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Ring Expansion of Cyclic α-Ethynyl Sulfonium Ylides by [2,3]-Sigmatropic Rearrangement: Formation of Thiocin, Thionin, and Thiecin Derivatives[1]

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The cyclic 1-ethoxycarbonylmethyl-2-ethynyl sulfonium salts (**15Aa—d**, **15Ba—d**, and **15Ca—d**), prepared from thiolane (**12A**), thiane (**12B**), and thiepane (**12C**), were treated with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) to result in ring expansion, giving thiocins (**18Aa—d**), thionins (**18Ba—d**), and thiecins (**18Ca—d**), respectively, presumably *via* the allenic intermediates (**17**) derived from the initially formed sulfonium ylides (**16**) by [2,3]-sigmatropic rearrangement. Similarly, the 1- (**27a—c**) and 3-benzothionins (**30a—c**) were obtained from 2-ethynylthiochromans (**21**) and 1-ethynylisothiochromans (**22**), respectively, *via* the sulfonium ylides (**25**, **28**) and the allenic compounds (**26**, **29**) successively.

Keywords——cyclic 2-ethynyl sulfide; cyclic *S*-ylide; sigmatropic rearrangement; ring-expansion; cyclic allene; thiocin; thionin; thiecin; benzothionin

Ylides have been used as reactive intermediates in organic synthesis, particularly in either thermal[2] or photochemical[3] rearrangements. The thermal sigmatropic rearrangements with ring-expansion of the cyclic allylamine *N*-methylides (**1a**),[4] *N*-imides (**1b**),[5] and *N*-oxides (**1c**)[6] have been well investigated, as have those of the cyclic allyl sulfonium ylides (**2**).[7] On the other hand, the open-chain propargylic *N*-methylides (**3a**),[8] *N*-oxides (**3b**),[9] and *S*-methylides (**3c**)[10] are known to undergo thermal [2,3]-sigmatropic rearrangement giving the corresponding allenic compounds (**4**). Therefore, we were interested in examining the thermal behavior of cyclic ethynyl ylides. We have already reported that the thermolysis of the 2-ethynylpyridine *N*-imides (**5**)[11] gave the 3-azaindolizines (**8**) *via* the zwitter-ionic (**6**) and the cyclic *N*-imide intermediates (**7**), and that of the 6-ethynyl-1,2,5,6-tetrahydropyridine *N*-imides (**9**)[12] resulted in ring-expansion to afford the dihydro-1,2-diazonines (**11**) *via* the allenic intermediates (**10**). In connection with these results, we studied the thermal reaction of five-, six-, and seven-membered cyclic sulfonium ylides having an ethynyl group at the α-position of the ring, and report the formation of the corresponding three-carbon ring enlargement products; thiocin, thionin, and thiecin derivatives.[13]

Thiolane (**12A**), thiane (**12B**), and thiepane (**12C**) were successively treated with *N*-chlorosuccinimide (NCS) and the ethynylmagnesium bromides (**13a—d**), according to the procedure reported for the preparation of α-alkyl cyclic sulfides,[14] to give the corresponding cyclic 2-ethynyl sulfides (**14Aa—d**, **14Ba—d**, and **14Ca—d**), respectively, in the yields shown in Table III.

Treatment of **14** with ethoxycarbonylmethyl trifluoromethanesulfonate ($TfOCH_2-CO_2Et$)[15] in acetonitrile gave the corresponding sulfonium salts (**15**) as viscous oils in high yeilds. However, each of the salts **15** obtained was a mixture of two stereoisomers (*ca.* 1 : 1), as confirmed by the proton nuclear magnetic resonance (^{1}H-NMR) spectral data, but it was difficult to separate the isomers and thus the mixture was used in the following reaction without separation.

