workup, VPC on column B (90–95 °C) afforded a colorless oil (4 mg, 33%; t_r = 5.5 min) which was identified as benzofuran by comparison of its IR and NMR spectra and VPC retention time with those of authentic benzofuran (Aldrich). Treatment of **5** with *p*-toluenesulfonic acid at 30 °C (2.5 days in benzene) or heating in toluene at 120 °C (1.7 days) in the absence of an acid catalyst resulted in very little decomposition and no benzofuran.

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are indebted to Mr. Eric Orava for technical assistance, Mr. Francis Picart for 300-MHz spectra, and Mr. S. T. Bella for microanalyses. The 300-MHz NMR spectrometer was purchased with assistance from the National Science Foundation and from the Camille and Henry Dreyfus Foundation. Low-resolution mass spectra were obtained on facilities supported by National Institutes of Health Grant RR-862.

Registry No. **1**, 85267-47-6; **1a**, 85267-48-7; **2**, 85316-99-0; **2a**, 85317-00-6; **3**, 85317-01-7; **3a**, 85317-02-8; **3b**, 85267-49-8; **3c**, 85267-50-1; **4**, 85267-51-2; **4a**, 85267-52-3; **5**, 85267-53-4; **5a** (isomer 1), 50356-49-5; **5a** (isomer 2), 50356-50-8; **6**, 50744-35-9; **7**, 68297-49-4; **8**, 7092-05-9; **9**, 85317-03-9; **10**, 85317-04-0; **12**, 50898-31-2; **13**, 85317-05-1; **14**, 85267-54-5; **16**, 65311-34-4; **16** (hydroxy derivative), 85267-55-6; **16** (hydroxyepoxy derivative), 85267-56-7; **17**, 17876-06-1; **24**, 85267-57-8; **25**, 85267-58-9.

Photochemical Cycloadditions of 2,3-Dihalobenzo[*b*]thiophenes: Stereochemical and Mechanistic Results

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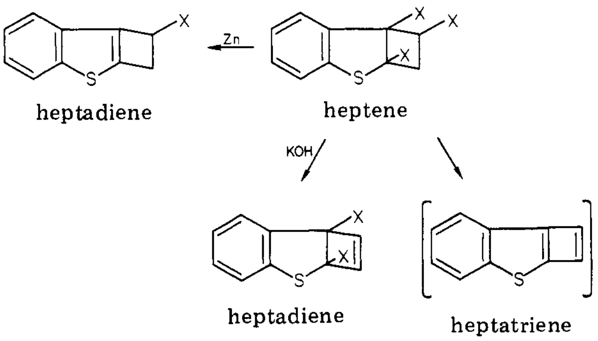
Synthetic approaches to 2-thia-3,4-benzobicyclo[3.2.0]-1,3,6-heptatriene and to 2-thia-3,4-benzobicyclo-[3.2.0]-1,3-heptadiene required halogenated cyclobutanes derived from [$_{\pi}2_{s}$ + $_{\pi}2_{s}$] photocycloadditions of 2,3-dichlorobenzo[*b*]thiophene and either vinyl bromide or 1,2-dichloroethylene. Addition reactions of vinyl bromide and dichloroethylene with 2,3-dichlorobenzo[*b*]thiophene and with 2,3-dibromobenzo[*b*]thiophene are reported. X-ray crystal structures of the two adducts derived from vinyl bromide and 2,3-dichlorobenzo[*b*]thiophene specify their stereochemistry. The adducts to 2,3-dibromobenzo[*b*]thiophene are linear, and structure determinations for these compounds are also reported.

The photocycloaddition of halo olefins to benzo[*b*]thiophene was first reported by Neckers and Dopper in 1970.[1] These authors reported that such cycloadditions were best carried out as triplet-sensitized processes, with sensitizers with triplet energies above 68 kcal/mol sufficing to catalyze the reaction. In early studies,[1] it was shown that the stereochemistry of the cyclic adducts reflected the stereochemistry of the starting olefins, though the reactions were not 100% stereospecific.

