dride; a vigorous evolution of gas accompanied the addition. The solution went from clear to cloudy upon further refluxing. The reaction was refluxed for an additional hour, cooled, and filtered: yield (M^+) 1.2 g (91.0%); mp 285–287 °C; mass spectrum, *m/e* 318 (M^+). The infrared and NMR spectra were also identical with **10a.**

Acknowledgments. The authors would like to thank Mr. Kenneth E. Kramer for his synthetic support, Mr. Paul Unger and associates for spectral measurements, and Mr. George Maciak and associates for microanalytical data. We would especially like to thank Professor Jack E. Baldwin, Oxford University, for his interest in our work and for his helpful mechanistic discussions.

Registry No.—**1,** 553-03-7; **3,** 68844-39-3; **5,** 68844-40-6; **6,** 68844-41-7; **7,** 35213-70-8; **8,** 68844-42-8; **9,** 68844-43-9; **10a,** 68844-44-0; **10b,** 68844-45-1; thionyl chloride, 7719-09-7; sodium azide, 26628-22-8.

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"One-Pot" Construction of the Bithiopyran Ring System from an Acyclic Precursor

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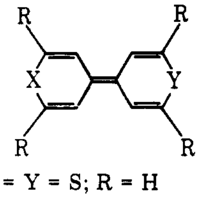
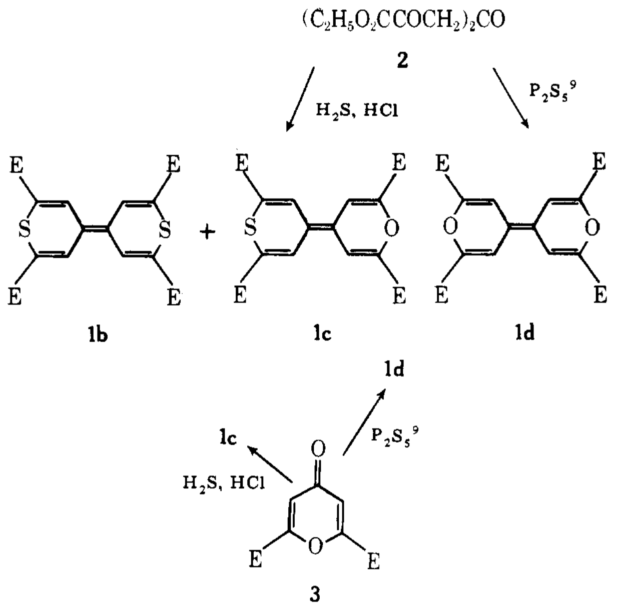
Synthetic procedures to derivatives of $\Delta^{4,4'}$-bithiopyran (BTP, **1a**), a ring system of interest to use in connection with our work on organic conductors,[1] and its benzannelated analogues typically involve a thiopyran derivative which is either reductively coupled[1–5] or induced to eliminate a chalcogen by either thermal[2,6] or photochemical[7] means. We now report the first procedure which yields a derivative of BTP from an acyclic precursor which does not contain sulfur.



1a, X = Y = S; R = H
b, X = Y = S; R = $CO_2C_2H_5$
c, X = O; Y = S; R = $CO_2C_2H_5$
d, X = Y = O; R = $CO_2C_2H_5$
e, X = Y = O; R = H
f, X = Y = O; R = C_6H_5
g, X = Y = S; R = C_6H_5

When an ethanol solution of the readily available acetonedioxalic ester[8] (**2**) is treated with a mixture of hydrogen chloride and an excess of hydrogen sulfide in a Paar autoclave (Scheme I), the dark green 2,2′,6,6′-tetracarboethoxybithiopyran (**1b**) is obtained in 60% yield after column chromatography. If the same reaction is carried out in conventional glassware at atmospheric pressure, a mixture of **1b** and the thiabipyran tetraester **1c**, a previously unknown ring system, is obtained. The known[9] bipyran tetraester **1d** could not be detected in these reaction mixtures by thin-layer chromatography (TLC). Further, **1d** is recovered unchanged from reaction mixtures which yield **1b** and **1c** and thus is not an intermediate in their formation. Moreover, diethyl chelidonate (**3**) reacts with H_2S and HCl to give a complex mixture from which **1c** may be isolated in ~10% yield. Thus, while **3** may be used to prepare **1c**, it is not useful for the preparation of **1b** and is not an intermediate in its synthesis.

