washed with saturated NaCl solution, dried, and concentrated on the rotary evaporator to give 12.5 g (80%) of white crystals. Recrystallization from CCl_4 gave 7.0 g of **8**, mp 58–58.5° (lit.[11a] mp 58–59°). A second crop was obtained from the mother liquors.

2-*tert*-Butyl-3-*p*-toluenesulfonoxy-1-propanol (9).—The diol **8** (7 g, 0.053 mol) and *p*-toluenesulfonyl chloride (10.05 g, 0.053 mol) were dissolved in 100 ml of pyridine. The solution was placed in the refrigerator for 3 days. The reaction mixture was poured onto ice–water and the product was extracted with ether. The ether extract was washed successively with dilute HCl, saturated $NaHCO_3$, and H_2O. The ether solution was dried and concentrated on the rotary evaporator to give 14 g (92%) of crude monotosylate **9**, which contains some ditosylate: nmr of **9**, δ 0.86 (s, 9 H), 2.44 (m, 1 H), 2.40 (s, 3 H), 3.60 (m, 2 H), 4.04 (m, 2 H), 7.26 (m, 2 H), 7.66 (m, 2 H).

3-*tert*-Butyl-4-hydroxybutyronitrile (10).—Sodium cyanide (2.9 g, 0.059 mol) was added to a solution of the crude monotosylate **9** (14 g) in 50 ml of DMSO. The mixture was stirred at room temperature for 6 days and was then poured on ice–water. The product was extracted with ether. Concentration of the ether extract yielded 6.1 g (88%, assuming that the 14 g of crude tosylate was all **9**) of crude **10**, which was distilled to give 4.9 g of product: bp 72° (0.08 mm); ir ν_{OH} 3500, $\nu_{C\equiv N}$ 2255 cm^{-1} (liquid film); nmr of **10**, δ 0.95 (s, 9 H), 1.6 (m, 1 H), 2.46 (m, 2 H), 3.00 (s, OH), 3.68 (m, 2 H). The nmr spectrum suggests the presence of about 20% of 3-*tert*-butylglutaronitrile. The dinitrile undoubtedly arose from the ditosylate impurity in **9**. The presence of the ditosylate in **9** could not be unequivocally established from the nmr spectrum of crude **9**. 3-*tert*-Butyl-1,5-pentanedioic acid is, however, isolated from the hydrolysis of the nitrile mixture, confirming the presence of the dinitrile in the hydroxynitrile **10**. See the preparation of **7** from **10** which follows.

3-(Hydroxymethyl)-4,4-dimethylpentanoic Acid γ-Lactone (7) from 3-*tert*-Butyl-4-hydroxybutyronitrile (10).—The procedure for the basic hydrolysis of nitriles outlined by Sandler and Karo[12] was used. The product was isolated by extraction with ether. The ether extract was washed with H_2O and then dried and the ether was removed on the rotary evaporator. The crude product was dissolved in ether–pentane and cooled. 3-*tert*-Butyl-1,5-pentanedioic acid (1 g) precipitated and was removed by filtration. The mother liquors were concentrated to give 2.5 g of **7** which had physical properties, *i.e.*, boiling point and ir and nmr spectra, identical with those obtained for **7** synthesized by another route (*vide supra*).

Registry No.—**3**, 16812-82-1; **4**, 36976-64-4; **5**, 36976-65-5; **6**, 36976-66-6; **7**, 22530-95-6; **9**, 36976-68-8; **10**, 36976-69-9; 2-*tert*-butyl-1,4-butanediol, 36976-70-2.

Acknowledgments.—The support of the University of Wyoming Division of Basic Research and the Research Coordinating Committee is appreciated. Our thanks to Mr. R. Mendoza for assistance in obtaining many of the mass and nmr spectra.

(12) S. R. Sandler and W. Karo, "Organic Functional Group Preparation," Vol. I, Academic Press, New York, N. Y., 1968, p 229.

Rearrangement of Dihalocyclopropanes Derived from Some 6,7-Dihydrobenzo[*b*]thiophenes

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Received July 11, 1972

1,1-Dihalocyclopropanes **10** have been prepared from 6,7-dihydrobenzo[*b*]thiophenes **4** derived from 4-oxo-4,5,6,7-tetrahydrobenzo[*b*]thiophene (**2**) through formation of either enol ethers **4a** and **4b** or dehydration of the tertiary alcohols **5**. These alcohols were obtained by reduction of **2** with sodium borohydride or Grignard reagents. The dihalocarbene adducts **10** rearranged with or without an organic base to afford 8*H*-cyclohepta[*b*]-thiophenes **11**.

The 1-thiaazulenium cation (the thienotropylium cation **1**, Scheme I) was reported[2a] to possess unusual stability relative to tropylium and the isoelectronic benzotropylium cations.[2b] Since this discovery, the expected publications describing other representatives of **1** have not appeared.[3] These two factors led us to consider the synthesis of substituted 1-thiaazulenium cations. The preparation of some 8*H*-cyclohepta[*b*]-thiophenes as possible precursors of such cations constitutes the subject of this report.

The 4,4-dialkoxy-4,5,6,7-tetrahydrobenzo[*b*]thiophenes **3a** and **3b** (Scheme I) were obtained by heating 4-oxo-4,5,6,7-tetrahydrobenzo[*b*]thiophene (**2**)[4] under reflux with the appropriate alcohol, a twofold molar excess of trialkyl orthoformate, and a catalytic amount of *p*-toluenesulfonic acid (TsOH). These ketals, unstable in air at room temperature, slowly eliminated alcohol to produce the respective 4-alkoxy-6,7-dihydrobenzo[*b*]thiophenes, **4a** and **4b**. The rate of conversion of **3a,b** to **4a,b** was enhanced by heating **3a,b** with TsOH for 10 min. The enol ethers **4a,b** required refrigeration under nitrogen to prevent reversion to the ketone **2**.

Treatment of **2** with sodium borohydride in ethanol gave an 81% yield of the alcohol **5a**, which readily underwent acid-catalyzed dehydration to 6,7-dihydrobenzo[*b*]thiophene (**4c**). Alkenyl-substituted thiophenes are known to exhibit instability leading to polymerization.[5] Likewise, **4c** polymerized so rapidly that a correct elemental analysis was prevented. The initial report[6] on the reduction of **2** with methylmagnesium bromide stated that only 4-methyl-6,7-dihydrobenzo[*b*]thiophene (**4d**) or the exocyclic isomer, 4-methylene-4,5,6,7-tetrahydrobenzo[*b*]thiophene (**6**) were produced. Subsequent publications[7,8a] described

(1) Taken, in part, from the doctoral dissertation of V. G. G., St. John's University, 1971.