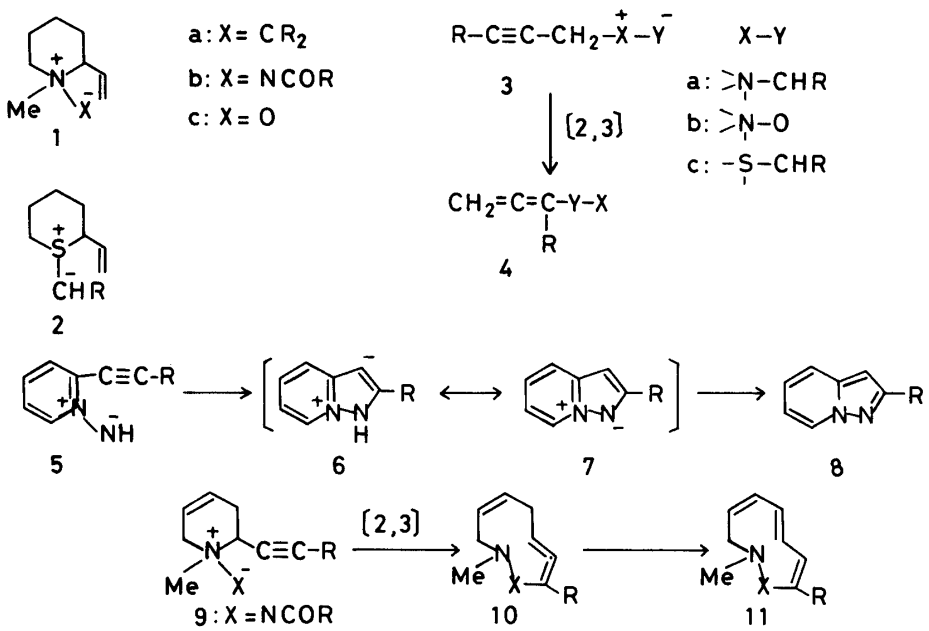


Chart 1

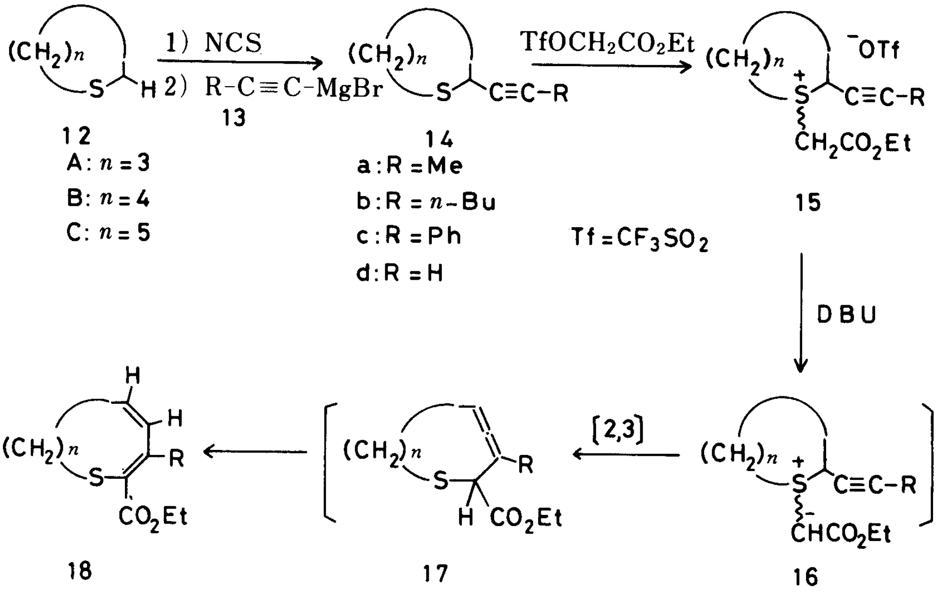
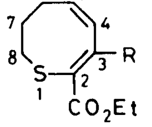
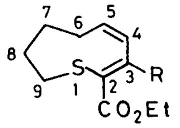
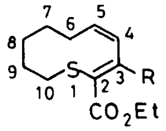


Chart 2

TABLE I. Yields[a] of the Ring-Expansion Products (18) from the Salts (15)

18[b]	R	 A (n=3) (%)	 B (n=4) (%)	 C (n=5) (%)
a	Me	38	73	62
b	n-Bu	40	75	63
c	Ph	68	61	75
d	H	33	26	24

a) Yields of isolated products. *b*) All compounds are colorless viscous oils except **18Cc**, mp 94—95 °C, colorless prisms (from n-hexane–CH_2Cl_2).

TABLE II. Spectral and Analytical Data for Thiocins (**18Aa**—**d**), Thionins (**18Ba**—**d**), and Thiecins (**18Ca**—**d**)

Compd. No.	IR ν_{max} cm^{-1} (C=O)	Formula (MS *m/z*: M$^+$)	Analysis (%) Calcd (Found)		^{1}H-NMR ($CDCl_3$) δ (*J*=Hz)
			C	H	
18Aa	1710	$C_{11}H_{16}O_2S$ (212)	62.26 (62.01	7.55 7.42)	1.50—2.41 (4H, m, 6- and 7-H_2), 1.99 (3H, s, 3-Me), 2.52—2.93 (2H, m, 8-H_2), 5.72 (1H, dt, *J*=11, 7, 5-H), 5.90 (1H, d, *J*=11, 4-H), 1.32 and 4.23 (3H, t, and 2H, q, CO_2Et)
18Ab	1720	$C_{14}H_{22}O_2S$ (254)	66.14 (65.86	8.66 8.87)	0.86 (3H, t, *J*=7, $-CH_2CH_2CH_2C\underline{H}_3$), 1.12—1.50 (4H, m, $-CH_2C\underline{H}_2C\underline{H}_2CH_3$), 2.01—2.40 (2H, m, $-C\underline{H}_2CH_2CH_2CH_3$), 1.53—1.80 (2H, m, 7-$H_2$), 2.02—2.41 (2H, m, 6-$H_2$), 2.59 (2H, t, *J*=6, 8-H_2), 5.77 (1H, dt, *J*=11, 7, 5-H), 5.88 (1H, d, *J*=11, 4-H), 1.30 and 4.21 (3H, t, and 2H, q, CO_2Et)
18Ac	1710	$C_{16}H_{18}O_2S$ (274)	70.07 (69.87	6.57 6.90)	1.52—1.73 (2H, m, 7-H_2), 2.22—2.41 (2H, m, 6-H_2), 2.70 (2H, t, *J*=6, 8-H_2), 5.78 (1H, dt, *J*=11, 7, 5-H), 6.01 (1H, d, *J*=11, 4-H), 7.21—7.29 (5H, m, Ph-H), 0.92 and 3.93 (3H, t, and 2H, q, CO_2Et)
18Ad	1710	$C_{10}H_{14}O_2S$ (198)	60.61 (60.39	7.07 6.99)	1.63—1.80 (2H, m, 7-H_2), 2.63—2.81 (2H, m, 6-H_2), 3.35 (2H, t, *J*=6, 8-H_2), 5.54 (1H, dt, *J*=11, 7, 5-H), 6.00 (1H, dd, *J*=11, 6, 4-H), 7.05 (1H, d, *J*=6, 3-H), 1.32 and 4.27 (3H, t, and 2H, q, CO_2Et)
18Ba	1720	$C_{12}H_{18}O_2S$ (226)	63.71 (63.72	7.96 7.78)	1.63—2.18 (6H, m, 6-, 7-, and 8-H_2), 1.96 (3H, s, 3-Me), 2.62 (2H, m, 9-H_2), 5.55 (1H, dt, *J*=11, 8, 5-H), 5.96 (1H, d, *J*=11, 4-H), 1.32 and 4.19 (3H, t, and 2H, q, CO_2Et)
18Bb	1720	$C_{15}H_{24}O_2S$ (268)	67.16 (67.00	8.96 8.73)	0.94 (3H, t, *J*=7, $-CH_2CH_2CH_2C\underline{H}_3$), 1.31—1.69 (4H, m, $-CH_2C\underline{H}_2C\underline{H}_2CH_3$), 2.19—2.23 (2H, m, $-C\underline{H}_2CH_2CH_2CH_3$), 1.60—2.01 (4H, m, 7- and 8-H_2), 2.31 (2H, m, 6-H_2), 2.58 (2H, m, 9-H_2), 5.63 (1H, dt, *J*=11, 8, 5-H), 5.94 (1H, d, *J*=11, 4-H), 1.31 and 4.21 (3H, t, and 2H, q, CO_2Et)
18Bc	1720	$C_{17}H_{20}O_2S$ (288)	70.83 (71.04	6.94 7.12)	1.72—1.98 (4H, m, 7- and 8-H_2), 2.28 (2H, m, 6-H_2), 2.73 (2H, m, 9-H_2), 5.79 (1H, dt, *J*=11, 8, 5-H), 6.12 (1H, d, *J*=11, 4-H), 7.22—7.26 (5H, m, Ar-H), 0.93 and 3.98 (3H, t, and 2H, q, CO_2Et)
18Bd	1710	$C_{11}H_{16}O_2S$ (212)	62.26 (62.43	7.55 7.31)	1.58—2.10 (4H, m, 7- and 8-H_2), 2.15—2.44 (2H, m, 6-H_2), 2.90 (2H, t, *J*=6, 9-H_2), 5.82 (1H, dt, *J*=11, 7, 5-H), 6.00 (1H, dd, *J*=11, 3, 4-H), 7.40 (1H, d, *J*=3, 3-H), 1.31 and 4.27 (3H, t, and 2H, q, CO_2Et)
18Ca	1710	$C_{13}H_{20}O_2S$ (240)	65.00 (65.07	8.33 8.21)	1.27—1.79 (6H, m, 7-, 8-, and 9-H_2), 1.99 (3H, s, 3-Me), 2.10 (2H, m, 6-H_2), 2.51 (2H, m, 10-H_2), 5.44 (1H, dt, *J*=11, 8, 5-H), 6.10 (1H, d, *J*=11, 4-H), 1.30 and 4.22 (3H, t, and 2H, q, CO_2Et)
18Cb	1710	$C_{16}H_{26}O_2S$ (282)	68.09 (67.94	9.22 9.03)	0.86 (3H, t, *J*=7, $-CH_2CH_2CH_2C\underline{H}_3$), 1.05—1.39 (4H, m, $-CH_2C\underline{H}_2C\underline{H}_2CH_3$), 2.30—2.35 (2H, m, $-C\underline{H}_2CH_2CH_2CH_3$), 1.37—1.81 (6H, m, 7-, 8-, and 9-H_2), 2.10 (2H, m, 6-H_2), 2.51 (2H, m, 10-H_2), 5.28 (1H, dt, *J*=11, 8, 5-H), 5.81 (1H, d, *J*=8, 4-H), 1.28 and 4.14 (3H, t, and 2H, q, CO_2Et)
18Cc	1710	$C_{18}H_{22}O_2S$ (302)	71.52 (71.48	7.28 7.49)	1.53—2.02 (6H, m, 7-, 8-, and 9-H_2), 2.29 (2H, m, 6-H_2), 2.63—2.66 (2H, m, 10-H_2), 5.56 (1H, dt, *J*=11, 8, 5-H), 6.27 (1H, d, *J*=11, 4-H), 7.30—7.35 (5H, m, Ar-H), 0.95 and 4.00 (3H, t, and 2H, q, CO_2Et)
18Cd	1710	$C_{12}H_{18}O_2S$ (226)	63.71 (64.01	7.96 7.77)	1.18—1.80 (6H, m, 7-, 8-, and 9-H_2), 1.92—2.23 (2H, m, 6-H_2), 2.66 (2H, t, *J*=6, 10-H_2), 5.43 (1H, dt, *J*=11, 8, 5-H), 5.95 (1H, dd, *J*=11, 3, 4-H), 7.78 (1H, d, *J*=3, 3-H), 1.34 and 4.24 (3H, t, and 2H, q, CO_2Et)