Scheme I

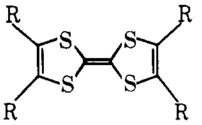


E = $CO_2C_2H_5$

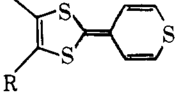
Table I lists the electrochemical and electronic spectral data for **1b, 1c,** and **1d,** along with the data for the unsubstituted compounds, **1a** and **1e,** and for the isoelectronic tetrathiafulvalene (TTF, **4**) and 2-(thiopyran-4-ylidene)-1,3-dithiole[10] (TPDT, **5**) derivatives.

The oxidation potentials ($E_{1/2}{}^{ox}$) of **1a** and **1e** are significantly increased by the introduction of four electron-attracting ester groups, as expected. This effect is somewhat bigger than that observed for the TTF derivatives **4a** and **4b.** The tetraester of BTP (**1b**) is more easily oxidized than the corresponding TTF tetraester **4b**, a trend found in the parent compounds.

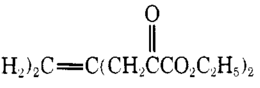
The major result of tetraester substitution on the absorption spectra of **1a** and **1e** is the shift of the major absorption band to longer wavelength. The effect is reminiscent of the behavior of phenyl substituents[4] in the same positions (**1f,g**). As with the electrochemical data, the absorption properties of **1c** are intermediate to those of **1b** and **1d.** While the major



4a, R = H
b, R = CO_2CH_3



5a, R = H
b, R = CO_2CH_3



$$(C_2H_5O_2C\overset{O}{\overset{\|}{C}}CH_2)_2C{=}C(CH_2\overset{O}{\overset{\|}{C}}CO_2C_2H_5)_2$$

6

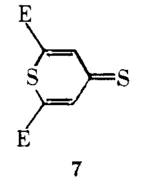


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Table I. Electrochemical and Electronic Spectra Data[11]

compound	E_1	E_2	λ_{max}, nm (log ϵ)
1a[1,4]	+0.20	+0.46	386 (4.81), 367 (4.63), 346 sh (4.25)[1]
1b	+0.75	+0.92	475 (4.70), 445 sh (4.45), 217 (4.46)
1c	+0.80	+1.02[a]	545 sh (3.27), 443 (4.66), 415 sh (4.57), 270 (4.52)
1d	+0.84	+1.14[a]	535 sh (3.10), 500 sh (3.50), 470 (3.73), 409 (4.74), 388 (4.58), 365 sh (4.24), 214 (4.32)
1e[4]	+0.21	+0.50	332 (4.71), 316 (4.60)
4a	+0.33[b]	+0.70[b]	446 (2.44), 355 sh (3.30), 315 (4.11), 306 (4.10)
4b	+0.80[c]	+1.07	445 (3.29), 315 (4.12), 284 (4.16)[d]
5a[10]	+0.28	+0.64	359 (4.5), 348 sh (4.4)
5b[10]	+0.47	+0.80	482 (3.01), 376 sh (3.91), 352 (4.56), 337 (4.44), 323 (4.21)

[a] This number represents the peak position (E_p) of an irreversible anodic wave. [b] E. M. Engler, F. B. Kaufman, D. C. Green, C. E. Klots, and R. N. Compton, *J. Am. Chem. Soc.*, **97,** 2921 (1975). [c] This value was also observed by B. A. Scott, F. B. Kaufman, and E. M. Engler, *J. Am. Chem. Soc.*, **98,** 4342 (1976). [d] Measured in ethanol solution: H. D. Hartzler, *J. Am. Chem. Soc.*, **95,** 4379 (1973).

effect of tetraester substitution in TTF (**4b**) is the intensification of a weak band, diester substitution in TPDT (**5b**) and tetraester substitution of bipyran introduce medium intensity low energy absorption not observed in the parent compounds. This medium intensity absorption is also present in **1c** but could not be detected in **1b**.

While we have not made a mechanistic study of the reactions described above, an intermediate such at **6**, or its enolic forms, obtainable by reductive coupling of **2**, could lead to **1b** and **1c**. However, this suggestion does not preclude the possible intermediacy of the thiopyran-4-thione **7** in the formation of **1b**.

In summary, we have described the first procedure which yields a derivative of the BTP ring system from an acyclic precursor. Also, the thiabipyran ring system has been synthesized for the first time. The electrochemical and spectral properties of the new compounds have been compared to related systems.