(2) (a) R. G. Turnbo, D. L. Sullivan, and R. Pettit, *J. Amer. Chem. Soc.*, **86**, 5630 (1964); see also D. L. Sullivan and R. Pettit, *Tetrahedron Lett.*, 401 (1963); (b) H. H. Rennhard, G. Modica, W. Simon, E. Heilbronner, and E. Eschenmoser, *Helv. Chim. Acta*, **40**, 957 (1957).

(3) Derivatives of the isomeric 2-thiaazulenium cation have been prepared by M. Winn and F. G. Bordwell, *J. Org. Chem.*, **32**, 1610 (1967), from the precursor, 2-thiaazulen-6-ones, and were found to be more stable than **1**.

(4) L. F. Fieser and R. G. Kennelly, *J. Amer. Chem. Soc.*, **57**, 1611 (1935).

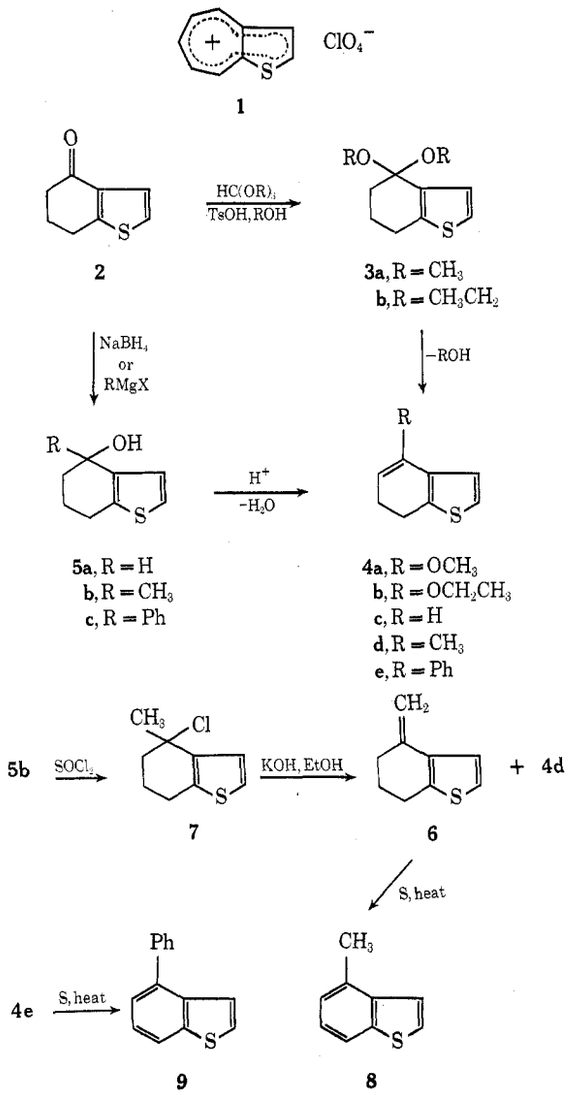
(5) P. Cagniant and G. Merle, *C. R. Acad. Sci., Ser. C*, **267**, 156 (1968).

(6) D. A. H. Taylor, *J. Chem. Soc.*, 2767 (1959).

(7) M. Kloetzel, J. Little, and D. Frisch, *J. Org. Chem.*, **18**, 1511 (1953).

(8) (a) M. Maillet and M. Sy, *C. R. Acad. Sci., Ser. C*, **264**, 1193 (1967). (b) For a detailed study on this type of disproportionation with dihydronaphthalenes, see J. P. Quillet, A. Duperrier, and J. Dreux, *Bull. Soc. Chim. Fr.*, 255 (1967), and J. Jaques and H. B. Kagan, *ibid.*, 128 (1956).

SCHEME I

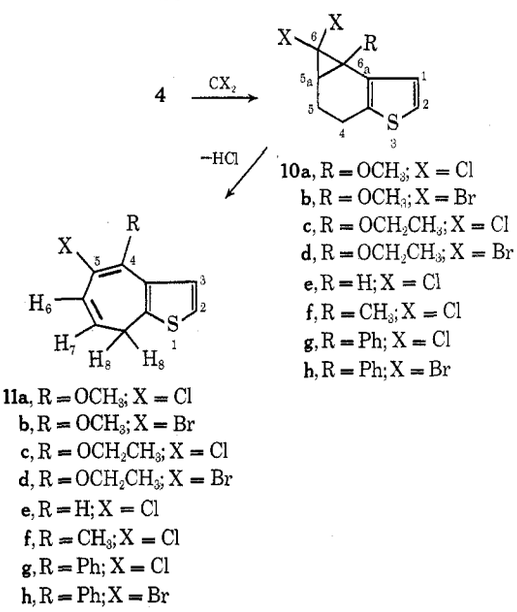


only the isolation of alcohol **5b**. This discrepancy simply resulted from the decomposition of the magnesium bromide complex of the alcohol **5b**, which we found afforded a 90% yield of **5b** if decomposed below 0° while at room temperature the alkenes **4d** and **6** were the only products. Dehydration of **5b** with hot glacial acetic acid gave **4d** and **6** in the isomer ratio of 2.3 (glc determination). Our attempt to minimize the vinylidene olefin **6** through conversion of **5b** to 4-chloro-4-methyl-4,5,6,7-tetrahydrobenzo[*b*]thiophene (**7**) with thionyl chloride followed by dehydrohalogenation also resulted in a mixture of **4d** and **6** with an isomer ratio of 1.9. Any of these mixtures could be separated by preparative gas chromatography. Either the separated components or the mixture of isomers **4d** and **6** gave 4-methylbenzo[*b*]thiophene (**8**) upon dehydrogenation with sulfur.[7] 4-Hydroxy-4-phenyl-4,5,6,7-tetrahydrobenzo[*b*]thiophene (**5c**) was obtained essentially as described,[7] again if the Grignard complex was decomposed below 0°. At room temperature a subsequent dehydration produced the cycloalkene **4e**.

The dehydration of **5c** with acidic reagents was reported[8a] to yield five products. We isolated only two of these, namely, the dihydrobenzothiophene **4e** and 4-phenylbenzo[*b*]thiophene (**9**). These products probably arise from a disproportionation between two molecules of **4e** or **4e** and the carbonium ion generated from **5c**.[8b] Dehydrogenation of **4e** with sulfur gave the benzothiophene **9**.