The salts **15** were treated with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) as a base in acetonitrile with stirring for *ca.* 1 h at room temperature to result in the formation of the corresponding ring-expansion products, thiocins (**18Aa—d**), thionins (**18Ba—d**), and thiecins (**18Ca—d**), in the yields shown in Table I. The structures of the products **18** were confirmed by their spectral and analytical data shown in Table II.

This three-carbon ring enlargement reaction of **15** to **18** may involve the allenic intermediates (**17**) which might be derived from the initially formed sulfonium ylides (**16**) by the [2,3]-sigmatropic rearrangement with the triple bond, by analogy with the cases of the open-chain propargylic ylides (**3**)[8-10] and the 2-ethynyltetrahydropyridine *N*-imides (**9**).[12] The intermediates **17** may then undergo a base-induced isomerization to give the products **18** with a conjugated diene system. Open-chain β-allenic esters are well known to undergo the base-induced rearrangement with reconjugation to 2,4-dienoates.[16] However, in the present cases, neither of the key intermediates **16** and **17** could be isolated, in contrast to the cases of **3** and **9** in which either ylide intermediates or allenic compounds were isolated.

The present results show that the sulfonium ylides (**16**) are very reactive toward the [2,3]-sigmatropic rearrangement, like the cyclic allyl sulfonium ylides (**2**),[7] and the resulting allenic compounds **17** are susceptible to the base-induced reconjugation to give the more stable diene compounds **18** under the reaction conditions used. The geometry of the double bond ($C_4=C_5$) in all products **18** was proved to be *cis* by the vicinal coupling constant ($J=11$ Hz) in the ^{1}H-NMR spectra of **18**. This stereochemistry is similar to that of the open-chain 2,4-dienoates formed from the β-allenic esters.[16] In addition, the same products **18** were obtained from **15** when potassium ethoxide or *tert*-butoxide was used as a base, but the yields of **18** were lower than those in the DBU-induced reaction.

Next, this ring-expansion reaction was applied to some benzo derivatives. Thiochroman (**19**) and isothiochroman (**20**) were successively treated with NCS and the ethynylmagnesium bromides (**13a—c**) to afford the corresponding 2-ethynylthiochromans (**21a—c**) and 1-ethynylisothiochromans (**22a—c**) in good yields. Treatment of **21** and **22** with $TfOCH_2CO_2Et$ gave the corresponding ethoxycarbonylmethylsulfonium salts (**23a—c** and **24a—c**) as mixtures of two stereoisomers in high yields, respectively. The salts were also used in the following base-induced reaction without separation of the isomers.