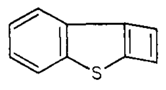
Photochemical [$_{\pi}2_{s}$ + $_{\pi}2_{s}$] cycloaddition reactions of electron-deficient olefins and benzo[*b*]thiophene derivatives generally provide high-yield routes to fused-ring systems, and 2-thia-3,4-benzobicyclo[3.2.0]-1,3-heptadiene and 2-thia-3,4-benzobicyclo[3.2.0]-3,6-heptadiene were both originally synthesized by this route.[2] Recent reports from our laboratories have applied similar processes to other fused-ring heterocyclic systems,[3-12] and the scope of such cycloadditions is now such that many heterocyclic derivatives can be produced by this general pathway. Some of the known photoreactions for monoheteroatom fused systems with alkynes and alkenes are outlined in Scheme I.

The 2-thia-3,4-benzobicyclo[3.2.0]heptene, -heptadiene, and -heptatriene ring skeletons are readily approached by such a photochemical process which builds a cyclobutane ring between a benzo[*b*]thiophene and a partner addend. If either or both possess a readily dissociable pair of functional groups, stereochemically positioned so that they are readily eliminated, the desired ring systems can be derived (eq 1).

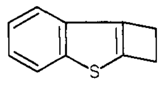


(1)

As part of a program seeking the highly strained heterocycles 2-thia-3,4-benzobicyclo[3.2.0]-1,3,6-heptatriene (**1**) and 2-thia-3,4-benzobicyclo[3.2.0]-1,3-heptadiene[2] (**2**)



1



2

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[1] Neckers, D. C.; Dopper, J. H.; Wynberg, H. *J. Org. Chem.* **1970**, *35*, 1582.

[2] Neckers, D. C.; Wagenaar, F. L. *J. Org. Chem.* **1981**, *46*, 3939. Murata, I.; Tatsuoka, T.; Sugihora, Y. *Tetrahedron Lett.* **1974**, 199.

[3] Dopper, J. H.; Neckers, D. C. *J. Org. Chem.* **1971**, *36*, 3722.

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[8] Davis, P. D.; Neckers, D. C.; Blount, J. R. *J. Org. Chem.* **1980**, *45*, 462.

[9] Ditto, S. R.; Davis, P. D.; Neckers, D. C. *Tetrahedron Lett.* **1981**, *22*, 521.

[10] Sindler-Kulyk, M.; Neckers, D. C. *Tetrahedron Lett.* **1981**, *22*, 525.

[11] Sindler-Kulyk, M.; Neckers, D. C.; Blount, J. R. *Tetrahedron* **1981**, *37*, 3377.

[12] Sindler-Kulyk, M.; Neckers, D. C. *J. Org. Chem.* **1982**, *47*, 4914.

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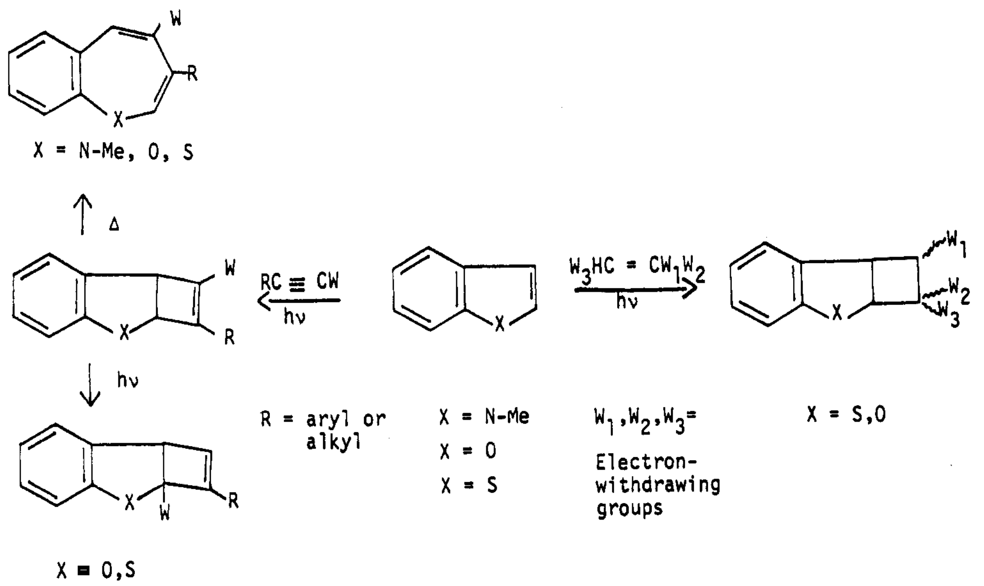
Scheme I. Photochemical Addition Reactions of Heteroaromatic Compounds with Alkynes and Alkenes



