolic sodium methoxide to give products of type 1, mixing the propiolate and thiol or selenol in a neat solution gave, exclusively, addition products of type 4.

The β -addition products cyclized to the corresponding thio- or selenoflavones (2) in phosphorus pentoxide-methanesulfonic acid,⁸ whereas the α -addition products gave the corresponding thio- and selenoaurones (5) under identical conditions.

Results and Discussion

Ionic Additions. Base-catalyzed additions of aromatic thiols to α,β -acetylenic esters⁹ and α,β -acetylenic ketones¹⁰

give β substitution, with the stereochemistry of addition being solvent dependent. Similarly, one would expect β substitution to be the regiochemical preference of additions of thiols and selenols to arylpropiolates under basic conditions. Not surprisingly, when the arylpropiolate was added to a methanolic solution of thiol or selenol and sodium methoxide, a mildly exothermic reaction ensued to give only the Michael adducts (eq 1). Saponification of the cinnamate esters with potassium hydroxide in aqueous methanol gave the acids described in Table I.



Two stereoisomers (*Z*)-1 and (*E*)-1 are possible from the aryl sulfide and aryl selenide additions. The phenyl selenide addition to arylpropiolates followed by saponification gave only one detectable stereoisomer in which the chemical shift of the olefinic protons α to the carbon was in the range δ 6.30-6.45. The similarity of the chemical shifts is indicative of a common stereoisomer. In most cases, the addition of sodium phenyl sulfide to arylpropiolates followed by saponification gave predominantly one stereoisomer with lesser amounts of the other stereoisomer. The chemical shift of the α protons of the predominant isomer was in the range δ 5.90-6.20, and that of the minor isomer was in the range δ 5.35-5.50. Similarly, the addition of sodium 1-naphthyl sulfide gave predominantly one isomer (δ 5.90-6.10) with minor amounts of a second isomer (δ 5.20-5.35).

¹H NMR is a sensitive probe for determining the presence of the stereoisomers of β -alkyl- β -(phenylthio)- α,β -ethylenic esters in which the α olefinic protons of *Z* isomers absorb around δ 5.6-5.9, and those of *E* isomers absorb around δ 5.1-5.3.⁹ With these values, the major products in the Michael additions can be assigned the *Z* stereochemistry (δ 5.90-6.45) and the minor isomers the *E* stereochemistry (δ 5.20-5.50). The observed stereochemical preference is consistent with minimizing steric interactions in the products. On the basis of *A* values,¹¹ arylthio and

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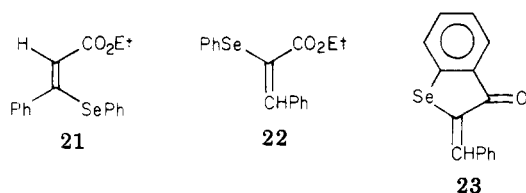
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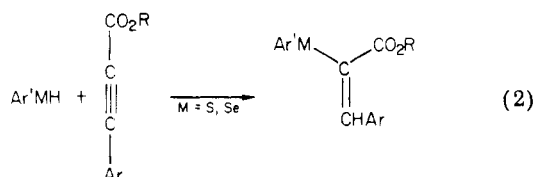
phenylseleno substituents are smaller than aryl substituents. Alternatively, a secondary interaction between the carbonyl oxygen and sulfur or selenium would also give the *Z* stereochemistry.

Radical Additions. The uncatalyzed addition of benzenethiol or benzeneselenol to various acetylenes gives regiochemical and stereochemical results different from those of base-catalyzed additions.¹² Presumably, a radical addition pathway is involved. Only one example of a radical addition of a thiol or selenol to an arylpropiolate has appeared in the literature⁷ in which the addition of benzeneselenol to ethyl phenylpropiolate gave only one product, assigned structure **21**, mp 30–31 °C.