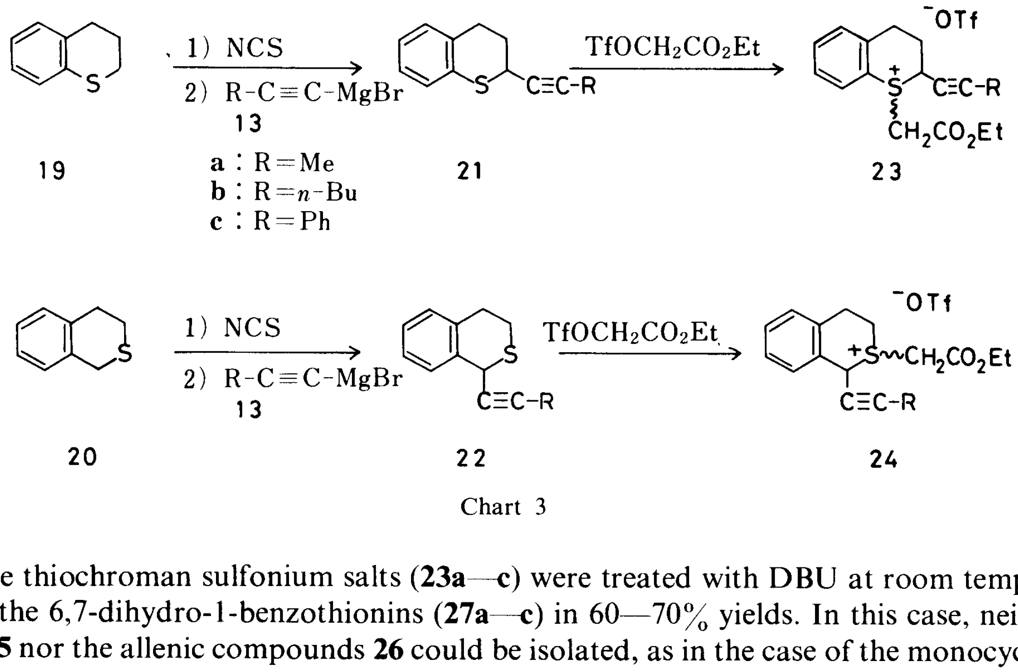


Chart 3

The thiochroman sulfonium salts (**23a—c**) were treated with DBU at room temperature to give the 6,7-dihydro-1-benzothionins (**27a—c**) in 60—70% yields. In this case, neither the ylides **25** nor the allenic compounds **26** could be isolated, as in the case of the monocyclic salts **15**. In contrast, the isothiochroman sulfonium salts (**24a, b**), upon treatment with DBU at room temperature, afforded the stable allenic compounds **29a**, **b** (60—80% yields), which showed absorptions at 1940—1945 cm^{-1} due to C=C=C in the infrared (IR) spectra. However, treatment of the salt (**24c**) with DBU gave directly the 1,2-dihydro-3-benzothionin (**30c**) in 64% yield and the allenic compound (**29c**) was not isolated even when the reaction was carried out at *ca.* −10 °C in an ice-salt bath.

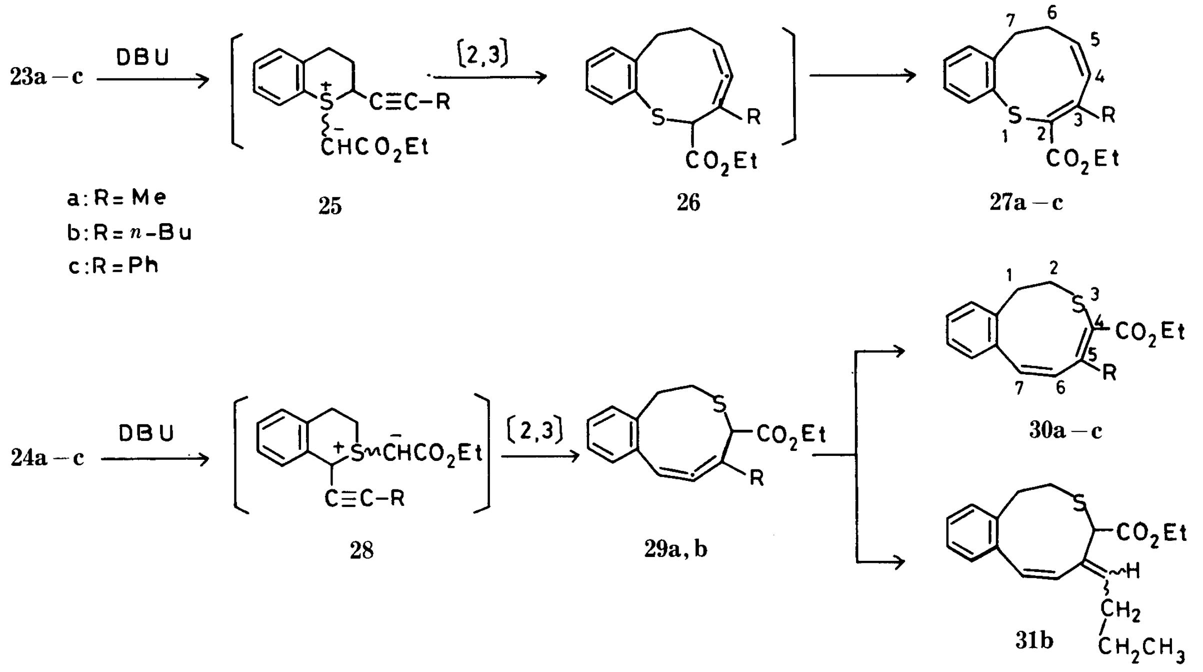


Chart 4

The allenic compound **29a** was further treated with DBU in refluxing benzene to result in isomerization, giving the 3-benzothionin (**30a**) in 70% yield as the sole product. However, under similar conditions, the allene **29b** (R = *n*-Bu) underwent two competing rearrangements involving C$_4$- and *n*-Bu-hydrogen elimination to result in the formation of two diene products, the 3-benzothionin **30b** (45% yield) and the *exo*-methylene compound **31b** (22% yield).

Although the reason why only the allenic compounds **29a**, **b** are stable at room temperature is not clear, the present results provide a new synthetic route for unsaturated medium-sized cyclic sulfides.

Experimental

Melting points were measured on a Yamato MP-21 apparatus and are uncorrected. IR spectra were determined with a Hitachi 270-30 spectrometer and mass spectra (MS) were recorded on a JEOL DX-300 instrument. ^{1}H-NMR spectra were recorded on a JEOL JNM-MH100 spectrometer in CDCl$_3$ using tetramethylsilane as an internal standard unless otherwise stated; spectral assignments were confirmed by spin-decoupling experiments. Coupling constants (*J*) are reported in Hz. Microanalyses were performed in the Microanalytical Laboratory of this School by Mrs. R. Igarashi.