Experimental Section[11]

2,2′,6,6′-Tetracarboethoxybithiopyran (1b). An ethanol (550 mL) solution of acetonedioxalic ester (**2**; 20 g, 0.088 mol) was stirred in a Paar autoclave which was evacuated using an aspirator. A mixture of hydrogen sulfide (30.6 g, 0.9 mol) and hydrogen chloride (3.6 g, 0.1 mol) which had been condensed with liquid nitrogen was simultaneously added to the above solution. The temperature of the reaction mixture did not rise above 30 °C, and stirring continued for 15 h. The autoclave was vented in the hood to remove excess gases. The crude reaction product in chloroform which contained **1b** by TLC was chromatographed on silica gel (200 g) with chloroform eluant. After evaporation of the chloroform, the product was recrystallized from carbon tetrachloride to give **1b**: 12.6 g (60%); mp 260–263 °C dec, softening at 245 °C. An analytical sample was obtained from this material by recrystallization from benzene. The NMR spectrum exhibited resonances at δ 1.25–1.52 (triplet, J = 7.5 Hz, 12 H, $-CH_2\mathbf{CH_3}$), 4.25–4.5 (quartet, J = 7.5 Hz, 8 H $-\mathbf{CH_2}CH_3$), and 7.85 (singlet, 4 H). The main features of the IR spectrum were at 1710, 1695, 1615, 1270, 1255, 1040, 795, 745, and 735 cm⁻¹. The mass spectrum exhibited a parent peak at *m/e* 480.

Anal. Calcd for $C_{22}H_{24}O_8S_2$: C, 54.99; H, 5.03; O, 26.63; S, 13.35. Found: C, 54.99; H, 4.96; S, 13.49.

2,2′,6,6′-Tetracarboethoxythiabipyran (1c). To an ethanol solution of acetonedioxalic ester (**2**; 20 g, 0.088 mol) stirred magnetically at room temperature continuously saturated with hydrogen sulfide was added hydrogen chloride gas. The reaction became mildly exothermic; continuous feeding of both gases proceeded for an hour, when TLC analysis (on silica gel with $CHCl_3$ elution) indicated the consumption of **2** and the presence of **1b** and **1c**. A dark precipitate was washed with ammonium sulfide, followed by water and ethanol, and the crude product (10 g) was chromatographed on silica gel in chloroform. Compound **1b** was eluted first, followed by fractions rich in **1c**. The impure **1c** was fractionally recrystallized from carbon tetrachloride, and a 1.5-g sample was then chromatographed on silica gel in benzene and eluted with a 50:50 v/v benzene–chloroform mixture to give **1c**: 1.3 g (6.4%); mp 234 °C dec. The mass spectrum of **1c** exhibited a parent peak at *m/e* 464. The NMR spectrum exhibited resonances at δ 1.20–1.50 (two overlapping triplets, J = 7 Hz, 12 H, $-CH_2\mathbf{CH_3}$), 4.21–4.55 (two overlapping quartets, J = 7 Hz, 8 H, $-\mathbf{CH_2}CH_3$), 7.16 (singlet, 2 H, vinylic protons in pyran ring), and 7.61 (singlet, 2 H, vinylic protons in thiopyran ring). The main features of the IR spectrum were at 1735, 1715, 1705, 1575, 1535, 1370, 1305, 1275, 1225, 1130, 1110, 1045, 1020, 945, 885, 870, 765, 755, 750, 735, and 725 cm⁻¹.

Anal. Calcd for $C_{22}H_{24}O_9S$: C, 56.89; H, 5.21; S, 6.90. Found: C, 56.82; H, 5.04; S, 6.70.

Reaction of Diethyl Chelidonate (3) with Hydrogen Sulfide and Hydrogen Chloride. To an ethanol (10 mL) solution of **3** (1 g, 4.2 mmol), prepared from **2** according to Willstätter and Pummerer,[12] continuously saturated with hydrogen sulfide was added hydrogen chloride gas. The reaction became mildly exothermic, as above. TLC analysis indicated a complex mixture which included **3** and **1c**. After being cooled in a refrigerator overnight, crude **1c** was isolated in ~10% yield; the product may be purified as described above to give identical material.