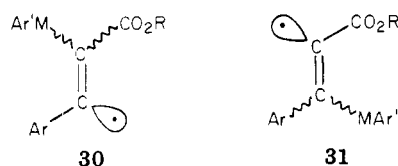


Authentic **21** (mp 107–109 °C) has been prepared by the Michael addition of potassium phenyl selenide to ethyl phenylpropiolate.¹³ In our work, warming a neat solution of benzeneselenol and the propiolate ester gave a single product, mp 37.5–40.0 °C. The ¹H NMR spectrum of this compound displayed a one-proton singlet at δ 8.10, signals for ten aromatic protons, and the proton signals for the ethyl ester. The structure of this compound was assigned as the regioisomer **22**, not **21** as originally described. The regiochemistry of addition was established unequivocally by saponification of **22** to the acid **24** and subsequent cyclization with phosphorus pentoxide–methanesulfonic acid⁸ to give the selenoaurone **23**.

The observed alteration of regiochemistry for radical additions of benzenethiol or benzeneselenol to arylpropiolates was general for the substrates examined (eq 2). Saponification of the initially formed esters gave the acids described in Table II.



The regiochemical preference for α substitution can be rationalized by assuming that a phenylthio or phenylseleno radical will add to the triple bond to give the more stable free radical. These results suggest that an aryl substituent is much better at stabilizing an adjacent radical in **30** than is a carboalkoxy group as in **31**. The stereochemistry cannot be assigned, although only one isomer is formed.



Cyclization Reactions. Friedel–Crafts acylation has been used to cyclize β -(arylthio)- or β -(arylseleno)cinnamic

Table II. Free Radical Additions of Benzenethiol and Benzeneselenol to Arylpropiolates. Preparation of $\text{ArC}=\text{C}(\text{MAr}')\text{CO}_2\text{H}^a$

compd ^d	Ar		% M yield ^b	mp, °C	¹ H NMR ^c
24	C ₆ H ₅	Se	73	113–115	8.29
25	4-CH ₃ OC ₆ H ₄	Se	78	126–129.5	8.38
26	2,5-(CH ₃ O) ₂ C ₆ H ₃	Se	62	146–148	8.53
27	2-CH ₃ OC ₁₀ H ₆	Se	82	183–187	8.51
28	C ₆ H ₅	S	86	139	8.15
29	2,5-(CH ₃ O) ₂ C ₆ H ₃	S	79	157	8.60

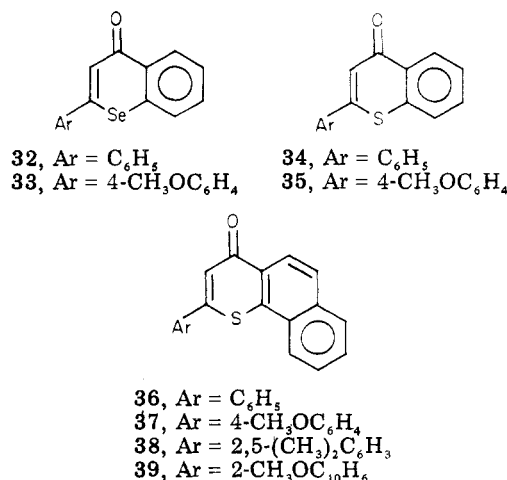
^a Suitable analytical data ($\pm 0.4\%$ for C, H, and S or Se) were obtained for all compounds except **28**, which gave the following data. Calcd for C₁₅H₁₁O₂S: C, 70.3; H, 4.7; S, 12.5. Found: C, 69.8; H, 4.5; S, 12.7. ^b Isolated yield. ^c In δ units with respect to Me₄Si, CDCl₃ solvent; chemical shift of olefinic proton β to the carboxyl. ^d Ar' was C₆H₅ in every case.