Starting Materials——Thiolane (**12A**) and thiane (**12B**) were obtained from Tokyo Kasei Kogyo Co., Japan. Thiepane (**12C**),[17] thiochroman (**19**),[18] and isothiochroman (**20**)[19] were prepared by the reported methods.

Cyclic 2-Ethynyl Sulfides (14Aa—d, 14Ba—d, 14Ca—d)——General Procedure: The procedure of Tuleen and Bennett[14] for the preparation of cyclic 2-alkyl sulfides was applied. NCS (6.75 g, 50 mmol) was added in small portions over a 30 min period to a solution of a cyclic sulfide **12** (50 mmol) in benzene (100 ml) with stirring. The temperature of the reaction mixture was maintained at 10—20 °C during the addition by cooling in an ice bath. The mixture was stirred for a further 1 h and then the resulting precipitate of succinimide was removed by filtration. The benzene solution containing the cyclic 2-chlorosulfide thus formed was used in the following reaction without isolation. The benzene solution was added under a nitrogen atmosphere at below 10 °C to an ether (200 ml) solution of an ethynylmagnesium bromide (**13**), which was freshly prepared from ethylmagnesium bromide (90 mmol) and the

Table III. Cyclic 2-Ethynyl Sulfides (**14**): 2-Ethynylthiolanes (**14Aa**—**d**), 2-Ethynylthianes (**14Ba**—**d**), and 2-Ethynylthiepanes (**14Ca**—**d**)

Compd. No.	Yield (%)	bp (°C) (mmHg)	IR ν_{max} cm^{-1} (C≡C)	Formula (MS m/z: M^+)	Analysis (%) Calcd (Found)	
					C	H
14Aa	47	87—90 (25)	2250	$C_7H_{10}S$ (126)	66.67 (66.39	7.94 7.91)
14Ab	49	99—102 (4)	2250	$C_{10}H_{16}S$ (168)	71.47 (71.53	9.52 9.31)
14Ac	61	130—140 (2)	2200	$C_{12}H_{12}S$ (188)	76.60 (76.91	6.38 6.14)
14Ad	18	65—74 (20)	2125	C_6H_8S (112)	64.29 (64.52	7.14 7.14)
14Ba	80	95—99 (20)	2250	$C_8H_{12}S$ (140)	68.57 (68.75	8.57 8.43)
14Bb	77	106—109 (5)	2250	$C_{11}H_{18}S$ (182)	72.53 (72.88	9.89 10.01)
14Bc	61	132—135 (1)	2200	$C_{13}H_{14}S$ (202)	77.23 (76.92	6.93 6.77)
14Bd	40	80—82 (25)	2125	$C_7H_{12}S$ (126)	66.67 (66.46	7.97 7.79)
14Ca	55	98—102 (10)	2250	$C_9H_{14}S$ (154)	70.13 (69.87	9.09 9.08)
14Cb	60	110—113 (4)	2250	$C_{12}H_{20}S$ (196)	73.47 (73.51	10.20 9.99)
14Cc	49	150—153 (1)	2225	$C_{14}H_{16}S$ (216)	77.78 (77.83	7.41 7.32)
14Cd	26	83—87 (20)	2125	$C_8H_{12}S$ (140)	68.57 (68.84	8.57 8.51)

corresponding acetylene derivative. The reaction mixture was stirred for an additional 1 h at room temperature and the excess reagent was decomposed by addition of 10% H_2SO_4 (150 ml). After separation of layers, the aqueous layer was extracted with ether. The combined organic layer was successively washed with satd. $NaHCO_3$ and satd. NaCl, dried over $MgSO_4$, and then evaporated *in vacuo*. The residue was distilled under reduced pressure to give **14** as a pale yellow oil.

Yields and physical, analytical, and spectral data of **14** are collected in Tables III and IV.

Cyclic 1-Ethoxycarbonylmethyl-2-ethynyl Sulfonium Trifluoromethanesulfonates (15Aa—d, 15Ba—d, 15Ca—d)——General Procedure: A solution of a cyclic 2-ethynyl sulfide **14** (4 mmol) in acetonitrile (5 ml) was added dropwise with stirring to a solution of $TfOCH_2CO_2Et$ (1.18 g, 5 mmol) in acetonitrile (5 ml) in an ice bath. The reaction mixture was stirred for a further 1 h at room temperature and then evaporated *in vacuo*. The viscous oily residue was washed with *n*-hexane to give the salt (**15**) in a nearly pure state, as a mixture (*ca.* 1 : 1) of two stereoisomers. It was difficult to separate the isomers and thus each mixture was used in the following reaction without separation.

Yields and IR spectra of the mixtures (**15**) are collected in Table V. ^1H-NMR spectra data for the a-series are given below.

15Aa ($n=3$): δ: 1.89 (3H, br d, $J=1$, C≡C-Me), 2.2—2.9 (4H, m, 3- and 4-H_2), 3.4—4.0 (2H, m, 5-H_2), 4.4—5.1 (3H, m, 2-H and S-CH_2-), 1.31 and 4.26 (3H, br t, and 2H, br q, CO_2Et).

15Ba ($n=4$): δ: 1.91 and 2.00 (each 1.5H, d, $J=1$, C≡C-Me), 1.6—2.5 (6H, m, 3-, 4-, and 5-H_2), 3.2—3.8 (2H, m, 6-H_2), 4.4—4.9 (3H, m, 2-H and S-CH_2-), 1.32 and 1.33 (each 1.5H, t, $CO_2CH_2C\underline{H}_3$), 4.26 and 4.27 (each 1H, q, CO_2CH_2-).

15Ca ($n=5$): δ: 1.90 and 2.04 (each 1.5H, d, $J=1$, C≡C-Me), 1.3—2.6 (8H, m, 3-, 4-, 5-, and 6-H_2), 3.6—4.0 (2H, m, 7-H_2), 4.40 and 4.57 (each 1H, s, S-CH_2-), 4.8—5.1 (1H, m, 2-H), 1.32 and 4.32 (3H, br t, and 2H, br q, CO_2Et).

Treatment of the Sulfonium Salts (15) with DBU——General Procedure: DBU (0.8 ml) was added dropwise to a solution of a salt **15** (3 mmol) in acetonitrile (10 ml) with stirring in an ice bath. The reaction mixture was sstirred for a further 1 h at room temperature and then diluted with water (20 ml). The mixture was extracted with CH_2Cl_2 and the extract was washed with satd. NaCl, dried, and evaporated *in vacuo*. The residue was chromatographed on silica gel using *n*-hexane-CH_2Cl_2 (1 : 1) as an eluent to give the ring-expansion product (**18**).

