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Ring Expansion Reaction of 2,2-Dimethyl-2,3-dihydrobenzo[*b*]-thiophene *N*-(*p*-Toluenesulfonyl)sulfilimine

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The ring expansion reactions of 2,2-dimethyl-2,3-dihydrobenzo[*b*]thiophene *N*-(*p*-toluenesulfonyl)sulfilimine (**5**) were investigated. Refluxing **5** in benzene gave the dihydrobenzo[*b*]thiophene **7** (60%) and the unsymmetrical dimer **13** (18%) as major products. Refluxing **5** in acetic acid gave a mixture of the dihydrobenzo[*b*]thiophene **8** and the thiochroman **11** in 76% total yield (ratio 2.6: 1), while refluxing **5** in methanol afforded the dihydrobenzo[*b*]thiophene **9** and the thiochroman **12** in 58% total yield (ratio 1: 5). The reaction of **5** with 2-mercaptobenzothiazole in refluxing toluene afforded exclusively the dihydrobenzo[*b*]thiophene **10**. These results were rationalized in terms of the intermediacy of the sulfenamide **15** and thiiranium ion **16**.

Keywords——2,2-dimethyl-2,3-dihydrobenzo[*b*]thiophene; thiochroman; sulfilimine; sulfoxide; sulfenamide; thiiranium ion; ring expansion; Pummerer reaction; cycloelimination; rearrangement

The conversion of penicillin sulfoxides into cephalosporins by acid-catalyzed rearrangement is now well documented.[2] Morin and co-workers,[3] in their investigation of this transformation, postulated initial ring opening to a sulfenic acid derivative (A) followed by formation of a thiiranium ion (B), which collapses to provide the observed products. This mechanistic scheme has now received experimental verification.

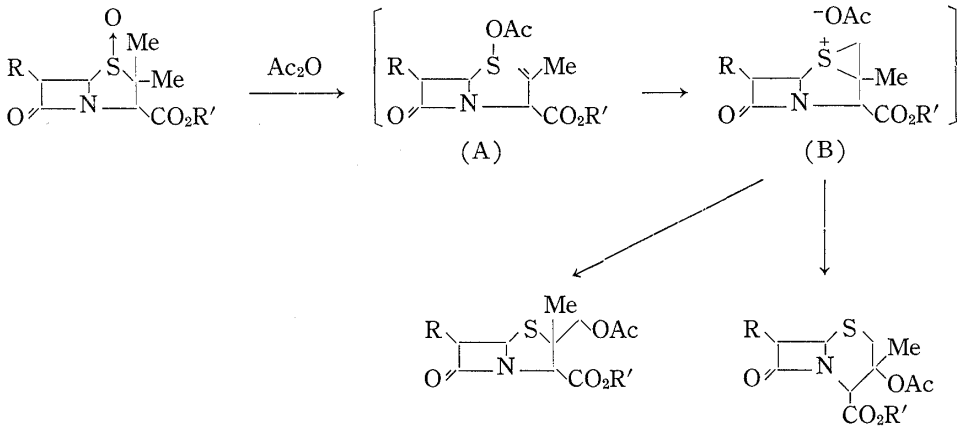

Chart 1

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3) R.B. Morin, B.G. Jackson, R.A. Mueller, E.R. Lavagnino, W.B. Scanlon, and S.L. Andrews, *J. Am. Chem. Soc.*, **91**, 1401 (1969).

In view of the well-known behavior of sulfilimines bearing a β-hydrogen atom, which undergo a cycloelimination reaction,[4] the sulfilimines of penicillin are also expected to undergo such a ring expansion reaction. However, attempts at this reaction have not given promising results, mainly because of difficulty in preparing the sulfilimines.[5,6] In connection with our interest in sulfilimine chemistry,[7] we planned to examine the ring expansion reaction in the sulfilimine series, and we now wish to report results obtained with the readily accessible 2,2-dimethyl-2,3-dihydrobenzo[*b*]thiophene *N*-(*p*-toluenesulfonyl)sulfilimine (**5**). In this paper a Pummerer-type reaction of the corresponding sulfoxide **6** is also described.