The use of carbene intermediates for the synthesis of a variety of carbocyclic and heterocyclic systems is well documented.[9,10] The work of Parham and his coworkers[11] with cyclic enol ethers was especially pertinent to our study as well as rearrangements of other 7,7-dihalobicyclo[4.1.0]heptanes.[12-14] The stereospecific cis addition[15] of dichlorocarbene (sodium methoxide and ethyl trichloroacetate[16] or potassium *tert*-butoxide and chloroform[15,17]) to the cyclic vinyl ethers **4a** and **4b** readily afforded the crude 6,6-dichloro-5,5a,6,6a-tetrahydro-6a-alkoxy-4*H*-cyclopropa[*e*][1]benzothiophenes, **10a** and **10c**, as dark brown oils (see Scheme II).[18]

SCHEME II



Their thermolability prevented purification and characterization. Likewise, the adducts **10b** and **10d** were obtained with bromoform and potassium *tert*-butoxide[17] but proved to be less stable[19] and offered no advantage in the rearrangements (*vide infra*). The addition of dichlorocarbene to the very unstable cycloalkene **4c** *possibly* yielded the adduct **10e**, which we were unable to characterize because of its instability. This was contrasted with the adduct of **10f**, which was sufficiently stable to be purified by fractional distillation. With the phenyl substituent in **4e**, a very stable adduct **10g** formed which was purified by distillation and subse-

(9) W. E. Parham and E. E. Schweizer, *Org. React.*, **13**, 55 (1956).
(10) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, Chapter 8.
(11) W. E. Parham, R. W. Soeder, J. R. Throckmorten, K. Kuncl, and R. M. Dodson, *J. Amer. Chem. Soc.*, **87**, 321 (1965), and preceding papers in this series.
(12) D. G. Lindsay and C. B. Reese, *Tetrahedron*, **21**, 1673 (1965).
(13) H. E. Wynberg, *J. Org. Chem.*, **24**, 264 (1959).
(14) G. C. Robinson, *ibid.*, **29**, 3433 (1964).
(15) P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, **78**, 5430 (1956).
(16) W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).
(17) W. v. E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, **76**, 6162 (1954).
(18) For a preliminary account of our effort in this area, see V. G. Grosso and C. V. Greco, *Chem. Commun.*, 771 (1970).
(19) This difference in stability between dichloro- and dibromocarbene adducts was first observed with the 7,7-dihalobicyclo[4.1.0]heptanes.[11,12]

quent recrystallization from pentane. Both compounds **10f** and **10g** were completely characterized by elemental and spectral analysis (see Experimental Section). It is of interest to note that the corresponding dibromocyclopropane, **10h**, was found thermally unstable and could not be purified.

The dichlorocyclopropanes described here showed no precipitation with alcoholic silver nitrate[20] at room temperature and failed to react with methanolic sodium methoxide.[21]

The rearrangement of the dihalocyclopropane adducts **10a–d** with or without an organic base gave 8*H*-cyclohepta[*b*]thiophenes **11a–d**. The results and conditions for these reactions are summarized in Table I. The ring expansions of **10a** and **10c** were accompanied by large amounts of polymerization products. In order to suppress this undesirable side reaction and increase the yield of the cyclohepta[*b*]thiophenes we took advantage of the increased thermolability of adducts **10b** and **10d** to facilitate the rearrangements at lower temperatures.[22] However, a study of the rearrangement of adducts **10a–d** at constant temperature with pyridine or triethylamine (see Table I) showed that the dichloro-

TABLE I

REARRANGEMENT OF DIHALOCYCLOPROPANES 10 TO 8*H*-CYCLOHEPTA[*b*]THIOPHENES 11

Dihalo adduct	R	X	Base[a]	Temp, °C	Time, hr	Yield,[b,c] %
10a	CH_3O	Cl	A	150–155	0.5	58.9
			B	115–116	6	57.4
			C	89–91	48	50.2
			D	120–125	0.25	40.0
10b	CH_3O	Br	A	120–130	0.5	26.4
			B	115–116	4	38.1
			C	89–91	24	34.2
			D	70–80	0.25	21.7
10c	CH_3CH_2O	Cl	A	190–200	0.5	20.0
			B	115–116	5	48.0
			C	89–91	48	45.0
			D	125–140	0.25	40.0
10d	CH_3CH_2O	Br	A	125–135	0.5	30.3
			B	115–116	3	35.4
			C	89–91	24	31.7
			D	70–75	0.25	25.9
10f	CH_3	Cl	A	190–200	0.5	34.7
			D	240–250	0.5	17.1
10g	C_6H_5	Cl	A	150–170	0.5	62.2
			D	190–200	0.5	38.6
10h	C_6H_5	Br	A	150–160	0.5	25.1
			D	200–210	0.5	16.5

[a] A, quinoline; B, pyridine; C, triethylamine; D, neat oil. [b] Per cent yields of cycloheptathiophenes **11a–d** are based on the original alkenes **4a** and **4b**, since the adducts were not purified. The yields of **11f–h** are based on the pure adducts **10f–h**. The products **11** turn dark if exposed to air. [c] Boiling points for products at 0.10 mm: **11a**, 111–115°; **11b**, 120–124°; **11c**, 87–91°; **11d**, 101–105°; **11f**, 104–106°; **11g**, 130–134°; **11h**, 135–140°.

carbene adducts **10a** and **10c** were better precursors for preparing the alkoxycycloheptathiophenes.

(20) It was reported[11] that 1-ethoxy-7,7-dichlorobicyclo[4.1.0]heptane failed to respond to silver nitrate.

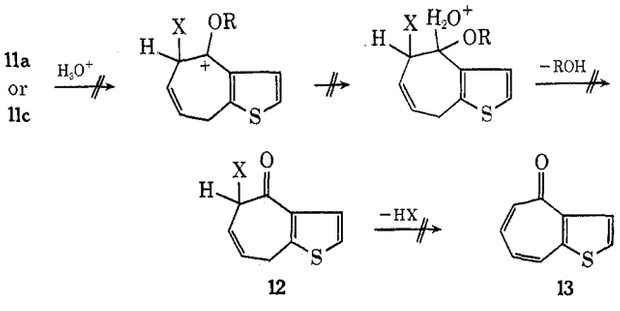
(21) A 3% yield of 1-ethoxy-1,3,5-cycloheptatriene and methyl phenetole were isolated[11] from a complex mixture obtained after treating 1-ethoxy-7,7-dichlorobicyclo[4.1.0]heptane with sodium methoxide.

(22) The 7,7-dibromobicyclo[4.1.0]heptanes[17] were reported[12] to expand more readily than the dichloro adducts and thus were better preparative precursors for ring-expanded products.