TABLE IV. ^{1}H-NMR Spectral Data[a)] for the Cyclic 2-Ethynyl Sulfides (**14**)

14Aa	1.79 (3H, d, $J=2$, C≡C-Me, 1.80—2.22 (4H, m, 3- and 4-H_2), 2.90 (2H, m, 5-H_2), 3.92 (1H, m, 2-H)
14Ab	0.93 (3H, t, $J=7$, $-CH_2CH_2CH_2C\underline{H}_3$), 1.30—1.62 (4H, m, $-CH_2C\underline{H}_2C\underline{H}_2CH_3$), 1.80—2.22 (2H, m, $-C\underline{H}_2CH_2CH_2CH_3$), 1.90—2.42 (4H, m, 3- and 4-H_2), 2.83—3.20 (2H, m, 5-H_2), 4.50 (1H, m, 2-H)
14Ac	1.90—2.33 (4H, m, 3- and 4-H_2), 2.80—3.22 (2H, m, 5-H_2), 4.30 (1H, m, 2-H), 7.20—7.40 (5H, m, Ar-H)
14Ad	1.92—2.30 (4H, m, 3- and 4-H_2), 2.40 (1H, d, $J=2$, C≡CH), 2.83—3.20 (2H, m, 5-H_2), 4.10 (1H, m, 2-H)
14Ba	1.30—2.21 (6H, m, 3-, 4-, and 5-H_2), 1.90 (3H, d, $J=2$, C≡C-Me), 2.40—2.95 (2H, m, 6-H_2), 3.56 (1H, m, 2-H)
14Bb	0.89 (3H, t, $J=7$, $-CH_2CH_2CH_2C\underline{H}_3$), 1.20—1.61 (4H, m, $-CH_2C\underline{H}_2C\underline{H}_2CH_3$), 2.10—2.32 (2H, m, $-C\underline{H}_2CH_2CH_2CH_3$), 1.62—2.03 (6H, m, 3-, 4-, and 5-H_2), 2.30—2.91 (2H, m, 6-H_2), 3.50—3.55 (1H, m, 2-H)
14Bc	1.22—2.21 (6H, m, 3-, 4-, and 5-H_2), 2.30—3.02 (2H, m, 6-H_2), 3.70—3.74 (1H, m, 2-H), 7.11—7.43 (5H, m, Ar-H)
14Bd	1.40—2.25 (6H, m, 3-, 4-, and 5-H_2), 2.36 (1H, d, $J=2$, C≡C-H), 2.85—3.10 (2H, m, 6-H_2), 3.45—3.60 (1H, m, 2-H)
14Ca	1.42—2.23 (8H, m, 3-, 4-, 5-, and 6-H_2), 1.82 (3H, d, $J=2$, C≡C-Me), 2.51—3.22 (2H, m, 7-H_2), 3.60—3.65 (1H, m, 2-H)
14Cb	0.90 (3H, t, $J=7$, $-CH_2CH_2CH_2C\underline{H}_3$), 1.31—1.50 (4H, m, $-CH_2C\underline{H}_2C\underline{H}_2CH_3$), 2.20—2.25 (2H, m, $-C\underline{H}_2CH_2CH_2CH_3$), 1.52—2.13 (8H, m, 3-, 4-, 5-, and 6-H_2), 2.40—3.12 (2H, m, 7-H_2), 3.51—3.55 (1H, m, 2-H)
14Cc	1.50—2.31 (8H, m, 3-, 4-, 5-, and 6-H_2), 2.52—3.23 (2H, m, 7-H_2), 3.92—3.96 (1H, m, 2-H), 7.20—7.40 (5H, m, Ar-H)
14Cd	1.30—2.31 (8H, m, 3-, 4-, 5-, and 6-H_2), 2.37 (1H, d, $J=2$, C≡C-H), 2.60—2.90 (2H, m, 7-H_2), 3.44—3.65 (1H, m, 2-H)

a) δ ($CDCl_3$), J = Hz.

TABLE V. Cyclic 1-Ethoxycarbonylmethyl-2-ethynyl Sulfonium Salts (**15**)

Compd. No.	Yield (%)	IR ν_{max} cm^{-1} (film) C≡C	C=O
15Aa	95	2250	1730
15Ab	96	2250	1730
15Ac	92	2250	1740
15Ad	98	2150	1730
15Ba	96	2250	1735
15Bb	99	2250	1740
15Bc	98	2250	1740
15Bd	94	2150	1730
15Ca	92	2250	1730
15Cb	86	2250	1740
15Cc	89	2250	1740
15Cd	88	2150	1730

Yields and physical, analytical, and spectral data of the thiocins (**18Aa**—**d**), thionins (**18Ba**—**d**), and thiecins (**18Ca**—**d**) thus obtained are collected in Tables I and II.

2-Ethynylthiochromans (21a—c)——Thiochroman **19** (7.5 g, 50 ml) was successively treated with NCS and one of the ethynylmagnesium bromides (**13a**—**c**) and worked up as described for the preparation of **14** from **12**. The residue was chromatogtaphed on silica gel using *n*-hexane–CH_2Cl_2 (1 : 1) as an eluent to give **21** as a pale yellow viscous oil.

21a: 5.83 g, 62% yield. MS *m/z*: 188 (M^+). IR ν_{max}^{film} cm^{-1}: 2225 (C≡C). NMR δ: 1.69 (3H, d, $J=2$, C≡C–Me), 1.9—2.2 (2H, m, 3-H_2), 2.5—3.0 (2H, m, 4-H_2), 3.8—4.0 (1H, m, 2-H), 6.7—7.0 (4H, m, Ar-H). *Anal.* Calcd for $C_{12}H_{12}S$: C, 80.85; H, 6.38. Found: C, 80.72; H, 6.41.