Reported syntheses[8] of 2,2-dimethyl-2,3-dihydrobenzo[*b*]thiophene (**4**), a precursor of **5** and **6**, have utilized the thio-Claisen rearrangement of β-methylallyl phenyl sulfide. The low yields of these procedures led us to investigate an alternative route to **4**. Thus, starting from benzo[*b*]thiophen-3(2*H*)-one 1,1-dioxide (**1**),[9] **4** could be obtained in about 53% yield as outlined in Chart 2. Dimethylation of **1** with methyl iodide in the presence of 1,8-diazabicyclo-[5.4.0]-7-undecene (DBU) gave the 2,2-dimethyl derivative **2** in 96% yield.[10] Sodium borohydride reduction of **2** gave the alcohol **3** in 92% yield. Treatment of **3** with thionyl chloride followed by lithium aluminum hydride reduction of the resulting 3-chloro derivative gave the desired dihydrobenzo[*b*]thiophene **4** in 61% yield.

The *N*-(*p*-toluenesulfonyl)sulfilimine **5** was prepared in 73% yield by treating **4** with chloramine-T·trihydrate in methylene chloride-methanol containing a catalytic amount of

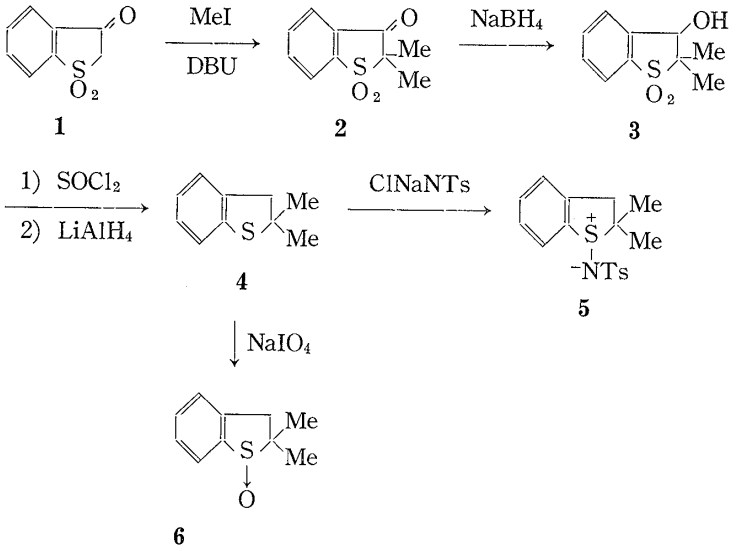


Chart 2

4) *a*) S. Oae and N. Furukawa, *Tetrahedron*, 33, 2359 (1977); *b*) T.L. Gilchrist and C.J. Moody, *Chem. Rev.*, 77, 409 (1977).
5) *a*) M.M. Campbell, G. Johnson, A.F. Cameron, and I.R. Cameron, *J.C.S. Perkin I*, **1975**, 1208; *b*) M. Numata, Y. Imashiro, I. Minamida, and M. Yamaoka, *Tetrahedron Lett.*, **1972**, 5097.
6) Very recently penicillin *N*-cyanosulfilimines have been prepared. However, the sulfilimines did not undergo ring expansion to cephalosporins. [J.E.G. Kemp, D. Ellis, and M.D. Closier, *Tetrahedron Lett.*, **1979**, 3781].
7) *a*) Y. Tamura, H. Matsushima, M. Ikeda, and K. Sumoto, *Synthesis*, **1974**, 277; *b*) Y. Tamura, S.M. Bayomi, M. Ikeda, and K. Sumoto, *Synthesis*, **1977**, 693; *c*) Y. Tamura, Y. Nishikawa, C. Mukai, K. Sumoto, and M. Ikeda, *J. Org. Chem.*, **44**, 1684 (1979); *d*) Y. Tamura, S.M. Bayomi, C. Mukai, M. Ikeda, M. Murase, and M. Kise, *Tetrahedron Lett.*, **1980**, 533.
8) *a*) H. Kwart and M.H. Cohen, *J. Org. Chem.*, **32**, 3135 (1967); *b*) D. Zhamalova, G. Danilova, T.A. Viktorova, *Zh. Org. Khim.*, **1974**, 76 [*C.A.*, **80**, 108281 (1974)].
9) S. Marmor, *J. Org. Chem.*, **42**, 2927 (1977).
10) The preparation of **2** will be described in a separate communication.

acetic acid. The structure of **5** was confirmed by its elemental analysis and spectral data (see "Experimental"). The corresponding sulfoxide **6** was prepared in 61% yield by oxidation of **4** with sodium metaperiodate.