2,2′,6,6′-Tetracarboethoxybipyran (1d). This compound was prepared as previously described[9] using **2** on a 10-g (44 mmol) scale. The crude product (7.6 g, 77%), mp 195–196 °C, was chromatographed on silica gel in chloroform with elution by ethyl acetate. The product was recrystallized from ethanol to give **4**, mp 201–203 °C (lit.[9] mp 203–204 °C). The NMR spectrum exhibited resonances at δ 1.25–1.50 (triplet, J = 7 Hz, 12 H, $-CH_2\mathbf{CH_3}$), 4.20–4.50 (quartet, J = 7 Hz, 8 H, $-\mathbf{CH_2}CH_3$), and 7.01 (singlet, 4 H). The main features of the IR spectrum were at 1720, 1590, 1345, 1325, 1290, 1220, 1150, 1110, 1025, 1005, 935, 880, 870, 765, 740, and 725 cm⁻¹.

Anal. Calcd for $C_{22}H_{24}O_{10}$: C, 58.93; H, 5.39; O, 35.68. Found: C, 58.70; H, 5.47.

2,3,6,7-Tetrakis(carbomethoxy)tetrathiafulvalene (4b).[13] To a benzene (25 mL) solution of dimethyl 1,3-dithiole-2-thione-4,5-dicarboxylate (10 g, 40 mmol) heated at reflex under nitrogen was added trimethyl phosphite (5.2 g, 44 mmol) via syringe. After reflux for 16 h, the mixture was cooled to room temperature and crude **4b** (8.3 g, 93% yield) was isolated by suction filtration. Slow crystallization of this material from benzene gave black prisms, mp 169–171 °C (lit.[13,14] mp 169–170 °C).

Acknowledgments. The authors wish to thank Professor H. K. Hall, University of Arizona, for useful discussions during the course of this work, Dr. R. J. Gruber for the use of his autoclave, A. P. Fisher, III, for technical assistance, and R. Crandall and F. Elder for the mass spectral data.

Registry No.—**1b,** 68854-14-8; **1c,** 68854-15-9; **1d,** 68854-16-0; **2,** 68854-18-2; **3,** 725-92-8; **4a,** 31366-25-3; **4b,** 68854-17-1; dimethyl 1,3-dithiole-2-thione-4,5-dicarboxylate, 7396-41-0.

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(11) Melting points are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Ultraviolet–visible spectra were recorded on a Cary 15 spectrophotometer in acetonitrile solution in 1-cm cells. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 283 instrument. Cyclic voltammetry measurements were carried out on a Princeton Applied Research PAR 170 instrument in acetonitrile solution using a platinum electrode with 0.1 M tetraethylammonium perchlorate as support electrolyte; potentials reported are vs. a saturated

calomel electrode. Proton nuclear magnetic resonance spectra were recorded on a Bruker WP-80 instrument in deuteriochloroform solution. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane.

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(14) Table I, footnote *d*.

Stereochemical Control of the Ynamine–Claisen Rearrangement

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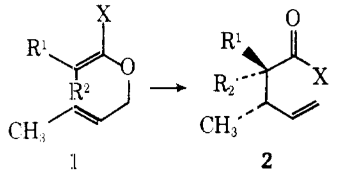
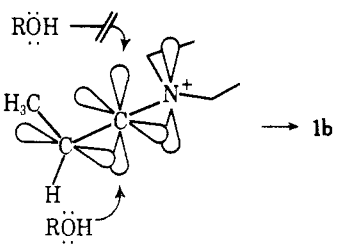
The Claisen rearrangement of carboxylic acid derivatives, proceeding via the ketene acetal tautomers **1**, has gained prominence as a means of introducing adjacent chiral centers in acyclic compounds in a stereoselective manner.[1] For example, the condensation of crotyl alcohol with 1-(diethylamino)-1-ethoxypropene[2] in refluxing xylene affords predominantly the erythro rearrangement product **2a** via the (*Z*)-ketene *N,O*-acetal **1a** in a reaction first developed by Eschenmoser.[3] In a more general procedure, Ireland has shown that either the *E* (**1c**) or *Z* (**1d**) enol trialkylsilyl ethers of allylic esters can be generated selectively as desired, giving the erythro (**2c**) or threo (**2d**) rearrangement products, respectively.[4] The condensation of crotyl alcohol with 1-(diethylamino)propyne also leads to a ketene *N,O*-acetal, and to a rearranged product;[5] however, a study of the stereochemistry of this reaction has not been reported.