21b: 9.82 g, 85% yield. MS *m/z*: 230 (M^+). IR ν_{max}^{film} cm^{-1}: 2225 ($C\equiv C$). NMR δ: 0.84 (3H, t, $J=7$, $-CH_2CH_2CH_2C\underline{H}_3$), 1.2—1.6 (4H, m, $-CH_2C\underline{H}_2C\underline{H}_2CH_3$), 2.0—2.3 (4H, m, $-C\underline{H}_2CH_2CH_2CH_3$ and 3-H_2), 2.5—3.1 (2H, m, 4-H_2), 3.9—4.1 (1H, m, 2-H), 6.8—7.1 (4H, m, Ar-H). *Anal.* Calcd for $C_{15}H_{18}S$: C, 78.26; H, 7.83. Found: C, 77.99; H, 7.74.

21c: 11.87 g, 95% yield. MS *m/z*: 250 (M^+). IR ν_{max}^{film} cm^{-1}: 2225 ($C\equiv C$). NMR δ: 2.1—2.3 (2H, m, 3-CH_2), 2.7—3.2 (2H, m, 4-H_2), 4.23 (1H, t, $J=6$, 2-H), 7.0—7.6 (9H, m, Ar-H). *Anal.* Calcd for $C_{17}H_{14}S$: C, 81.60; H, 5.60. Found: C, 81.48; H, 5.77.

1-Ethynylisothiochromans (22a—c)——Isothiochroman **20** (7.5 g, 50 mmol) was successively treated with NCS and the ethynylmagnesium bromides (**13a—c**), and worked up as described for **21** to give **22**.

22a: 4.98 g, 53% yield, pale yellow viscous oil. MS *m/z*: 188 (M^+). IR ν_{max}^{film} cm^{-1}: 2250 ($C\equiv C$). NMR δ: 1.79 (3H, d, $J=2$, $C\equiv C$-Me), 2.7—3.2 (4H, m, 3- and 4-H_2), 4.63 (1H, q, $J=2$, 1-H), 6.9—7.4 (4H, m, Ar-H). *Anal.* Calcd for $C_{12}H_{12}S$: C, 80.85; H, 6.38. Found: C, 80.93; H, 6.58.

22b: 8.28 g, 72% yield, pale yellow viscous oil. MS *m/z*: 230 (M^+). IR ν_{max}^{film} cm^{-1}: 2250 ($C\equiv C$). NMR δ: 0.86 (3H, t, $J=7$, $-CH_2CH_2CH_2C\underline{H}_3$), 1.2—1.7 (4H, m, $-CH_2C\underline{H}_2C\underline{H}_2CH_3$), 2.1—2.4 (2H, m, $-C\underline{H}_2CH_2CH_2CH_3$), 2.7—3.2 (4H, m, 3- and 4-H_2), 4.66 (1H, t, $J=2$, 1-H), 7.0—7.6 (4H, m, Ar-H). *Anal.* Calcd for $C_{15}H_{18}S$: C, 78.26; H, 7.83. Found: C, 78.22; H, 7.97.

22c: 11.08 g, 89% yield, mp 51—52 °C, pale yellow prisms (from EtOH). MS *m/z*: 250 (M^+). IR ν_{max}^{KBr} cm^{-1}: 2250 ($C\equiv C$). NMR δ: 2.7—3.2 (4H, m, 3- and 4-H_2), 4.89 (1H, s, 1-H), 6.9—7.6 (9H, m, Ar-H). *Anal.* Calcd for $C_{17}H_{14}S$: C, 81.60; H, 5.60. Found: C, 81.64; H, 5.53.

1-Ethoxycarbonylmethyl-2-ethynylthiochromanium Trifluoromethanesulfonates (23a—c)——The 2-ethynylthiochromans **21** (5 mmol) were treated with $TfOCH_2CO_2Et$ (1.52 g, 6.5 mmol) and worked up as described for **15** to give the viscous oily salts (**23a—c**) as mixtures of two stereoisomers. It was difficult to separate the isomers and thus each mixture was used in the following reaction without separation.

Yields and IR spectral data of the salts are given below.

23a: 1.74 g, 82% yield. IR ν_{max}^{film} cm^{-1}: 2250 ($C\equiv C$), 1740 ($C=O$).

23b: 1.98 g, 85% yield. IR ν_{max}^{film} cm^{-1}: 2230 ($C\equiv C$), 1730 ($C=O$).

23c: 2.11 g, 87% yield. IR ν_{max}^{film} cm^{-1}: 2250 ($C\equiv C$), 1740 ($C=O$).

2-Ethoxycarbonylmethyl-1-ethynylisothiochromanium Trifluoromethanesulfonates (24a—c)——The 1-ethynylisothiochromans **22** (5 mmol) were treated with $TfOCH_2CO_2Et$ (1.52 g, 6.5 mmol) and worked up as described for **23** to give the viscous oily salts (**24a—c**) as mixtures of two stereoisomers. The mixtures were used in the following reaction without separation of the isomers.

Yields and IR spectral data of the salts are given below.

24a: 1.80 g, 85% yield. IR ν_{max}^{film} cm^{-1}: 2250 ($C\equiv C$), 1740 ($C=O$).

24b: 2.05 g, 88% yield. IR ν_{max}^{film} cm^{-1}: 2225 ($C\equiv C$), 1730 ($C=O$).

24c: 1.95 g, 80% yield. IR ν_{max}^{film} cm^{-1}: 2240 ($C\equiv C$), 1740 ($C=O$).

Treatment of the Salts (23a—c) with DBU——The salts **23** (4 mmol) were treated with DBU (1 ml) in acetonitrile (15 ml) and worked up as described for **15** to give the 6,7-dihydro-1-benzothionins (**27a—c**).

27a: 679 mg, 62% yield, pale yellow oil. MS *m/z*: 274 (M^+). IR ν_{max}^{film} cm^{-1}: 1710 ($C=O$). NMR δ: 1.61 (3H, s, 3-Me), 2.2—3.4 (4H, m, 6- and 7-H_2), 5.2—5.5 (2H, m, 4- and 5-H), 7.0—7.5 (4H, m, Ar-H), 1.23 and 4.12 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{16}H_{18}O_2S$: C, 70.07; H, 6.57. Found: C, 70.09; H, 6.78.