When the sulfilimine **5** was refluxed in benzene, at least three products were obtained, of which two major products, **7** (60%) and **13** (18%), could be obtained as pure compounds. The structure of **7** was readily confirmed by the spectral data (see Table I). The second major product was assigned the dimeric structure **13**. The mass spectrum and elemental analysis data indicated the molecular formula $C_{27}H_{29}NO_2S_3$. The nuclear magnetic resonance (NMR) spectrum of **13** showed three methyl singlets at δ 1.46, 1.50, and 2.40, three AB quartets centered at δ 3.11 (J_{AB}=16 Hz), 3.12 (J_{AB}=16 Hz), and 3.85 (J_{AB}=16 Hz), a singlet (2H) at δ 3.88 (CH_2NTs), and a multiplet (12H) in the aromatic region. Thus, the NMR spectrum is consistent with the unsymmetrical structure **13** and eliminates the possibility of an alternative structure **13'**. The minor oily products could not be isolated in pure forms and were not further examined. A similar result was obtained on refluxing **5** in toluene.

When the reaction was carried out in refluxing acetic acid, two isomeric products **8** and **11** (ratio 72: 28) were obtained in 76% total yield and were separated by careful column chromatography. The structures of **8** and **11** were readily ascertained by examination of the NMR spectra (Tables I and II).

The sulfilimine **5**, on refluxing in methanol, afforded three products which were separated by preparative thin-layer chromatography (TLC). Two of them were found to be isomeric and were assigned the structures **9** (10%) and **12** (48%) on the basis of the NMR spectral evidence (Tables I and II). The third minor product could not be identified.

The reaction of **5** with 2-mercaptobenzothiazole (**14**) in refluxing toluene afforded a single product in quantitative yield, which was assigned the structure **10** on the basis of the NMR spectral data (see Table I).

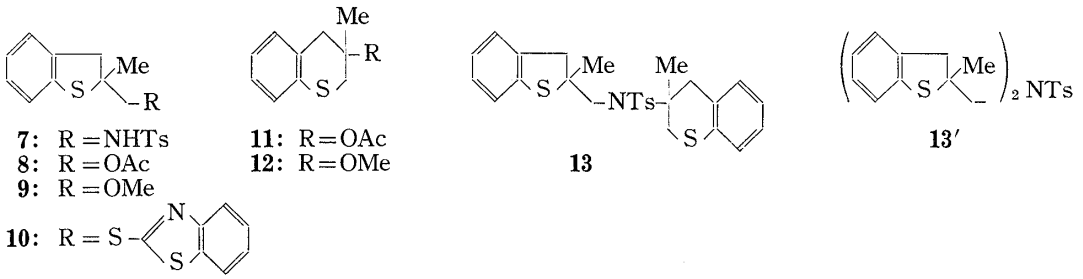


Chart 3

Based on the documented behavior of penicillin sulfoxides[2] and 2,2-dimethylthiochroman *N*-(*p*-toluenesulfonyl)sulfilimine (**17**),[11] it would appear that the reaction of **5** also proceeds through the sulfenamide **15** and thiiranium ion **16**.

Experiments designed to trap the sulfenamide **15** using 2-mercaptobenzothiazole (**14**)[12] as a nucleophile or dimethyl acetylenedicarboxylate (DAC)[13] as an electrophile were unsuccessful.[14] Thus, the reaction of **5** with **14** in refluxing toluene produced a quantitative yield of **10**, and refluxing **5** in toluene in the presence of DAC gave **7** and **13** as major products.

11) *a*) M. Kise, M. Murase, M. Kitano, T. Tomita, and H. Murai, *Tetrahedron Lett.*, **1976**, 691; *b*) M. Kise, M. Murase, M. Kitano, and H. Murai, *Tetrahedron Lett.*, **1976**, 4355; *c*) M. Murase, M. Kitano, M. Kise, and H. Murai, *Chem. Lett.*, **1976**, 849.