Table III. Cyclization of β -(Arylthio)- and β -(Arylseleno)cinnamic Acids with Phosphorus Pentoxide–Methanesulfonic Acid^a

compd	% yield ^b	mp, °C	lit. mp, °C	¹ H NMR ^c
32	64	127–130	133 ^d	7.35
33	40	130–132	150–152 ^e	7.22
34	80	122–123	124–126 ^f	7.35
35	74	127–128		7.31
36	74	180–184		7.43
37	64	170–171		7.22
38	42	150–153		7.20
39	78	137–140		7.31

^a Suitable analytical data ($\pm 0.4\%$ for C, H, and S or Se) were obtained for all new compounds except **39**, which gave the following data. Calcd for C₂₄H₁₆O₃S: C, 78.2; H, 4.4; S, 8.7. Found: C, 77.7; H, 4.8; S, 8.9. ^b Isolated yield. ^c In δ units with respect to Me₄Si, CDCl₃ solvent; chemical shift of enone proton in flavone. ^d Rawet, A.; Renson, M. *Bull. Soc. Chim. Belg.* 1966, 75, 260. ^e Reference 1a. ^f Reference 1c.

acids to the corresponding flavones with various degrees of success.^{4,5} One of the more recent modifications of the Friedel–Crafts reaction, phosphorus pentoxide–methanesulfonic acid,⁸ has not been investigated for such transformations. We have found that it is the method of choice for cyclizing most of the β -(arylthio)- or β -(arylseleno)-cinnamic acid derivatives (compounds **32–39**, Table III).



Competitive cyclization into the cinnamyl aromatic ring, rather than the selenium- or sulfur-bearing ring, became important when the cinnamyl ring was strongly activated by methoxy substituents. Thus, cyclization of the 2,5-

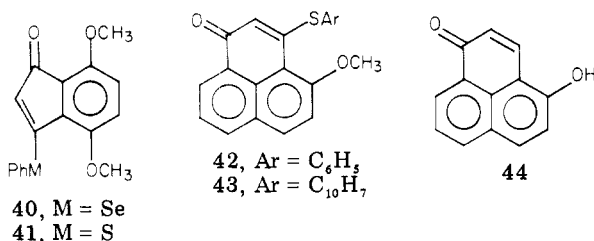
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 (13) Detty, M. R. *Tetrahedron Lett.* 1978, 5087.

Table IV. Cyclization of α -(Arylthio)- and α -(Arylseleno)cinnamic Acids with Phosphorus Pentoxide-Methanesulfonic Acid^a

compd	% yield ^b	mp, °C	lit. mp, °C	¹ H NMR ^c
45	47	119–122	122 ^d	8.18
46	89	156–159		8.02
47	84	117–118	117 ^d	8.26
48	65	127–129		8.52

^a Suitable analytical data ($\pm 0.4\%$ for C, H, and S or Se) were obtained for all new compounds. ^b Isolated yield. ^c In δ units with respect to Me₄Si, CDCl₃ solvent; chemical shift of enone proton. ^d Reference 6a.

dimethoxyphenyl derivatives **10** and **14** gave preferential attack at the 6-position of the doubly activated ring to give the benzocyclopentenones **40** and **41** in 70 and 92% yields,



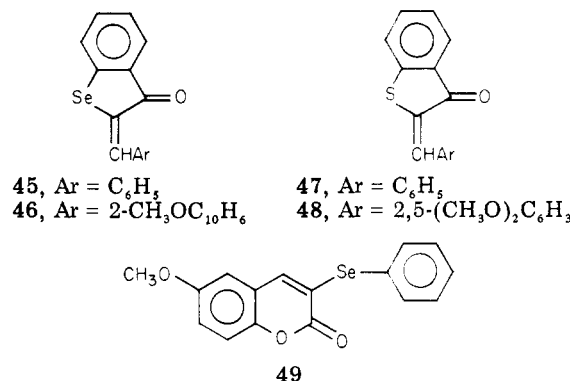
respectively. Similarly, the 2-methoxynaphthyl derivatives **15** and **20** gave the phenalenones **42** and **43** (as a minor product with **39**) in 41% and 7% yields, respectively. The necessary isomerization of the cinnamic acids (*Z* to *E*) to give products of this type could occur by protonation at the α carbon, rotation, and proton loss. No experimental evidence is available for isomerization.