27b: 885 mg, 70% yield, pale yellow oil. MS *m/z*: 316 (M^+). IR ν_{max}^{film} cm^{-1}: 1710 ($C=O$). NMR δ: 0.83 (3H, t, $J=7$, $-CH_2CH_2CH_2C\underline{H}_3$), 1.2—1.5 (4H, m, $-CH_2C\underline{H}_2C\underline{H}_2CH_3$), 1.8—2.4 (2H, m, $-C\underline{H}_2CH_2CH_2CH_3$), 2.4—3.2 (4H, m, 6- and 7-H_2), 5.7—6.1 (2H, m, 4- and 5-H), 7.0—7.4 and 7.72 (3H, m, and 1H, d, $J=7$, Ar-H), 1.26 and 4.24 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{19}H_{24}O_2S$: C, 72.15; H, 6.01. Found: C, 71.96; H, 6.08.

27c: 847 mg, 63% yield, mp 55—59 °C, pale yellow prisms (from *n*-hexane). MS *m/z*: 336 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1720 ($C=O$). NMR δ: 2.5—3.2 (4H, m, 6-, and 7-H_2), 5.9—6.2 (2H, m, 4- and 5-H), 7.1—7.3 and 7.79 (3H, m, and 1H, d, $J=7$, Ar-H), 0.74 and 3.85 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{21}H_{20}O_2S$: C, 75.00; H, 5.95. Found: C, 75.21; H, 6.41.

Treatment of the Salts (24a—c) with DBU——The salts **24** (4 mmol) were treated with DBU (1 ml) in acetonitrile and worked up as described for **15** to give the allenic compounds (**29a**, **b**) from **24a**, **b** and the 1,2-dihydro-3-benzothionin derivative (**30c**) from **24c**.

29a: 675 mg, 60% yield, mp 77—80 °C, colorless prisms (from *n*-hexane). MS *m/z*: 274 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1940 ($C=C=C$), 1730 ($C=O$). NMR δ: 1.87 (3H, d, $J=3$, 5-Me), 2.5—3.1 (4H, m, 1- and 2-H_2), 3.73 (1H, s, 4-H), 6.45 (1H, d, $J=3$, 7-H), 7.0—7.3 (4H, m, Ar-H), 1.21 and 4.10 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{16}H_{18}O_2S$: C, 70.07; H, 6.57. Found: C, 70.03; H, 6.66.

29b: 986 mg, 78% yield, pale yellow oil. MS *m/z*: 316 (M^+). IR ν_{max}^{film} cm^{-1}: 1945 ($C=C=C$), 1730 ($C=O$). NMR δ: 0.88 (3H, t, $J=7$, $-CH_2CH_2CH_2C\underline{H}_3$), 1.1—1.6 (4H, m, $-CH_2C\underline{H}_2C\underline{H}_2CH_3$), 2.0—2.3 (2H, m, $-C\underline{H}_2CH_2CH_2CH_3$), 2.6—3.2 (4H, m, 1- and 2-H_2), 3.78 (1H, s, 4-H), 6.5—6.6 (1H, m, 7-H), 7.0—7.3 (4H, m, Ar-H), 1.21 and 4.10 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{19}H_{24}O_2S$: C, 72.15; H, 7.59. Found: C, 72.00; H, 7.32.

30c: 874 mg, 64% yield, mp 127—128 °C, colorless prisms (from *n*-hexane–CH_2Cl_2). MS *m/z*: 336 (M^+). IR

ν_{max}^{KBr} cm^{-1}: 1710 (C=O). NMR δ: 2.7—3.2 (4H, m, 1- and 2-H_2), 6.6—7.2 (11H, 6-, 7-, and Ar-H), 0.78 and 3.79 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{21}H_{20}O_2S$: C, 75.00; H, 5.95. Found: C, 74.76; H, 5.95.

Treatment of the Allenic Compounds (29a, b) with DBU in Refluxing Benzene——A solution of **29** (0.5 mmol) and DBU (0.1 ml) in benzene (10 ml) was refluxed for 12 h. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel using *n*-hexane–CH_2Cl_2 (1 : 1) as an eluent. From **29a**, the 1,2-dihydro-3-benzothionin (**30a**) was obtained as the sole product. From **29b**, both the 3-benzothionin (**30b**) and the *exo*-methylene compound (**31b**) were obtained successively.

30a: 95 mg, 69% yield, colorelss oil. MS *m/z*: 274 (M^+). IR ν_{max}^{film} cm^{-1}: 1715 (C=O). NMR δ: 1.83 (3H, s, 5-Me), 2.9—3.2 (4H, m, 1- and 2-H_2), 6.51 (1H, d, J=11, 6-H), 6.83 (1H, d, J=11, 7-H), 6.9—7.3 (4H, m, Ar-H), 1.19 and 4.08 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{16}H_{18}O_2S$: C, 70.07; H, 6.57. Found: C, 69.89; H, 6.57.

30b: 71 mg, 45% yield, pale yellow oil. MS *m/z*: 316 (M^+). IR ν_{max}^{film} cm^{-1}: 1720 (C=O). NMR δ: 0.87 (3H, t, J=7, $-CH_2CH_2CH_3C\underline{H}_3$), 1.1—1.6 (4H, m, $-CH_2C\underline{H}_2C\underline{H}_2CH_3$), 1.8—2.4 (2H, m, $-C\underline{H}_2CH_2CH_2CH_3$), 2.9—3.2 (4H, m, 1- and 2-H_2), 6.54 (1H, d, J=11, 6-H), 6.89 (1H, d, J=11, 7-H), 6.9—7.3 (4H, m, Ar-H), 1.20 and 4.08 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{19}H_{24}O_2S$: C, 72.15; H, 7.59. Found: C, 72.36; H, 7.55.

31b: 35 mg, 22% yield, pale yellow oil. MS *m/z*: 316 (M^+). IR ν_{max}^{film} cm^{-1}: 1720 (C=O). NMR δ: 0.87 (3H, t, J=7, $-CH_2CH_2C\underline{H}_3$), 1.1—1.5 (2H, m, $-CH_2C\underline{H}_2CH_3$), 2.04 (2H, dt, J=8 and 8, $-C\underline{H}_2CH_2CH_3$), 2.7—3.3 (4H, m, 1- and 2-H_2), 4.16 (1H, s, 4-H), 5.51 (1H, t, J=8, $=C\underline{H}-CH_2CH_2CH_3$), 6.47 (1H, d, J=11, 6-H), 6.73 (1H, d, J=11, 7-H), 7.0—7.3 (4H, m, Ar-H), 1.18 and 4.09 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{19}H_{24}O_2S$: C, 72.15; H, 7.59. Found: C, 71.91; H, 7.33.

References and Notes

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