12) T. Kamiya, T. Teraji, Y. Saito, M. Hashimoto, O. Nakaguchi, and T. Oku, *Tetrahedron Lett.*, **1973**, 3001.

13) D.H.R. Barton, I.H. Coates, P.G. Sammes, and C.M. Cooper, *J.C.S. Chem. Commun.*, **1973**, 303.

14) In another attempt to trap the sulfenic acid intermediate, refluxing a solution of the sulfoxide **6** and **14** in toluene gave the sulfide **4** (41%), bis-2-benzothiazolyl disulfide (100%), and a trace amount of **10**.

Table I. NMR Data for Dihydrobenzo[*b*]thiophene Derivatives ($CDCl_3$, δ)

Compd	2-CH_3	2-CH_2R	3-CH_2	R	Arom. H
7	1.55(s)	3.08(s) (J=7 Hz)	3.08, 3.22 (ABq) (J=16 Hz)	2.41(s) (CH_3), 4.82(t) (NH) (J=7 Hz)	7.03(s) 7.26, 7.68 (ABq) (J=9 Hz)
8	1.56(s)	4.18(s)	3.07, 3.28 (ABq) (J=16 Hz)	2.04(s) ($COCH_3$)	6.8—7.2(m)
9	1.56(s)	3.46(s)	3.00, 3.30 (ABq) (J=16 Hz)	3.38(s) (OCH_3)	6.8—7.2(m)
10	1.66(s)	3.87(s)	3.07, 3.33 (ABq) (J=16 Hz)		6.8—7.9(m)

Table II. NMR Data for Thiochroman Derivatives ($CDCl_3$, δ)

Compd	2- or 4-CH_2	4- or 2-CH_2	3-CH_3	R	Arom. H
11	2.90, 3.20[a] (ABq) (J=16 Hz)	3.10,[a] 3.50[a] (ABq) (J=13 Hz)	1.70(s)	1.92(s) ($COCH_3$)	6.7—7.2(m)
12	2.76, 2.96 (ABq) (J=16 Hz)	2.88, 3.02[a] (ABq) (J=13 Hz)	1.36(s)	3.31(s) (OCH_3)	6.9—7.2(m)

a) Further splitting with J=2 Hz.