The structural assignments to **40** and **41** followed directly from spectral data. Mass spectra indicated that **40** and **41** were isomeric with the expected flavones, although the fragmentation patterns were quite different. In particular, **40** and **41** gave large ions for the loss of PhSe- and PhS-, respectively, which the flavones did not. The IR spectra of **40** and **41** displayed strong carbonyl stretching at 1670 and 1690 cm⁻¹, respectively. The UV spectra are consistent with an extended chromophore with λ_{\max} (log ϵ) of 398 nm (3.95) for **40** and 393 nm (3.91) for **41**. In the ¹H NMR spectra, the α proton of the enone appeared as a singlet at δ 5.26 for **40** and at δ 5.08 for **41**, two distinct methoxyl proton singlets were apparent for each compound, the phenylthio and phenylseleno multiplets were distinct, and the two protons on the dimethoxybenzo ring appeared as narrow multiplets at δ 7.07 in both **40** and **41**. The spectral data are consistent only with the benzocyclopentenone structures **40** and **41**.

The structural assignments to **42** and **43** were made from spectral data, although they are not unequivocal. Mass spectra were indicative of compounds isomeric with the expected flavones with different fragmentation patterns. The observed fragmentations, however, did not show loss of ArS- or ArSH, which is somewhat disturbing. The ¹H NMR spectra displayed singlets for the α proton in the enone system at δ 6.08 for **42** and at δ 6.15 for **43**, singlets for the methoxyl protons, and the expected aromatic signals. The IR spectra showed strong carbonyl stretching at 1630 cm⁻¹ for **42** and 1640 cm⁻¹ for **43**, which is indicative of conjugated carbonyls. The UV spectra of **42** and **43** were similar. For **42**: λ_{\max} 461 nm (sh), 432 (sh), 387, 342 (log ϵ 3.58, 3.92, 4.15, and 4.26, respectively). For **43**: λ_{\max} 461 nm (sh), 431 (sh), 390, 348 (log ϵ 3.57, 3.90, 4.15, and 4.17, respectively). The phenalenone **44** is the compound most structurally similar to **42** and **43** that appears in the lit-

erature.¹⁴ The UV spectrum of **44** showed the following absorptions: λ_{\max} 423 nm, 338, 320 (log ϵ 4.12, 3.52, and 3.50, respectively).

The Friedel-Crafts cyclization of α -(arylthio)- or α -(arylseleno)cinnamic acids has not been studied extensively. Cyclization of these substrates with phosphorus pentoxide-methanesulfonic acid⁸ gave the aurones **45–48**



in good yield (Table IV). . The only problem encountered in the cyclization of the α -substituted cinnamates was attack of the acylium species at the oxygen of the 2-methoxy substituent in acid **26**. Coumarin **49** was the only isolable product.

Conclusions

The regiochemistry of addition of the elements of aryl selenols or aryl thiols across the triple bond of aryl-propiolates can be easily controlled. Basic conditions favor Michael additions to give β -substituted cinnamates, and neutral conditions promote radical additions to give α -substituted cinnamates.

β -Substituted cinnamates treated with phosphorus pentoxide-methanesulfonic acid gave good-to-excellent yields of thio- or selenoflavones unless the cinnamyl aromatic ring was strongly activated, in which case cyclization into this ring became possible. Similarly, α -substituted cinnamates cyclized to give the thio- or selenoaurone dyes. The aurone dyes had not been prepared before by cinnamate cyclization.

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are corrected. Boiling points are uncorrected. ¹H NMR spectra were run on Varian T-60 and EM-390 instruments. IR spectra were recorded on a Perkin-Elmer 137 spectrophotometer. UV spectra were run on a Cary 17 instrument. Mass spectra were recorded on a Du Pont 21-491 instrument. Microanalyses were performed on a Perkin-Elmer 240 C, H, and N analyzer. Benzeneselenol, benzenethiol, and 1-naphthalenethiol were obtained from Eastman Organic Chemicals and were distilled before use.