The freshly distilled 5-chloro-4-alkoxy-8*H*-cyclohepta[*b*]thiophenes **11a** and **11c** are stable for long periods if refrigerated under nitrogen; otherwise they polymerize at room temperature on exposure to air. The analytical samples, obtained by preparative glc, showed the confirmatory spectral data (see Experimental Section). The structures of **11a–d** were particularly evident from the nmr spectra, which showed, in addition to alkoxy group and thiophene ring absorptions, a sharp doublet (δ 6.00–6.08) for the 6-methine proton, a multiplet (5.40–5.47) for the 7-methine hydrogen, and a sharp doublet (3.08–3.16) for the two methylene protons at position eight. The observed shift in absorption of these latter protons compared to the cycloheptatriene methylene hydrogens (δ 2.20)[23] can be ascribed to paramagnetic shielding by the adjacent thiophene ring.

Our initial synthetic plan envisioned hydrolysis of **11a** to the α-halo ketone **12** (Scheme III) which after

SCHEME III



dehydrohalogenation would yield 1-thiaazulen-4-one (**13**). Derivatives of **1** would have been obtained by applying the procedure of Winn and Bordwell[3] to the ketone **13**. While no reports on the hydrolysis of cyclic β-haloalkenyl ethers are available, the acyclic analogs do undergo hydrolysis.[24] Neither **11a** or **11c** responded to mild acid hydrolysis and more drastic conditions led to polymers. Also, the 2,4-dinitrophenylhydrazone of **12** could not be obtained from either **11a** or **11c**.[25] This resistance to hydrolysis may be attributed to conjugation of the enol ether with the thiophene ring.

Our attention was then directed to the rearrangement of adducts **10e–h**. The inability to observe any change of adduct **10e** to **11e**, by either neat thermal degradation or by refluxing with an organic base below 300°, left doubt as to whether adduct **10e** formed at all (*vide supra*) or if the product **11e** was unstable. At temperatures above 300°, decomposition to polymeric products resulted.[26] The rearrangements of **10f–h** are summarized in Table I. These adducts would not rearrange in refluxing pyridine or triethylamine.[26] This

(23) G. Frankel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, **82**, 5846 (1960).

(24) M. Shostakovskie and A. Bogdanova, *J. Gen. Chem. USSR*, **17**, 565 (1947); *Chem. Abstr.*, **42**, 4519 (1948).

(25) A dinitrophenylhydrazone was reported[11] isolated from 2-ethoxy-3-chloro-1,3-cycloheptadiene. However, a hydrolysis which formed the corresponding ketone was described only for the dibromobicycloheptane on reaction with alcoholic silver nitrate.

(26) In quinoline at 140–150°, 2-oxa-7,7-dichlorobicyclo[4.1.0]heptane gave 2,3-dihydro-6-chlorooxepin [E. E. Schweizer and W. E. Parham, *J. Amer. Chem. Soc.*, **82**, 4085 (1960)] while 1-ethoxy-7,7-dichlorobicyclo[4.1.0]-heptane required 160° with quinoline or refluxing pyridine. This is contrasted with the rearrangement of 7,7-dihalobicyclo[4.1.0]heptane, which required temperatures of 500° [13] or 444° with calcium oxide.[14]

depressed reactivity compared to the accelerating effect of the alkoxy group in **10a–d** clearly reflects the importance of such groups in stabilizing the transition state, which must be essentially polar in nature.[27] The lone-pair electrons on oxygen increased the electron density of the cyclopropane ring, thereby polarizing the carbon–chlorine bond; *i.e.*, the electronic effect of the alkoxy group was transmitted through the cyclopropane ring.[27] The contribution from hyperconjugation by the methyl group in **10f** and from the resonance effect by the phenyl group in **10g** relative to the effect of the alkoxy groups in **10a–d** clearly follows the usual order of activation found in the formation of such incipient cationic transition states, *i.e.*, OR > C_6H_5 > CH_3. Our interpretation of the fate of such transition states is similar to that described by others.[27,28] With ionization of the carbon–chlorine bond trans to the C_{5a} and C_{6a} substituents,[29] the formed cyclopropyl cation underwent a concerted electrocyclic transformation to an alkyl cation by a disrotatory process,[30] the C_{5a} and C_{6a} substituents moving outward. Finally, the alkyl cation lost a proton from the 7 position to afford the 8*H*-cyclohepta[*b*]thiophenes.

Treatment of compounds **11** with either trityl perchlorate or fluoroborate[31] to obtain the substituted 1-thiaazulenium cations resulted in unstable products which have not yet been fully characteirzed.

Experimental Section

All melting points (uncorrected) were determined on a Mel-Temp melting point apparatus. Combustion analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and Childers Microanalytical Laboratories, Milford, N. J. Infrared spectra were determined on a Perkin-Elmer Model 137. Ultraviolet absorption spectra were determined with a Bausch and Lomb Spectronic 505 spectrophotometer. Nmr spectra were obtained on a Varian A-60A spectrometer. Chemical shifts are given in δ (parts per million) downfield from Me_4Si as an internal standard. Gas chromatographic analyses were obtained on a A-700 Varian Aerograph gas chromatography apparatus using helium as a carrier gas and equipped with a thermal conductivity detector. A 6 ft × 0.25 in. i.d. stainless steel column of 5% Apiezon L supported on 60–80 mesh Chromosorb G was used for all separations and purifications.

All reactions were performed under dry nitrogen unless indicated otherwise. The *p*-toluenesulfonic acid was dried by azeotroping off the water by refluxing with benzene and collecting the distillate in a Dean-Stark trap. Sodium methoxide was purchased from Fisher Chemical Co. Trityl perchlorate and fluoroborate were prepared as described.[31] The pentane, bromoform, chloroform, methanol, and ethanol were purified by the procedure of Perrin, Armarego, and Perrin.[32]

4-Oxo-4,5,6,7-tetrahydrobenzo[*b*]thiophene (2).—This compound was prepared according to the procedure of Fieser and Kennelly,[4] bp 81–84° (0.25 mm) [lit.[4] bp 102–110° (2.00 mm)].