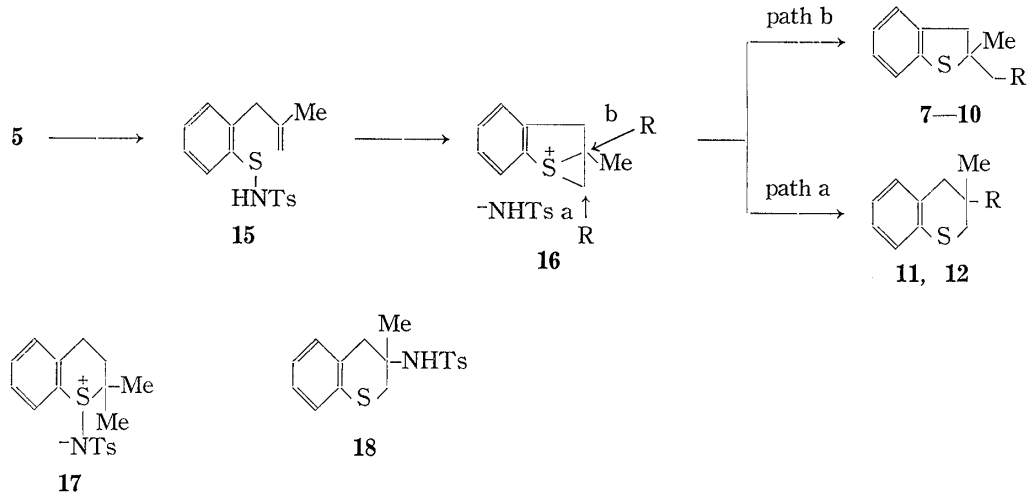


Chart 4

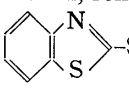
These results are in contrast to the case of the thiochroman sulfilimine **17**[11] and penicillin sulfoxides,[2] in which the initially formed sulfenic acid derivatives react with thiols to give disulfides and with DAC to afford addition products. Failure to trap the sulfenamide **15** in the reaction of **5**, however, does not necessarily rule out this species as a reaction intermediate. Cyclization of **15** to **16** may be too fast for trapping by external reagents to occur, for the following reasons: i) the electrophilic sulfur atom of **15** is held in closer proximity to the nucleophilic olefin than is the case in the thiochroman sulfilimine **17**, and ii) the *p*-toluenesulfonamide anion is a better leaving group than the hydroxide ion from sulfenic acids (transformation of a sulfenic acid to a thiiranium ion usually requires acid catalysts[2,15]).

The ring opening of the possible intermediate **16** may occur either by path a or by path b, leading to the five-membered products or the rearranged products (see Chart 4), and the

15) An exception to this is the ring expansion reaction of 1,3-dithiolanes to dihydro-1,4-dithiins. [C.H. Chen, *Tetrahedron Lett.*, **1976**, 25].

product distributions are highly dependent upon the nature of the nucleophile and the reaction conditions.[16] As can be seen in Table III, reaction of **5** with stronger nucleophiles such as the *p*-toluenesulfonamide anion (entries 1 and 2) and 2-mercaptobenzothiazole (**14**) (or its anion) (entry 6) gave exclusively the five-membered products (ring opening by path a), while the reaction in refluxing methanol (entry 5) gave predominantly the ring-expansion product **12** (ring opening by path b). The formation of the unsymmetrical dimer **13** from **5** takes on special interest, since it may be the result of an alternative ring opening (*i.e.* path b) of **16** by the *p*-toluenesulfonamide anion to give **18** as an intermediate. However, it is more likely that a part of **7** formed by path a reacted with **16** by path b, which would be favored if it is assumed that the nucleophile is the *p*-toluenesulfonamide **7** rather than its anion. This route is supported by the fact that **18** was not found in the reaction mixture. The reaction of **5** in acetic acid might be complicated by a concomitant isomerization of the products under the reaction conditions used. Indeed, pure **8** or **11** in refluxing acetic acid gave an equilibrium mixture consisting of **8** and **11** in a ratio of 80: 20 after 10 hr.

Table III. Product Distribution in the Reaction of **5**

Entry	Reaction conditions	Products (%)[a]
1	C_6H_6, reflux, 5 hr	**7** (60%), **13** (18%)[b]
2	$C_6H_5CH_3$, reflux, 1 hr	**7** (58%), **13** (11%)[b]
3	AcOH, reflux, 0.5 hr	**8**+**11** (76%; 72: 28[c])
4	MeOH, reflux, 33 hr	**9** (10%), **12** (48%)[b] (17: 83[c])
5	 –SH (**14**), $C_6H_5CH_3$, reflux,1 hr	**10** (100%)

a) Isolation yield.
b) Small amounts of unidentified products were formed.
c) The ratio was determined by integration of the methyl signals in the NMR spectrum of the crude reaction mixture.

For comparison, we have also examined the Pummerer-type reaction[2] of the sulfoxide **6** with acetic anhydride. A solution of **6** in acetic anhydride was refluxed until the starting material disappeared (5 hr). Removal of acetic anhydride by evaporation, and column chromatography of the resulting black residue, gave a mixture of **8** and **11** in only 15% total yield and in a 2: 1 ratio. A similar reaction of the sulfilimine **5** with acetic anhydride proceeded cleanly to give **8** and **11** (69% total yield and a 2: 1 ratio) together with **7** (12%).