General Procedure for the Preparation of β -(Arylseleno)- and β -(Arylthio)cinnamic Acids. Ionic Additions. A solution of sodium methoxide in dry methanol (~ 0.5 M) was treated with an equivalent amount of the aryl selenol or aryl thiol. The resulting solution was added to the arylpropiolate in methanol (~ 0.5 M) and warmed briefly on a steam bath. The reaction mixture was then treated with an equal volume of 3 M potassium hydroxide solution. The solution was refluxed for ~ 2 h. Acidification of the hydrolysis solution with cold 10% hydrochloric acid furnished the crude acid, which was recrystallized from aqueous methanol (Table I).

Several of the (arylthio)cinnamic acids were isomeric mixtures and could not be conveniently purified by recrystallization.

Examination of the crude esters after addition of the sodium aryl sulfide, but before hydrolysis, gave the isomer ratios in Table I. Representative spectral descriptions follow.

For 7: ^1H NMR (CDCl_3) δ 10.9 (br s, 1 H), 7.30–6.80 (m, 10 H), 6.30 (s, 1 H); IR (KBr) 3000, 1650, 1550, 1300, 765, 735, 690 cm^{-1} ; mass spectrum, m/e 304 ($\text{C}_{15}\text{H}_{12}\text{O}_2^{80}\text{Se}$).

For 8: ^1H NMR (CDCl_3) δ 10.4 (br s, 1 H), 7.3–6.7 (m, 7 H), 6.46 (d, 2 H, $J = 7$ Hz), 6.30 (s, 1 H), 3.70 (s, 3 H); IR (KBr) 3000, 1670 cm^{-1} ; mass spectrum, m/e (relative intensity) 334 ($\text{C}_{16}\text{H}_{14}\text{O}_3^{80}\text{Se}$), 177 (100).

For 16: ^1H NMR (CDCl_3) δ 9.50 (br, 1 H), 8.54 (m, 1 H), 7.70 (m, 5 H), 7.50–6.80 (m, 6 H), 6.27 (s, 1 H); IR (KBr) 3000, 1620, 1560, 1240, 1205 cm^{-1} ; mass spectrum, m/e 306 ($\text{C}_{19}\text{H}_{14}\text{O}_2\text{S}$).

General Procedure for the Preparation of α -(Arylseleno)- and α -(Arylthio)cinnamic Acids. Radical Additions. Equimolar amounts of the appropriate arylpropionate ester and benzenethiol or benzeneselenol were mixed and warmed neat for 15 min on a steam bath. The reaction mixture was diluted with methanol or isopropyl alcohol (~10 mL/mmol), and an equal volume of 3 M potassium hydroxide was added. The hydrolysis mixture was warmed on a steam bath for ~2 h. Acidification with cold 10% hydrochloric acid furnished the crude acid. Recrystallization from aqueous methanol gave the pure acids (Table II). Representative spectral descriptions follow.

For 24: ^1H NMR (CDCl_3) δ 9.0 (br s, 1 H), 8.29 (s, 1 H), 7.63 (m, 4 H), 7.25 (m, 6 H); IR (KBr) 3000, 1670, 1290, 770, 740, 683 cm^{-1} ; mass spectrum, m/e (relative intensity) 304 ($\text{C}_{15}\text{H}_{12}\text{O}_2^{80}\text{Se}$), 259 (100).

For 25: ^1H NMR (CDCl_3) δ 11.4 (s, 1 H), 8.38 (s, 1 H), 7.86 (d, 2 H, $J = 9$ Hz), 7.35 (m, 2 H), 7.20 (m, 3 H), 6.90 (d, 2 H, $J = 9$ Hz), 3.86 (s, 3 H); IR (KBr) 2900, 1695, 1610, 1600, 1180, 833, 800, 740 cm^{-1} ; mass spectrum, m/e 334 ($\text{C}_{16}\text{H}_{14}\text{O}_3\text{Se}$).