4,4-Dimethoxy-4,5,6,7-tetrahydrobenzo[*b*]thiophene (3a).—Into a 200-ml flask was added 15.2 g (0.10 mol) of **2**, 44 g (0.41 mol) of trimethyl orthoformate, 50 ml of dry methanol, and 0.50 g of *p*-toluenesulfonic acid. This mixture was stirred at room temperature for 24 hr and refluxed for 5 hr. The solution gradually changed from light yellow to a dark purple. The reaction was cooled to room temperature and neutralized with alcoholic sodium methoxide, whereupon the color of the solution changed from dark purple to light yellow. After concentration of the solution under reduced pressure, the yellow oil was distilled (6-in. Vigreux), giving 17.1 g (86%) of **3a** as a colorless oil, bp 69–72° (0.10 mm). The oil, which solidified upon standing (mp 52–57°), was recrystallized twice from pentane to yield 15 g (75.8%) of **3a**: mp 58–60°; ir (KBr) disappearance of carbonyl absorption at 1690 cm^{-1}, ketal bands at 1055, 1100, and 1160 cm^{-1}; uv max (95% EtOH) 235 nm (ϵ 4100); nmr ($CDCl_3$) δ 7.05 (d, 2, thiophene), 3.24 (s, 6, $-OCH_3$), 2.78 (t, 2, $-CH_2-$), 2.00 (m, 4, $-CH_2CH_2-$).

Anal. Calcd for $C_{10}H_{14}O_2S$: C, 60.57; H, 7.11; S, 16.17. Found: C, 60.49; H, 7.21; S, 16.37.

4,4-Diethoxy-4,5,6,7-tetrahydrobenzo[*b*]thiophene (3b) was prepared by the same method as **3a** using ethanol, triethyl orthoformate, and sodium ethoxide to yield 19.2 g (85%) of the diketal **3b**, bp 70–74° (0.10 mm). In seven runs the average yield was 80%. The purified oil, which solidified upon standing (mp 62–66°), was recrystallized from methanol to give a white solid: mp 66–67°; ir (neat) disappearance of carbonyl band at 1690 cm^{-1}; uv max (95% EtOH) 236 nm (ϵ 4090); nmr ($CDCl_3$) δ 7.10 (d, 2, thiophene), 3.62 (m, 4, $-OCH_2-$), 2.78 (m, 2, $-CH_2-$), 2.01 (m, 4, $-CH_2CH_2-$), 1.15 (t, 6, CH_3-).

Anal. Calcd for $C_{12}H_{18}O_2S$: C, 63.68; H, 8.00; S, 14.16. Found: C, 63.76; H, 8.01; S, 14.29.

4-Methoxy-6,7-dihydrobenzo[*b*]thiophene (4a).—Into a 100-ml round-bottom flask fitted with a magnetic stirrer was added 19.8 g (0.10 mol) of **3a** and 0.10 g of *p*-toluenesulfonic acid. The reaction was heated to 80°, the methanol was distilled off, and the dark oil that remained was distilled (6-in. Vigreux) to give 10.1 g (60.2%) of a colorless oil, bp 74–76° (0.10 mm). Gas chromatography showed only one component (conditions: column temperature 175°, helium flow 80 ml/min, retention time 4.2 min): ir (neat) doublet at 1695, 1680 (C–C stretch in vinyl ether), 1255 cm^{-1} (=COC); uv max (95% EtOH) 225 nm (ϵ 14,800), 288 (1800); nmr (neat) δ 7.00 (q, 2, thiophene), 4.50 (t, 1 $=CHCH_2-$), 3.49 (s, 3, $-OCH_3$), 2.50 (m, 4, $-CH_2CH_2-$).

Anal. Calcd for $C_9H_{10}OS$: C, 65.02; H, 6.06; S, 19.28. Found: C, 65.21; H, 6.13; S, 19.20.

4-Ethoxy-6,7-dihydrobenzo[*b*]thiophene (4b) was prepared in the same manner as described for **4a** to afford 9.0 g (50%) of a colorless oil **4b**, bp 57–59° (0.10 mm). In seven preparations the average yield was 40%. Gas chromatography showed the product to contain only one component (conditions: column temperature 175°, helium flow 60 ml/min, retention time 6.2 min): ir (neat) 1685 (C–C stretch of vinyl ether), 1250 cm^{-1} (=COC); uv max (95% EtOH) 225 nm (ϵ 14,700), 288 (1820); nmr (neat) δ 6.99 (q, 2, thiophene), 4.52 (t, 1, $=CHCH_2-$), 3.68 (q, 2, $-OCH_2CH_3$), 2.50 (m, 4, $-CH_2CH_2-$), 1.24 (t, 3, $-OCH_2CH_3$).

Anal. Calcd for $C_{10}H_{12}OS$: C, 66.73; H, 6.70; S, 17.78. Found: C, 66.81; H, 6.88; S, 17.98.

4-Hydroxy-4,5,6,7-tetrahydrobenzo[*b*]thiophene (5a).—Into a 250-ml round bottom flask was added 10.0 g (0.065 mol) of **2**, 150 ml of absolute ethanol, and 2.66 g (0.07 mol) of sodium borohydride. After the solution was stirred at room temperature for 24 hr, 100 ml of water was added and the ethanol was evaporated at reduced pressure. The remaining aqueous solution was extracted with ether (2 × 25 ml). The ether extract was washed with water (2 × 10 ml) and dried ($MgSO_4$) overnight, and the ether was evaporated at reduced pressure. The remaining 9.2 g of colorless oil was dissolved in 100 ml of pentane and placed in the refrigerator overnight to deposit white crystals, 8.2 g (81%), mp 63–64°. The reaction was run four times with an average yield of 75%: ir (KBr) 3400 cm^{-1} (OH); nmr ($CDCl_3$) δ 6.84 (s, 2, thiophene), 4.65 (m, 1, HCOH), 2.70 (m, 2, $-CH_2-$), 2.10 (s, 1, OH), 1.92 (m, 4, $-CH_2CH_2-$). Upon shaking with D_2O the band at δ 2.10 disappeared.

Anal. Calcd for $C_8H_{10}OS$: C, 62.31; H, 6.53; S, 20.78. Found: C, 62.18; H, 6.45; S, 20.95.

4-Hydroxy-4-methyl-4,5,6,7-tetrahydrobenzo[*b*]thiophene (5b) was prepared according to the procedure of Kloetzel, Little, and Frisch:[7] yield 83.5%; mp 74–76° (lit.[7] yield 91% mp 75–76°); ir (KBr) 3400 cm^{-1} (OH); nmr ($CDCl_3$) δ 7.00 (s, 2, thiophene), 2.74 (m, 2, $-CH_2-$), 2.31 (s, 1, OH), 1.85 (m, 4, $-CH_2-CH_2-$), 1.48 (s, 3, $-CH_3$). The band at δ 2.31 disappeared when the compound was shaken with D_2O.