Experimental[17]

2,2-Dimethyl-2,3-dihydro-3-hydroxybenzo[*b*]thiophene 1,1-Dioxide (3)——$NaBH_4$ (0.57 g, 0.015 mol) was added portionwise to an ice-cooled solution of **2**[10] (2.9 g, 0.013 mol) in methanol (25 ml). After stirring the reaction mixture at room temperature for 2 hr, the solvent was evaporated off and the residue was dissolved in $CHCl_3$. The solution was washed with dil. HCl and H_2O, dried ($MgSO_4$), and concentrated to give crude **3** (2.68 g, 92%). Recrystallization from ether–cyclohexane gave **3** as needles, mp 69—70°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3200—3600 (OH), 1300 and 1150 (SO_2). NMR ($CDCl_3$) δ: 1.35 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 3.25 (b, 1H, OH, disappeared on D_2O exchange), 4.87 (bs, 1H, H-3), and 7.3—7.8 (m, 4H, arom. protons). *Anal.* Calcd for $C_{10}H_{12}O_3S$: C, 56.58; H, 5.89. Found: C, 56.22; H, 5.69.

2,2-Dimethyl-2,3-dihydrobenzo[*b*]thiophene (4)——Thionyl chloride (2.5 g) was added dropwise to a solution of **3** (2.5 g, 0.001 mol) in toluene (15 ml) with stirring at room temperature. After refluxing the

16) D.H.R. Barton, F. Comer, D.G.T. Greig, P.G. Sammes, C.M. Cooper, G. Hewitt, and W.G.E. Underwood, *J. Chem. Soc.*(*C*), **1971**, 3540.
17) All melting points are uncorrected. The IR spectra were determined with a Hitachi EPI-G2 spectrophotometer, and NMR spectra with a Hitachi R-20 spectrometer with tetramethylsilane as internal standard. Low and high resolution mass spectra were obtained with Hitachi RMU-6D and RMU-6M instruments at 70 eV, respectively.

reaction mixture for 4 hr, excess thionyl chloride and toluene were evaporated off *in vacuo*, and anhydrous benzene was then added and removed in the same way. The residue was dissolved in ether–benzene (1: 1) (100 ml) and added to a stirred suspension of $LiAlH_4$ (4 g) in anhydrous ether (100 ml). The reaction mixture was stirred under reflux for 7 hr and then treated with 10% HCl to decompose excess $LiAlH_4$. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried ($MgSO_4$) and concentrated. The residual oil was distilled to give **4** (1.17 g, 61%), bp 130° (bath temperature)/6 mmHg. NMR ($CDCl_3$) δ: 1.52 (s, 6H, $2\times CH_3$), 3.05 (s, 2H, 2-CH_2), and 6.8—7.2 (m, 4H, arom. protons).[8a]

2,2-Dimethyl-2,3-dihydrobenzo[*b*]thiophene *N*-(*p*-Toluenesulfonyl)sulfilimine (5)——Chloramine-T·$3H_2O$ (1.31 g, 5 mmol) was added as a single batch to a stirred solution of **4** (0.82 g, 5 mmol) in methanol (25 ml) and methylene chloride (12 ml) containing acetic acid (0.05 ml) at room temperature. A white precipitate was soon formed. The reaction mixture was stirred at room temperature for 1 hr then concentrated *in vacuo*. The residue was dissolved in $CHCl_3$ and the solution was washed with a saturated $NaHCO_3$ solution and H_2O, then dried ($MgSO_4$), and concentrated. The residual oil was passed through a short silica gel column with ethyl acetate–benzene (5: 1) as an eluent to give **5** (1.22 g, 73%), mp 115—116° (from benzene–*n*-hexane). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1300, 1280, 1140, 1080 (SO_2), 970, and 960 (S^+–N^-). NMR ($CDCl_3$) δ: 1.43 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 2.40 (s, 3H, toluene ring CH_3), 2.98, 3.55 (ABq, $J=16$ Hz, 1H each, CH_2), and 7.0—7.9 (m, 8H, arom. protons). MS *m/e*: 333 (M^+). *Anal.* Calcd for $C_{17}H_{19}NO_2S_2$: C, 61.23; H, 5.74; N, 4.20. Found: C, 60.79; H, 5.64; N, 4.22.