1 **2**

a, R^1 = H, R^2 = CH$_3$, X = NEt$_2$; b, R^1 = CH$_3$, R^2 = H, X = NEt$_2$; c, R^1 = H, R^2 = CH$_3$, X = OSiR$_3$; d, R^1 = CH$_3$, R^2 = H, X = OSiR$_3$

A reasonable step in the ynamine–Claisen rearrangement is the addition of the alcohol (or alkoxide) to the keteniminium intermediate **3**. Because the alcohol must approach this intermediate in the plane of the carbon–carbon double bond, we reasoned that steric interference by the methyl group would favor formation of the (*E*)-ketene *N,O*-acetal **1b**, as depicted. Rearrangement of this kinetically formed *E* isomer to the threo product **2b** would be a useful complement to the Eschenmoser procedure.



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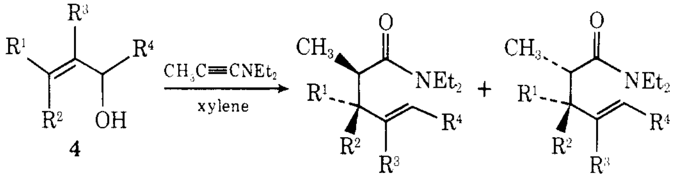
The reaction of crotyl alcohol with 1-(diethylamino)propyne at room temperature in benzene with catalysis by boron trifluoride etherate gives a better than 20:1 ratio of stereoisomeric products, favoring the *same* isomer (**2a**) as does the Eschenmoser reaction. Apparently, in the presence of a Lewis acid, equilibration of the initially formed adduct to the thermodynamically favored *Z* stereoisomer (**1a**) takes place before rearrangement. Similar high stereoselectivity is observed with a variety of allylic alcohols, as shown in Table I.[6]

On the other hand, equilibration of the ketene *N,O*-acetals can be avoided, and rearranged products arising from the *E* isomer (e.g., **1b**) can be obtained by adding the alcohol slowly to a refluxing solution of the ynamine in xylene. Under these conditions, in the absence of acid and with a low concentration of alcohol at all times, equilibration is slowed and rearrangement occurs predominantly via the kinetically formed (*E*)-ketene *N,O*-acetal. This reversal of stereoselectivity with choice of rearrangement conditions is observed for all of the acyclic allylic alcohols examined (see Table I). Moreover, in some instances the stereoselectivity of the uncatalyzed, thermal rearrangement is quite good. Poorer stereoselectivity is observed if the alcohol is added to the ynamine all at once, suggesting that isomerization may be proceeding via the amide acetal (by addition, then elimination, of a second molecule of alcohol).

2-Cyclohexenol reacts with the ynamine in refluxing xylene to give a 10:1 ratio of rearranged products **7** and **8** in 64% yield. The BF$_3$-catalyzed reaction results in dehydration only;[5] however, the condensation of this alcohol with 1-ethoxy-1-(diethylamino)propene affords a 50:50 mixture of **7** and **8**. The fact that the (*Z*)-ketene *N,O*-acetal, formed in the latter reaction, leads to a mixture of products while the intermediate in the neutral ynamine reaction gives essentially a single isomer is further confirmation that this intermediate has the *E* geometry. The major isomer formed in the ynamine–Claisen rearrangement is **7**, and it must arise via a boat-like transition state. The rearrangement of the (*E*)-ketene *N,O*-acetal may

Table I. Stereocontrol of the Ynamine–Claisen Rearrangement



4 **5** **6**

entry	R^1	R^2	R^3	R^4	ratio[a] of 5/6 (yield,[b] %) catalyzed by BF$_3$·Et$_2$O, 25 °C	ratio[a] of 5/6 (yield,[b] %) slow addition of alcohol, 140 °C
a	CH$_3$	H	H	H	1:20 (44)	2:1 (62)
b	H	CH$_3$	H	H	1:5 (37)	2.5:1 (74)
c	CH$_3$	H	CH$_3$	H	1:10 (50)	10:1 (56)
d	CH$_3$	H	H	CH$_3$	1:3 (19)	4:1 (38)
e	Ph	H	H	H	1:10 (60)	2:1 (61)

[a] Lower limit, determined by ^{13}C NMR. [b] Isolated yield of distilled material.