4-Hydroxy-4-phenyl-4,5,6,7-tetrahydrobenzo[*b*]thiophene (5c) was prepared according to the procedure of Kloetzel, Little, and

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Frisch:[7] yield 77%; mp 64–66° (lit.[7] yield 89%, mp 65–67°); ir (KBr) 3400 cm^{-1} (OH); nmr ($CDCl_3$) δ 7.25 (s, 5, phenyl), 6.78 (q, 2, thiophene), 2.83 (m, 2, $-CH_2-$), 2.35 (s, 1, OH), 2.01 (m, 4, $-CH_2CH_2-$). The proton at δ 2.35 disappeared when the compound was shaken with D_2O.

Anal. Calcd for $C_{14}H_{14}OS$: C, 73.01; H, 6.13; S, 13.91. Found: C, 72.90; H, 6.22; S, 14.01.

6,7-Dihydrobenzo[*b*]thiophene (4c).—In a 100-ml round-bottom flask was added 15.4 g (0.10 mol) of **5a** and 0.10 g of *p*-toluenesulfonic acid. The mixture was heated on a steam bath with stirring for 15 min. The dark blue solution was distilled, giving 3.2 g (23.5%) of a colorless oil, bp 68–71° (0.10 mm), ir (neat) 1625 cm^{-1} (C=C), disappearance of OH band at 3400 cm^{-1}.

The oil polymerizes very rapidly upon standing in air and less rapidly under nitrogen or with refrigeration. However, it had to be used immediately for the carbene insertion reactions.

4-Methyl-6,7-dihydrobenzo[*b*]thiophene (4d). A. Dehydration of 5b.—Into a 100-ml round-bottom flask was added 16.8 g (0.10 mol) of **5b** and 30 ml of glacial acetic acid. The mixture was heated on a steam bath overnight, during which the solution turned dark yellow. The acetic acid was evaporated at reduced pressure to give 14 g of a yellow oil. Distillation of the crude oil gave 13 g (86.6%) of a colorless oil, bp 51–53° (0.25 mm). Gas chromatography showed two components in a ratio of 70:30. Preparative gas chromatography (conditions: column temperature 170°, helium flow 75 ml/min, retention time 4.10 min for major component, 4.18 min for minor component) separated 4-methyl-6,7-dihydrobenzo[*b*]thiophene (**4d**) (70%) from the exocyclic isomer (30%) **6**: ir of **4d** (neat) 1625 cm^{-1} (C=C) and the disappearance of OH at 3400 cm^{-1}; nmr (neat) δ 6.75 (s, 2, thiophene), 5.35 (m, 1, HC=C), 2.60 (m, 2, $-CH_2-$), 2.25 (m, 2, $-CH_2-$), 1.90 (s, 3, CH_3-).

Anal. Calcd for $C_9H_{10}S$: C, 71.94; H, 6.71; S, 21.34. Found: C, 71.76; H, 6.51; S, 21.28.

B. From 4-Chloro-4-methyl-4,5,6,7-tetrahydrobenzo[*b*]thiophene (7).—Into a 250-ml round-bottom flask was added 50 ml of dry benzene and 8.4 g (0.05 mol) of **5b**. To this solution was added, over a 1-hr period, 11.9 g (0.10 mol) of thionyl chloride. The solution turned dark yellow after the addition and was then refluxed for 1 hr. Upon cooling to room temperature the excess thionyl chloride and benzene were removed at reduced pressure to yield 8.8 g of a yellow oil. This oil was dissolved in 40 ml of absolute ethanol and 2.5 g of potassium hydroxide was added. The mixture was stirred at room temperature overnight (12–15 hr), then refluxed for 1 hr. The potassium chloride was filtered off and the ethanol filtrate was evaporated at reduced pressure to yield 4.8 g of an oil distilling at 50–52° (0.10 mm). Gas chromatography (conditions: column temperature 170°, helium flow 75 ml/min, retention time 4.10 min for major component, 4.18 min for minor component) showed this to be a 65:35 mixture of **4d** and **6**.

4-Phenyl-6,7-dihydrobenzo[b]thiophene (4e).—Into a 300-ml round-bottom flask was added 23 g (0.10 mol) of **5c** and 100 ml of glacial acetic acid. This solution was heated on a steam bath for 12 hr, during which it turned dark yellow. The acetic acid was evaporated at reduced pressure to give 20 g of a yellow oil. Distillation gave 3 g of 4-phenylbenzo[*b*]thiophene (**9**), bp 55–70° (0.10 mm), and 18.2 g (86%) of a colorless oil, bp 115–120° (0.10 mm). This oil solidified upon standing and was recrystallized from pentane to give 17 g of white crystals of **4e**: mp 54–55°; average yield for five preparations was 80%; ir (KBr) 1620 cm^{-1} (C=C); nmr ($CDCl_3$) δ 7.22 (s, 5, phenyl), 6.80 (d, 2, thiophene), 5.77 (t, 1, $CH_2=CHC_6H_5$), 2.58 (complex m, 4, $-CH_2CH_2-$).

Anal. Calcd for $C_{14}H_{12}S$: C, 79.20; H, 5.69; S, 15.10. Found: C, 79.41; H, 5.66; S, 15.28.

4-Methylbenzo[*b*]thiophene (8).—To 1.5 g (0.01 mol) of **4d** was added 0.36 g of elemental sulfur and the mixture was heated in a test tube to 250° and kept there for 5 min. The black mixture was distilled to give 0.8 g (54%) of a colorless oil, bp 50–53° (1.00 mm), picrate mp 133–136° (lit.[7] mp 135–136°).

4-Phenylbenzo[*b*]thiophene (9).—To 4.2 g (0.02 mol) of **4e** was added 0.61 g (0.02 mol) of elemental sulfur. The mixture was heated in a bomb at 240–250° for 20 min and cooled, and the black oil was distilled to give 3.1 g of a light yellow oil, bp 65–75° (0.10 mm). The purified oil solidified and was recrystallized from 95% ethanol to give 2.5 g (60%) of white crystals, mp 45–47° (lit.[7] mp 48°).

Anal. Calcd for $C_{14}H_{10}S$: C, 79.96; H, 4.79. Found: C, 79.90; H, 4.79

The sulfone had mp 137–139° (lit.[7] mp 139°).

General Procedure for the Preparation of 6,6-Dihalo-5,5a,6,6a-tetrahydro 6a-Substituted 4*H*-Cyclopropa[*e*][1]benzothiophenes. A. Haloform–Potassium *tert*-Butoxide Method. 10a–e.—A solution of the appropriate cycloalkene **4** (0.05 mol) in 50 ml of dry pentane was cooled to 0° and treated with an equimolar amount of potassium *tert*-butoxide. The appropriate haloform (1.5 molar equiv) was added dropwise over 1 hr, which gave a dark brown solution. After stirring overnight (12–15 hr), initially in an ice bath and then at room temperature, the precipitated salts were filtered off and washed with 10 ml of dry pentane. The combined pentane filtrates were evaporated (30°) at reduced pressure to afford the crude dihalocarbene adducts **10a–e**.