2,2-Dimethyl-2,3-dihydrobenzo[*b*]thiophene 1-Oxide (6)——Sodium metaperiodate (106 mg, 1.8 mmol) was added as a single portion to a stirred solution of **4** (300 mg, 1.8 mmol) in 50% aqueous alcohol (50 ml). After stirring at room temperature for 8 hr, the reaction mixture was concentrated *in vacuo* and the residue was dissolved in $CHCl_3$. The solution was washed with dil. HCl and H_2O, dried ($MgSO_4$), and concentrated to give an oily product which was subjected to short-path silica gel column chromatography. Elution with benzene–*n*-hexane (1: 5) gave **6** (200 mg, 61%), mp 84—86° (from benzene–*n*-hexane). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1025 (S→O). NMR (CCl_4) δ: 1.28 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 2.90, 3.40 (ABq, $J=16$ Hz, 1H each, CH_2), and 7.1—7.8 (m, 4H, arom. protons).[18]

Thermolysis of 5——(A) In Benzene: A solution of **5** (0.66 g, 2 mmol) in benzene (10 ml) was refluxed for 5 hr. Removal of the solvent by evaporation gave a crude mixture which consisted of at least three products as indicated by TLC. This mixture was chromatographed on silica gel. Elution with *n*-hexane gave an unidentified oily mixture (17 mg). Elution with benzene–*n*-hexane (8: 2) gave the dimer **13** (90 mg, 18%), mp 135—137° (from benzene–*n*-hexane). IR ν_{max}^{KCl} cm^{-1}: 1330 and 1150 (SO_2). NMR ($CDCl_3$) δ: 1.46 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 2.40 (s, 3H, toluene ring CH_3), 2.92, 3.24 (ABq, $J=16$ Hz, 1H each, CH_2), 2.92, 3.29 (ABq, $J=16$ Hz, 1H each, CH_2), 3.70, 3.96 (ABq, $J=16$ Hz, 1H each, CH_2), 3.88 (s, 2H, CH_2NTs), and 6.7—7.8 (m, 12H, arom. protons). MS *m/e*: 495 (M^+). *Anal.* Calcd for $C_{27}H_{29}NO_2S_3$: C, 65.42; H, 5.89; N, 2.82. Found: C, 65.24; H, 5.82; N, 2.82.

Further elution with benzene–ethyl acetate (8: 2) afforded 2-methyl-2-*N*-(*p*-toluenesulfonyl)amidomethyl-2,3-dihydrobenzo[*b*]thiophene (**7**) (398 mg, 60%) as white cubes, mp 122—124° (from ethyl acetate–*n*-hexane). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3300 (NH), 1345, and 1160 (SO_2). MS *m/e*: 333 (M^+). *Anal.* Calcd for $C_{17}H_{19}NO_2S_2$: C, 61.23; H, 5.74; N, 4.20. Found: C, 61.06; H, 5.76; N, 4.22.

(B) in Toluene: A solution of **5** (110 mg) in toluene (2 ml) was refluxed for 1 hr. Work-up as described above gave **7** (64 mg, 58%), **13** (18 mg, 11%) and a trace amount of unidentified products.

Reaction of 5 in Acetic Acid——A solution of **5** (100 mg, 3 mmol) in acetic acid (5 ml) was heated under reflux for 30 min. The solution was concentrated *in vacuo* and the residue was dissolved in ethyl acetate. The solution was washed with saturated $NaHCO_3$ and H_2O, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel. Elution with *n*-hexane–benzene (1: 1) afforded a mixture of 2-acetoxymethyl-2-methyl-2,3-dihydrobenzo[*b*]thiophene (**8**) and 3-acetoxy-3-methylthiochroman (**11**) (50 mg, 76%) in a ratio of 72: 28 (by NMR spectroscopy). Rechromatography of this mixture on silica gel with *n*-hexane–benzene (2: 1) as an eluent gave pure samples of **11** and **8**.

Compound **11** gave mp 68—69° (from *n*-hexane). IR ν_{max}^{KCl} cm^{-1}: 1720 (C=O). MS *m/e*: 222 (M^+). *Anal.* Calcd for $C_{12}H_{14}O_2S$: C, 64.83; H, 6.34. Found: C, 64.73; H, 6.34.

Compound **8** was an oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1740 (C=O). This was analyzed by high-resolution mass spectrometry: Calcd for $C_{12}H_{14}O_2S$, 222.0714; Found: 222.0721.