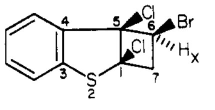
we have synthesized halogenated derivatives of 2-thia-3,4-benzobicyclo[3.2.0]-3-heptene by the well-known [$_{\pi}2_{s}$ + $_{\pi}2_{s}$] photocycloaddition of electron-poor olefins to halogenated benzo[*b*]thiophenes.

Full X-ray structural analysis of the two isolated adducts of 2,3-dichlorobenzo[*b*]thiophene and vinyl bromide show the addition to be regiospecific and outline the stereochemistry to be expected in related systems; stereochemical assignments in adducts from 1,2-dichloroethylene and dichlorobenzo[*b*]thiophene are also then obtainable by analogy. Reactions of all olefins with 2,3-dibromobenzo[*b*]thiophene give linear rather than cyclic adducts. We report structure determinations in these systems as well.

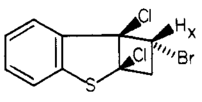
In this paper two processes are compared: the reaction of 2,3-dichlorobenzo[*b*]thiophene with vinyl bromide, with 1,2-dichloroethylene, and with ethylene and the photochemical reactions of 2,3-dibromobenzo[*b*]thiophene with these same alkenes. In general, reactions with 2,3-dichlorobenzo[*b*]thiophene give cyclic products, whereas the reactions with 2,3-dibromobenzo[*b*]thiophene give linear addition products. Both processes provide clues as to the mechanism of the addition reactions.

Results

Photocycloaddition of vinyl bromide to 2,3-dichlorobenzo[*b*]thiophene sensitized with benzophenone and carried out in the presence of the inhibitor 2,6-di-*tert*-butyl-*p*-cresol gave two adducts (3, 4) in about 75% overall



3



4

yield as a 1:1 mixture of stereoisomers.[2] Crystals of both adducts, which could be separated by column chromatography, were millimeters in size. Two crystalline forms of one adduct (3) were found; one contained 4 molecules per cell while photographs of the other indicated that it contained 32. A complete structure determination was carried out only on the former. The stereoscopic ORTEP drawings of 3 and 4 are given in Figures 1 and 2, respectively, and the X-ray data are reported in the Experimental Section.

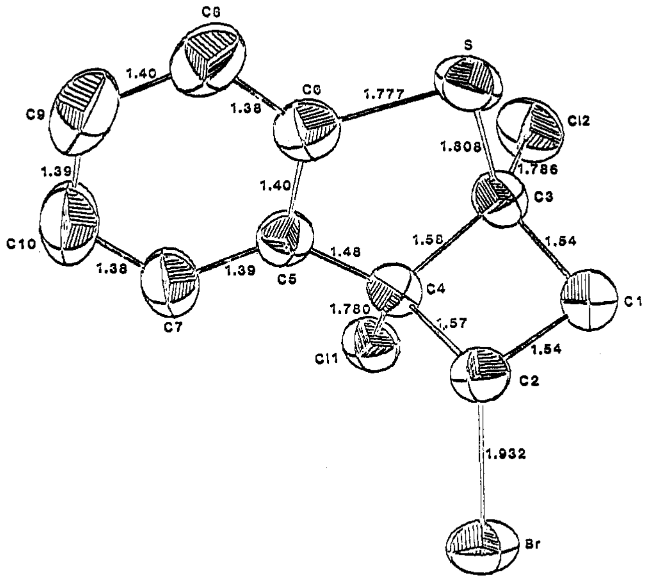


Figure 1. View of the $BrCl_2SC_{10}H_7$ molecule 3 showing 50% probability ellipsoids.