General Procedure for Cyclization of Arylseleno- and Arylthio-Substituted Cinnamic Acids with Phosphorus Pentoxide–Methanesulfonic Acid.⁸ For every 2 mmol of substrate to be cyclized, 1 g of phosphorus pentoxide was dissolved in 10 g of methanesulfonic acid. After the phosphorus pentoxide was completely dissolved (~3 h at 20 °C), the substrate was added in one portion as a powder. The resulting mixture was stirred under nitrogen for 3–6 h and then added dropwise to a saturated sodium bicarbonate solution (100 mL for every 10 g of methanesulfonic acid) with rapid stirring. The product was extracted with methylene chloride, and the extracts were dried over sodium sulfate and concentrated. Recrystallization from methanol gave the products described in Tables III and IV. Representative spectral descriptions follow.

For 32: ^1H NMR (CDCl_3) δ 8.61 (m, 1 H), 7.48 (m, 8 H), 7.35 (s, 1 H); IR (KBr) 1605, 1590, 1330, 778, 760 cm^{-1} ; mass spectrum m/e 286 ($\text{C}_{15}\text{H}_{10}\text{OSe}$).

For 34: ^1H NMR (CDCl_3) δ 8.55 (m, 1 H), 7.45 (m, 8 H), 7.35 (s, 1 H); IR (KBr) 1605, 1590, 1330, 775 cm^{-1} ; mass spectrum, m/e 238 ($\text{C}_{15}\text{H}_{10}\text{OS}$).

For 36: ^1H NMR (CDCl_3) δ 8.64 (d, 1 H, $J = 10$ Hz), 8.47 (m, 1 H), 8.15–7.50 (m, 9 H), 7.43 (s, 1 H); ^{13}C NMR (CDCl_3) δ 180.4, 150.6, 136.8, 136.3, 133.5, 130.4, 128.9, 128.5, 127.5, 126.9, 126.7, 123.6, 123.4, 123.1; IR (KBr) 1600, 1350, 1120 cm^{-1} ; mass spectrum, m/e (relative intensity) 288 ($\text{C}_{19}\text{H}_{12}\text{OS}$), 260 (100).

For 45: ^1H NMR (CDCl_3) δ 8.18 (s, 1 H), 7.83 (br d, 1 H), 7.7–7.0 (m, 8 H); ^{13}C NMR (CDCl_3) δ 190.2, 141.2, 136.4, 134.7, 134.2, 131.6, 129.8, 129.5, 129.1, 128.5, 127.8, 126.2, 125.6; IR (KBr) 1680, 1590, 1280, 1060, 746 cm^{-1} ; λ_{max} (EtOH) 439 nm (log ϵ 3.93), 315 (4.30); mass spectrum, m/e 346 ($\text{C}_{17}\text{H}_{14}\text{O}_3^{80}\text{Se}$).

For 47: ^1H NMR (CDCl_3) δ 8.26 (s, 1 H), 7.85 (m, 1 H), 7.55–7.10 (m, 8 H); IR (KBr) 1680, 1280, 745, 735 cm^{-1} ; λ_{max} (EtOH) 433 nm (log ϵ 3.90); mass spectrum, m/e 238 ($\text{C}_{15}\text{H}_{10}\text{OS}$).

Cyclization of Cinnamate 10. Preparation of Benzo-cyclopentenone 40. A 0.90-g (2.5 mmol) sample of 10 was cyclized in 12 g of the phosphorus pentoxide–methanesulfonic acid mixture as described. Workup and recrystallization from methanol gave 0.57 g (70%) of 40 as yellow needles: mp 129–133 °C; ^1H NMR (CDCl_3) δ 7.81 (m, 2 H), 7.56 (m, 3 H), 7.07 (m, 2 H), 5.26 (s, 1 H), 4.00 (s, 3 H), 3.95 (s, 3 H); ^{13}C NMR (CDCl_3) δ 191.7, 162.4, 150.2, 147.5, 136.1, 135.8, 135.5, 130.2, 129.4, 129.2, 126.5, 120.5, 119.5, 117.6, 116.6, 56.3; IR (KBr) 1670, 1270, 1060, 812, 745 cm^{-1} ;

λ_{max} (EtOH) 398 nm (log ϵ 3.95), 299 (3.89); mass spectrum, m/e 346 ($\text{C}_{17}\text{H}_{14}\text{O}_3^{80}\text{Se}$).