Reaction of 5 in Methanol——A solution of 5 (100 mg, 0.3 mol) in absolute methanol (5 ml) was heated under reflux for 33 hr then concentrated. The residual oil was subjected to preparative TLC on silica gel and developed with benzene to give 2-methoxymethyl-2-methyl-2,3-dihydrobenzo[*b*]thiophene (**9**) as an oil (6 mg, 10%), 3-methoxy-3-methylthiochroman (**12**) as an oil (28 mg, 48%), and a trace of an unidentified oily product. Both **9** and **12** gave a molecular ion peak at *m/e* 194.

Reaction of 5 with 2-Mercaptobenzothiazole (14)——A solution of **5** (110 mg, 0.33 mmol) and **14** (55 mg, 0.33 mmol) in toluene (5 ml) was refluxed for 1 hr. The oily product obtained after removal of the toluene was chromatographed on silica gel, using a mixture of benzene–*n*-hexane (1: 1) as an eluent, to give a viscous

18) G. Kresze and W. Amann, *Spectrochemica Acta*, **26A**, 637 (1970).

oil of 2-(2-benzothiazolyl)thiomethyl-2-methyl-2,3-dihydrobenzo[*b*]thiophene (**10**) (108 mg, quantitative yield). This was analyzed by high-resolution mass spectrometry: Calcd for $C_{17}H_{15}NS_3$, 329.0366; Found: 329.0383.

Reaction of 6 with 2-Mercaptobenzothiazole (14)——A solution of **6** (80 mg, 0.4 mmol) and **14** (85 mg, 0.5 mmol) in toluene (3 ml) was refluxed for 4 hr. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel. Elution with benzene–*n*-hexane (1: 1) gave **4** (30 mg, 41%). Further elution with benzene afforded a trace amount of **10** and finally bis-2-benzothiazolyl disulfide (82 mg), mp 184—186° (from ethyl acetate) (lit.[19] 186°). MS *m/e*: 332 (M^+).

Isomerization of 8 and 11——A solution of **11** (20 mg) in acetic acid (1 ml) was refluxed for 10 hr. Usual work-up gave a mixture of **8** and **11** in a ratio of 80: 20 (by NMR spectroscopy).

Similar treatment of **8** gave a mixture of **8** and **11** in the same ratio.

Reaction of 6 with Acetic Anhydride——A solution of **6** (150 mg, 0.8 mmol) in acetic anhydride (5 ml) was heated under reflux for 5 hr. The color of the reaction mixture became black. After removal of excess acetic anhydride *in vacuo*, the residue was dissolved in ethyl acetate. The solution was washed with saturated $NaHCO_3$ and H_2O, dried (Na_2SO_4), and concentrated. The residual oil was chromatographed on silica gel. Elution with *n*-hexane–benzene (4: 1) gave a mixture of **4** and an unidentified olefinic compound (23 mg). Further elution with the same solvent system gave a mixture of **8** and **11** (28 mg, 15%) in *ca.* 2: 1 ratio (by NMR spectroscopy).

Reaction of 5 with Acetic Anhydride——A solution of **5** (300 mg, 0.9 mmol) in acetic anhydride (10 ml) was heated under reflux for 1 hr and then excess acetic anhydride was evaporated off *in vacuo*. The residue was dissolved in ethyl acetate and the solution was washed with saturated $NaHCO_3$ and H_2O, dried (Na_2SO_4), and concentrated. The residue, which consisted of a mixture of three major components (as indicated by TLC), was chromatographed on silica gel. Elution with *n*-hexane–benzene (2: 1) gave an unidentified oil (3 mg) and then pure **11** (16 mg), mp 68—69° (from *n*-hexane). Further elution with the same solvent system afforded a mixture of **11** and **8** (82 mg) and then pure **8** (40 mg) as an oil. Finally, elution with benzene–ethyl acetate (2: 1) gave **7** (35 mg).

In a separate experiment, a solution of **5** (130 mg, 0.39 mmol) in acetic anhydride (3 ml) was refluxed for 1 hr. After work-up as described above, the crude mixture was subjected to preparative TLC on silica gel with benzene–*n*-hexane (5: 1) to give a mixture of two isomeric products **8** and **11** (57 mg) in a 2: 1 ratio (by NMR spectroscopy). The other products were not isolated.

19) M. Gordon, *J. Polymer Sci.*, 7, 485 (1951).