B. Ethyl Trichloroacetate–Sodium Methoxide Method with 4b.—To 4.5 g (0.02 mol) of **4b** in 40 ml of dry pentane cooled to 0–10° was added 1.3 g (0.024 mol) of sodium methoxide and 4.7 g (0.025 mol) of ethyl trichloroacetate, which gave a yellow mixture. After 4 hr stirring in an ice bath followed by 12–15 hr at room temperature the dark brown solution was filtered and the residue was washed with 10 ml of pentane. The combined pentane filtrates were evaporated (25°) at reduced pressure to afford 6 g of crude 6,6-dichloro-6a-ethoxy-5,5a,6,6a-tetrahydro-4*H*-cyclopropa[*e*][1]benzothiophene (**10c**) as a dark orange oil.

6,6-Dichloro-5,5a,6,6a-tetrahydro-6a-methyl-4*H*-cyclopropa[*e*]-[1]benzothiophene (10f).—Into a 100-ml round-bottom flask fitted with a magnetic stirrer was added 4.5 g (0.03 mol) of **4d** and 50 ml of dry pentane. The reaction flask was placed in an ice bath and 3.4 g (0.03 mol) of potassium *tert*-butoxide was added followed by dropwise addition over a 1-hr period of 6.0 g (0.05 mol) of purified chloroform, whereupon the mixture turned dark brown. The reaction was stirred at room temperature overnight (12–15 hr), then filtered and the residue was washed with 10 ml of pentane. The pentane filtrates were combined and evaporated at reduced pressure, yielding 4.7 g of a dark brown oil. Distillation (6-in. Vigreux) gave 2.3 g (36.4%) of a colorless oil, bp 80–85° (0.10 mm), ir (neat) 1010 (cyclopropane), 815 cm^{-1} (CCl).

Anal. Calcd for $C_{10}H_{10}Cl_2S$: C, 51.51; H, 4.32; Cl, 30.41; S, 13.75. Found: C, 51.79; H, 4.24; Cl, 30.20; S, 13.84.

6,6-Dichloro-5,5a,6,6a-tetrahydro-6a-phenyl-4*H*-cyclopropa[*e*]-[1]benzothiophene (10g).—Into a 100-ml round-bottom flask fitted with a magnetic stirrer was added 6.3 g (0.03 mol) of **4e**, 50 ml of dry pentane, and 1.62 g (0.03 mol) of sodium methoxide. The reaction was cooled in an ice bath and 5.8 g of purified ethyl trichloroacetate was added in one portion. The reaction mixture turned dark yellow. It was stirred in an ice bath for 4 hr and then at room temperature overnight (12–15 hr). The solution was filtered and the residue was washed with 10 ml of pentane. The pentane filtrates were combined and evaporated at reduced pressure to give 7.0 g of a dark, thick, orange oil. The oil was dissolved in 100 ml of hot pentane and cooled in the refrigerator to give 1.8 g (20.4%) of a white solid: mp 110–112°; ir (KBr) 1020 (cyclopropane), 810 cm^{-1} (CCl); nmr ($CDCl_3$) δ 7.31 (m, 5, phenyl), 6.82 (s, 2, thiophene), 2.85 (m, 2, $-CH_2-$), 2.34 (m, 2, $-CH_2-$), 1.00 (m, 1, HCCCl).

Anal. Calcd for $C_{15}H_{12}Cl_2S$: C, 61.03; H, 4.09; Cl, 24.02; S, 10.86. Found: C, 60.95; H, 4.03; Cl, 24.05; S, 10.93.

6,6-Dibromo-5,5a,6,6a-tetrahydro-6a-phenyl-4*H*-cyclopropa[*e*]-[1]benzothiophene (10h).—Into a 200-ml round-bottom flask fitted with a magnetic stirrer was added 10.6 g (0.05 mol) of **4e**, 100 ml of dry pentane, and 5.6 g (0.05 mol) of potassium *tert*-butoxide. The reaction was cooled to 0° in an ice bath and 12.6 g (0.05 mol) of bromoform was added dropwise over a 1-hr period. The reaction turned black and was stirred at 0° for 5 hr and then at room temperature overnight (12–15 hr). The reaction was filtered and the residue was washed with 10 ml of pentane. The pentane filtrates were combined and evaporated at reduced pressure to give 11.5 g of a dark brown oil which would not be further purified.

General Procedure for the Rearrangement of Dihalocyclopropanes 10 to the 8*H*-Cyclohepta[*b*]thiophenes 11. A. Pyrolysis in Base.—The dihalocarbene adduct **10** was added to an excess of freshly distilled organic base and heated for the stated time at the designated temperature (consult Table I), then cooled to room temperature, and the amine hydrohalide salt was filtered off. The residue was washed with ether and the combined ether–organic base filtrate was evaporated at reduced pressure. The residual dark oil was vacuum distilled.

B. Neat Pyrolysis.—The adduct **10** was heated at atmospheric pressure at the designated temperature and time (Table I), cooled to room temperature, and vacuum distilled. An alternate method was to heat the adduct under a slight vacuum, during which the exothermic rearrangement evolved a gas (vacuum decrease observed), and then to raise the temperature gradually until distillation of the colorless oil commenced.

In all cases, analytical samples were obtained by preparative glc. The conditions required, spectral data of the products, and their elemental analyses, respectively, are described below for the individual cyclohepta[*b*]thiophenes.

5-Chloro-4-methoxy-8*H*-cyclohepta[*b*]thiophene (11a) (column temperature 175°, helium flow rate 80 ml/min, retention time 18.2 min) had ir (neat) 1625 (C=C), 1225, 1025 cm^{-1} (=COC); uv max (95% EtOH) 225 nm (ϵ 21,000), 278 (8200), 360 (650); nmr (neat) δ 7.02 (s, 2, thiophene), 6.00 (d, 1, H-6), 5.40 (m, 1, H-7) 3.62 (s, 3, $-OCH_3$), 3.08 (d, 2, H-8).

Anal. Calcd for $C_{10}H_9ClOS$: C, 56.46; H, 4.26; Cl, 16.67; S, 15.07. Found: C, 56.38; H, 4.10; Cl, 16.40; S, 15.00.