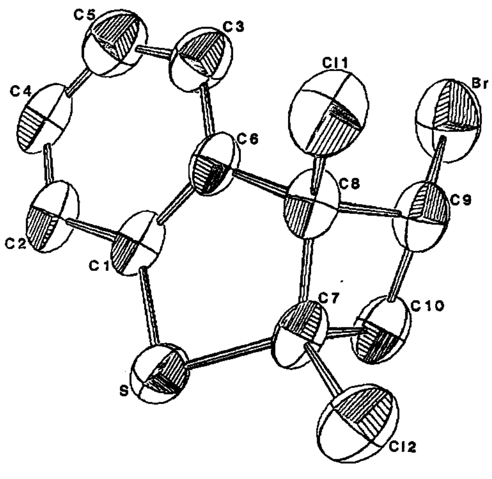
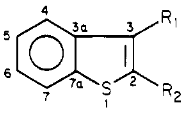


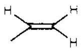
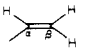
Figure 2. View of the $BrCl_2SC_{10}H_7$ molecule 4 showing 50% probability ellipsoids.

The crystal and molecular structures of $BrCl_2SC_{10}H_7$ (3) have been determined by single-crystal, three-dimensional, X-ray analysis and refined by successive structure factor and electron density map calculations. The material crystallizes in the monoclinic space group $P2_1/n$ with a =

Table I. ^{13}C NMR Spectral Data for Various $[_{\pi}2_s + _{\pi}2_s]$ Adducts of Benzo[*b*]thiophene and Halo Olefins[15]



I

compd	chemical shift, δ (carbon no.) A	B[a]	C	D
3	139.76 (3a), 136.14 (7a)	130.87, 130.06 (4, 7), 125.62, 121.88 (5, 6)	81.56 (3), 77.46 (2)	50.76 (3α), 50.33 (2)
4	139.07 (3a), 137.46 (7a)	130.43, 125.79 (4, 7), 125.19, 121.59 (5, 6)	86.63 (3), 78.95 (2)	50.91 (3α, t), 47.36 (2α, d)
5	138.48 (3a), 136.33 (7a)	130.66, 126.03 (4, 7), 125.19, 121.81 (5, 6)	86.08 (3), 83.79 (2)	69.38 (3α), 64.73 (2α)
6	138.96 (3a), 134.57 (7a)	131.30, 130.07 (4, 7), 125.74, 122.22 (5, 6)	81.79 (3), 78.18	68.80 (3α), 67.36 (2α)
11	137.44 (7a), 133.62 (3a)	125.55, 125.03 (5, 6),[b] 123.10, 122.16 (4, 7)	109.03 (3)	44.95 (2α, t), 41.40 (2β, d)
12	138.07 (2), 136.41 (7a), 134.27 (3a)	129.48 (2α), 126.30, 125.32 (5, 6), 123.37, 122.16 (4, 7)	110.06 (2β), 108.29 (3)	
I, $R_1 = R_2 = Br$	138.80 (7a), 137.35 (3a)	125.53, 125.39 (4, 7), 123.19, 121.68 (5, 6)	114.15 (2), 111.66 (3)	
I, $R_1 = H$; $R_2 =$ 	143.25 (2), 140.28 (7a), 139.16 (3a)	130.82 (2α, d), 124.95, 124.55 (5, 6), 123.78 (4), 123.36 (9), 122.41 (3)	115.87 (2β, t)	
I, $R_1 = H$; $R_2 = CHBrCH_2Br$	142.92 (2), 139.90 (3a), 138.73 (7a)	125.32, 124.75, 124.33, 124.15, 122.56		45.94 (2α, d), 35.53 (2β, t)
I, $R_1 =$ ; $R_2 = H$	140.44 (7a), 137.59 (3a), 134.45 (3)	129.15 (3α, d), 124.32, 124.14 (5, 6), 122.74 (4), 122.21 (2), 121.84 (7)	115.32 (3β, t)	
I, $R_1 = C^{\alpha}HBrC^{\beta}H_2Br$; $R_2 = H$	140.51 (7a), 136.64 (3a), 132.59 (3)	125.66, 124.93, 124.35, 122.99, 122.00		44.11 (3α, d) 33.48 (3β, t)
7	138.42 (3a), 136.85 (3a), 136.06 (2a), 134.92 (7a)	130.23, 126.17 (4, 7), 125.46, 121.99 (5, 6)	84.78 (3), 82.28 (2)	

[a] Carbon assignments are based on trends noted in: Geneste, P.; et al. *J. Org. Chem.* **1979**, *44*, 2887. No attempt was made to distinguish the aromatic absorptions unambiguously. [b] Carbon 2 was buried under the other aromatic absorptions.