Anal. Calcd for $\text{C}_{17}\text{H}_{14}\text{O}_3\text{Se}$: C, 59.1; H, 4.1; Se, 22.9. Found: C, 59.0; H, 4.1; Se, 23.3.

Cyclization of Cinnamate 14. Preparation of Benzo-cyclopentenone 41. A 0.95-g (3.0 mmol) sample of 14 was cyclized in 15 g of the phosphorus pentoxide–methanesulfonic acid mixture as described. Workup and recrystallization from methanol gave 0.82 g (92%) of 41 as yellow needles: mp 132–134 °C; ^1H NMR (CDCl_3) δ 7.75 (m, 2 H), 7.60 (m, 3 H), 7.07 (m, 2 H), 5.08 (s, 1 H), 3.97 (s, 3 H), 3.99 (s, 3 H); ^{13}C NMR (CDCl_3) δ 191.6, 165.5, 150.2, 147.6, 134.4, 129.8, 129.6, 129.0, 119.7, 118.0, 116.9, 116.6, 56.5, 56.3; IR (KBr) 1690, 1540, 1275, 813 cm^{-1} ; λ_{max} (EtOH) 393 nm (log ϵ 3.91), 286 (3.92); mass spectrum, m/e 298 ($\text{C}_{17}\text{H}_{14}\text{O}_3\text{S}$).

Anal. Calcd for $\text{C}_{17}\text{H}_{14}\text{O}_3\text{S}$: C, 68.4; H, 4.7; S, 10.7. Found: C, 68.2; H, 4.8; S, 10.1.

Cyclization of Cinnamate 15. Preparation of Phenalenone 42. A 0.34-g (1.0 mmol) sample of 15 was cyclized in 5 g of the phosphorus pentoxide–methanesulfonic acid mixture as described. Workup and recrystallization from methanol gave 0.13 g (41%) of 42 as a gold-brown solid: mp 198–201 °C; ^1H NMR (CDCl_3) δ 8.69 (d, 1 H, $J = 8$ Hz), 8.00 (d, 2 H, $J = 9$ Hz), 7.80–7.20 (m, 7 H), 6.08 (s, 1 H), 4.17 (s, 3 H); IR (KBr) 1630, 1600, 1580, 1560, 1265, 1170, 836 cm^{-1} ; λ_{max} (EtOH) 387 (log ϵ 4.15), 342 (4.26); mass spectrum, m/e 318 ($\text{C}_{20}\text{H}_{14}\text{O}_2\text{S}$).

Anal. Calcd for $\text{C}_{20}\text{H}_{14}\text{O}_2\text{S}$: C, 75.4; H, 4.4; S, 10.1. Found: C, 75.1; H, 4.4; S, 10.3.

Cyclization of Cinnamate 20. Minor Product Phenalenone 43. Chromatography of the reaction mixture from the cyclization of 20 on silica gel eluted with 20% ether–hexane gave 43 in 7% yield as a yellow solid (mp 212–216.5 °C) in addition to flavone 39. For 43: ^1H NMR (CDCl_3) δ 8.65 (d, 1 H, $J = 8$ Hz), 8.2–7.1 (m, 11 H), 6.15 (s, 1 H), 4.10 (s, 3 H); IR (KBr) 1640, 1565, 1270, 835 cm^{-1} ; λ_{max} (EtOH) 390 nm (log ϵ 4.15); mass spectrum, m/e 368 ($\text{C}_{24}\text{H}_{16}\text{O}_2\text{S}$).