5-Bromo-4-methoxy-8*H*-cyclohepta[*b*]thiophene (11b) (column temperature 170°, helium flow 140 ml/min, retention time 20 min) had ir (neat) 1630 (C=C), 1225 and 1025 cm^{-1} (=COC); uv max (95% EtOH) 225 nm (ϵ 20,700), 278 (7800), 365 (645); nmr ($CDCl_3$) δ 7.00 (s, 2, thiophene), 6.02 (d, 1, H-6), 5.47 (m, 1, H-7), 3.67 (s, 3, $-OCH_3$), 3.16 (d, 1, H-8).

Anal. Calcd for $C_{10}H_9BrOS$: C, 46.70; H, 3.53; Br, 31.08; S, 12.47. Found: C, 46.48; H, 3.40; Br, 30.77; S, 12.30.

5-Chloro-4-ethoxy-8*H*-cyclohepta[*b*]thiophene (11c) (column temperature 200°, helium flow 100 ml/min, retention time 20.2 min) had ir (neat) 1620 (C=C), 1225, and 1050 cm^{-1} (=COC); uv max (95% EtOH) 228 nm (ϵ 20,900), 282 (8000), 362 (690); nmr (neat) δ 7.00 (s, 2, thiophene), 5.95 (d, 1, H-6), 5.42 (m, 1, H-7), 3.85 (q, 2, $-OCH_2CH_3$), 3.11 (d, 2, H-8), 1.24 (t, 3, $-OCH_2CH_3$).

Anal. Calcd for $C_{11}H_{11}ClOS$: C, 58.28; H, 4.89; Cl, 15.64; S, 14.14. Found: C, 58.30; H, 4.73; Cl, 15.50; S, 14.42.

5-Bromo-4-ethoxy-8*H*-cyclohepta[*o*]thiophene (11d) (column temperature 200°, helium flow 140 ml/min, retention time 22 min) had ir (neat) 1625 (C=C), 1220, and 1025 cm^{-1} (=COC); uv max (95% EtOH) 232 nm (ϵ 20,850), 280 (7500), 365 (680); nmr ($CDCl_3$) δ 7.05 (s, 2, thiophene), 6.08 (d, 1, H-6), 5.45 (m, 1, H-7), 3.92 (q, 2, $-OCH_2CH_3$), 3.15 (d, 2, H-8), 1.30 (t, 3, OCH_2CH_3).

Anal. Calcd for $C_{11}H_{11}BrOS$: C, 48.72; H, 4.08; Br, 29.46; S, 11.82. Found: C, 48.65; H, 4.21; Br, 29.20; S, 11.71.

5-Chloro-4-methyl-8*H*-cyclohepta[*b*]thiophene (11f) (column temperature 200°, helium flow 140 ml/min, retention time 18.6 min) had ir (neat) 1630 (C=C), 3060 cm^{-1} (=CH); uv max (CH_3CN) 225 nm (ϵ 20,000), 280 (7500); nmr ($CDCl_3$) δ 7.02 (s, 2, thiophene), 6.08 (d, 1, H-6), 5.59 (m, 1, H-7), 3.12 (d, 2, H-8), 2.40 (s, 3, $-CH_3$).

Anal. Calcd for $C_{10}H_9ClS$: C, 61.06; H, 4.61; Cl, 18.02; S, 16.30. Found: C, 61.28; H, 4.71; Cl, 17.90; S, 16.27.

5-Chloro-4-phenyl-8*H*-cyclohepta[*b*]thiophene (11g) (column temperature 200°, helium flow 180 ml/min, retention time 21 min) had ir (neat) 1630 (C=C), 3060 cm^{-1} (=CH); uv max (CH_3CN) 230 nm (ϵ 22,000), 270 (8600); nmr ($CDCl_3$) δ 7.18 (s, 5, C_6H_5), 6.52 (q, 2, thiophene), 6.10 (d, 1, H-6), 5.55 (m, 1, H-7), 3.18 (d, 2, H-8).

Anal. Calcd for $C_{15}H_{11}ClS$: C, 69.62; H, 4.28; Cl, 13.70; S, 12.38. Found: C, 69.69; H, 4.39; Cl, 13.87; S, 12.40.

5-Bromo-4-phenyl-8*H*-cyclohepta[*b*]thiophene (11h) (column temperature 200°, helium flow 200 ml/min, retention time 16 min) had ir (neat) 1625 (C=C), 3060 cm^{-1} (=CH); uv max (CH_3CN) 230 nm (ϵ 22,200), 275 (8500); nmr ($CDCl_3$) δ 7.28 (s, 5, C_6H_5), 6.60 (d, 2, thiophene), 6.30 (d, 1, H-6), 5.53 (m, 1, H-7), 3.15 (d, 2, H-8).

Anal. Calcd for $C_{15}H_{11}BrS$: C, 59.41; H, 3.65; Br, 26.36; S, 10.57. Found: C, 59.68; H, 3.89; Br, 26.04; S, 10.33.

Registry No.—**3a**, 36914-02-0; **3b**, 28857-19-4; **4a**, 36914-04-2; **4b**, 28857-20-7; **4c**, 36914-06-4; **4d**, 36914-07-5; **4e**, 36914-08-6; **5a**, 36914-09-7; **5b**, 36914-10-0; **5c**, 36914-11-1; **10a**, 36914-12-2; **10b**, 36914-13-3; **10c**, 28857-21-8; **10d**, 36914-15-5; **10f**, 36914-16-6; **10a**, 36914-17-7; **10h**, 36895-15-5; **11a**, 36917-68-7; **11b**, 36917-69-8; **11c**, 28857-22-9; **11d**, 36917-71-2; **11f**, 36917-72-3; **11g**, 36917-73-4; **11h**, 36917-74-5.

Notes

New Phenolic Hasubanan Alkaloids from *Stephania abyssinica*[1]

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Received July 19, 1972

Stephania abyssinica Walp. is a creeping plant indigenous to southern and eastern Africa which is reputed to possess a variety of medicinal uses.[2] An examination of *S. abyssinica* from Natal revealed the presence of an alkaloid[3] subsequently characterized as metaphanine (**1b**).[4] Earlier studies in this laboratory of roots and rhizomes from Ethiopia resulted in isolation and structural elucidation of the alkaloids oxoxylopine[5] ("lanuginosine"[6]) and stephavanine.[7] We report herein the isolation and structure elucidation of three new phenolic hasubanan alkaloids, stephabyssine (**1a**), stephaboline (**2**), and prostephabyssine (**3a**).

A concentrated ethanolic extract of *S. abyssinica* roots and rhizomes was partitioned between 5% hydrochloric acid and chloroform (fraction A). The acid solution was partially basified to pH 5 with ammonium hydroxide and extracted with chloroform to yield fraction B. Further basification with excess am-

(1) This investigation was supported by Public Health Service Grant No. HE-02952 and CA-12059 from the National Institutes of Health.

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