8.415 (3) Å, *b* = 11.466 (5) Å, *c* = 11.742 (11) Å, β = 96.70 (6)°, and *Z* = 4. The structure was refined by a least-squares procedure to a conventional residual index of *R* = 0.045.

The carbon–carbon and carbon–halogen bond distances are all within the expected range. The sulfur–carbon bond lengths, 1.777 (16) Å to a carbon in the benzene ring (C6) and 1.808 (5) Å to an sp^3-hybridized carbon (C3), can be compared to those found in 1,4-thiophthene and 1,4-dithiane.[13] In the former the C–S single bond distance averages 1.73 Å to an sp^2-hybridized carbon, whereas in the latter this distance is 1.81 Å to an sp^3-hybridized carbon.

The crystal and molecular structure of $BrCl_2SC_{10}H_7$ (**4**) has also been determined by single-crystal, three-dimensional, X-ray analysis and refined by successive structure factor and electron density map calculations. The material crystallizes in the monoclinic space group $P2_1/n$ with *a* = 8.380 (11) Å, *b* = 19.320 (11) Å, *c* = 7.455 (5) Å, β = 111.46 (5)°, and *Z* = 4. The structure was refined by a least-squares procedure to a conventional residual index of *R* = 0.071 (0.058 for reflections limited to 2θ ≤ 45°).

The ^1H NMR spectra of both **3** and **4** were ABX spectra. In **3**, an AB was centered at δ 3.05 (2 H): H_A at δ 3.35 (J_{AX} = 9.0 Hz), H_B at δ 2.73 (J_{BX} = 10.0 Hz and J_{AB} (gem coupling) = 13 Hz). H_X was centered at δ 5.02. In **4**, an AB was centered at δ 3.33: H_A, δ 3.45 (J_{AX} = 7.0 Hz); H_B, δ 3.13 (J_{BX} = 8.2 Hz, J_{AB} (gem coupling) = 12.5 Hz). H_X was centered at δ 4.69, thus indicating that H_X in **4** is in a more shielded environment.

Photocycloaddition of dichloroethylene to 2,3-dichlorobenzo[*b*]thiophene proceeds similarly to that of vinyl bromide and also is stereoselective. When the heterocyclic compound is irradiated with *cis*-1,2-dichloroethylene for a short period of time with benzophenone as the sensitizer, only one product predominates, that being the cis/syn adduct **5**. The proton NMR spectra of **5** shows an AB pattern, a one-proton doublet at δ 4.78, and a second single proton doublet centered at δ 4.46.

A second adduct, **6**, is produced competitively with **5** when 2,3-dichlorobenzo[*b*]thiophene is irradiated in *trans*-1,2-dichloroethylene. Its proton NMR spectrum is like that of **5**, but the coupling constant J_{AB} is somewhat larger, consistent with other four-membered-ring systems, and the proton attached to carbon 6 is more shielded, which is consistent with the analogous proton (H_X) in **4**. Its carbon spectrum is consistent with a structure in which the chlorine atoms are trans in the added dichloroethylene function (Table I).

The similarity of the NMR spectra and J_{AX} and J_{BX} assign 3-dimensional structures to the two cycloadducts of dichloroethylene and 2,3-dichlorobenzo[*b*]thiophene as

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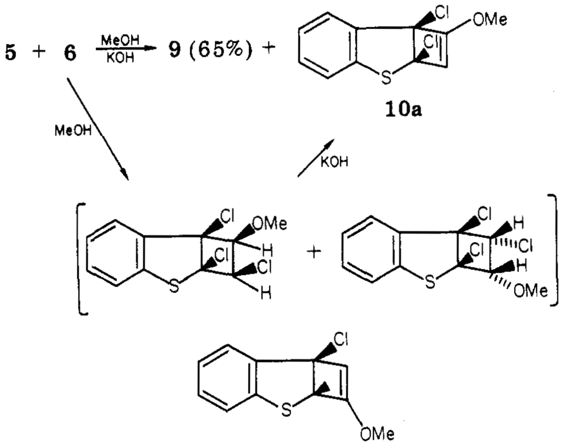
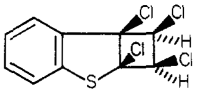
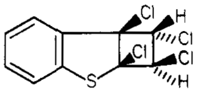
[13] "Tables of Interatomic Distances and Configurations in Molecules and Ions"; Burlington House: London, 1958; Spec. Publ.—Chem. Soc. No. 11, p W.1.