Cyclization of Cinnamate 26. Preparation of Coumarin 49. A 0.20-g (0.55 mmol) sample of 26 was cyclized in 3 g of phosphorus pentoxide–methanesulfonic acid as described. Chromatography on silica gel (CH_2Cl_2) followed by recrystallization from methanol gave 0.10 g (55%) of 49 as yellow needles: mp 98–100 °C; ^1H NMR (CDCl_3) δ 7.48 (m, 2 H), 7.24 (m, 3 H), 6.99 (d, 1 H, $J = 9$ Hz), 6.75 (dd, 1 H, $J = 2.5, 9$ Hz), 6.76 (s, 1 H), 6.33 (d, 1 H, $J = 2.5$ Hz), 3.63 (s, 3 H); IR (KBr) 1705, 1270, 1156, 975, 807, 755, 740, 688 cm^{-1} ; λ_{max} (EtOH) 352 nm (log ϵ 3.93); mass spectrum, m/e 332 ($\text{C}_{16}\text{H}_{12}\text{O}_3^{80}\text{Se}$).

Preparation of Ethyl α -(Phenylseleno)cinnamate (22). Benzeneselenol (1.58 g, 0.0100 mol) and ethyl phenylpropionate (1.74 g, 0.0100 mol) were mixed neat, giving an exothermic reaction. The reaction mixture was warmed for 15 min on a steam bath. Crystallization and recrystallization of the reaction mixture gave 2.65 g (80%) of 22 as a white solid: mp 37.5–40.0 °C; ^1H NMR (CDCl_3) δ 8.10 (s, 1 H), 7.57 (m, 2 H), 7.33 (m, 5 H), 7.13 (m, 3 H), 4.00 (q, 2 H, $J = 7$ Hz), 1.02 (t, 3 H, $J = 7$ Hz); IR (KBr) 1700, 1580, 1240, 1030, 765, 732, 685 cm^{-1} ; mass spectrum, m/e 332 ($\text{C}_{17}\text{H}_{16}\text{O}_2^{80}\text{Se}$).

Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2\text{Se}$: C, 61.6; H, 4.9. Found: C, 62.0; H, 4.8.

Registry No. 7, 74877-27-3; 8, 74877-28-4; 9, 74877-29-5; 10, 74877-30-8; 11, 74877-31-9; (E)-12, 34874-98-1; (Z)-12, 34874-91-4; (E)-13, 74877-32-0; (Z)-13, 74877-33-1; (E)-14, 74877-34-2; (Z)-14, 74877-35-3; 15, 74877-36-4; (E)-16, 74877-37-5; (Z)-16, 74877-38-6; 17, 74877-39-7; 18, 74877-40-0; (E)-19, 74877-41-1; (Z)-19, 74877-42-2; 20, 74877-43-3; 22, 74877-44-4; 24, 74877-45-5; 25, 74877-46-6; 26, 74877-47-7; 27, 74877-48-8; 28, 60805-23-4; 29, 74877-49-9; 32, 4512-97-4; 33, 4512-98-5; 34, 784-62-3; 35, 893-10-7; 36, 29869-13-4; 37, 74877-50-2; 38, 74877-51-3; 39, 74877-52-4; 40, 74877-53-5; 41, 74877-54-6; 42, 74877-55-7; 43, 74877-56-8; 45, 36251-50-0; 46, 74877-57-9; 47, 3139-42-2; 48, 74877-58-0; 49, 74877-59-1; benzenethiol, 108-98-5; 1-naphthalenethiol, 529-36-2; benzeneselenol, 645-96-5; phenylpropionic acid, 637-44-5; (p-methoxyphenyl)propionic acid, 2227-57-8; (2,5-dimethylphenyl)propionic acid, 74877-60-4; (2,5-dimethoxyphenyl)propionic acid, 71797-88-1; 2-methoxy-1-naphthalenepropionic acid, 74877-61-5; ethyl phenylpropionate, 2216-94-6.