Scheme II

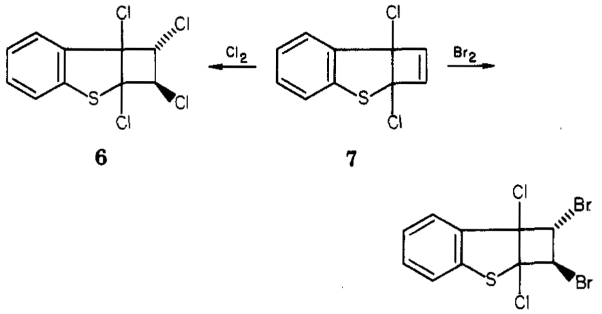


well. The NMRs of the adducts both show AB patterns, and on the basis of analogy with 3 and 4, these compounds are the cis and trans isomers 5 and 6.


5

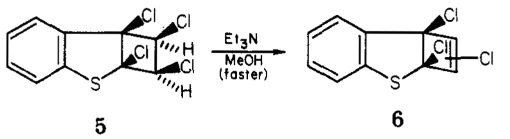

6

That 6 has trans chlorine functionalities is confirmed chemically. Addition of Cl_2 to 7 resulted almost exclusively in one isomer whose NMR spectrum matched that of 6. Addition of Br_2 also gave predominantly one isomer, 8, which had an identical AB pattern and differed only in chemical shift from the isomer in the chlorine case (eq 2).



8 (2)

Treatment of a 50:50 mixture of 5 and 6 with triethylamine destroys 5 more rapidly than 6 because, we suggest, of the trans-positioned H–Cl and cis-positioned chlorines in the former isomer (eq 3).



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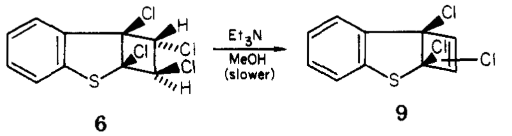


(3b)

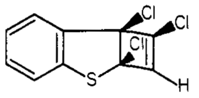
The olefin produced by elimination, 9, can be produced quantitatively from the mixture of 5 and 6 with potassium *tert*-butoxide in Me_2SO (eq 4). When 5 and 6 are treated

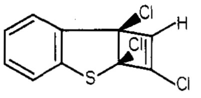
$$5 + 6 \xrightarrow[\mathrm{Me_2SO}]{\mathrm{KO}\text{-}t\text{-}\mathrm{Bu}} 9 \qquad (4)$$

with potassium hydroxide in methanol under previously developed standard conditions for such eliminations, the methyl ether **10a** is formed in about 20% overall yield (Scheme II). We suggest S_N2 attack inverts one carbon atom in either 5 or 6, thereby facilitating HCl elimination and resulting in the production of the corresponding vinyl ether.

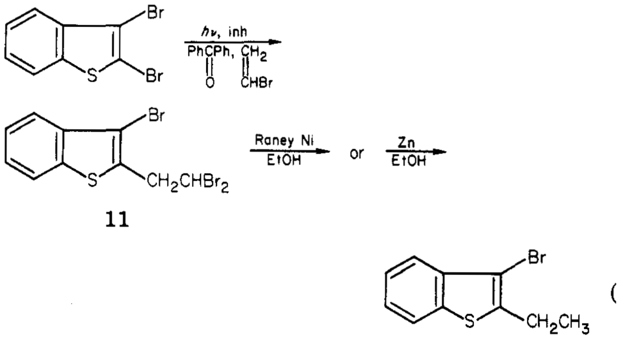
Elimination products 9 and 10 are produced in a 3:1 ratio from an equimolar mixture of 5 and 6. This suggests competitive elimination/substitution processes are possible with both stereoisomers. As crystal structures of 3 and 4 show, the cyclobutane ring is rather distorted, such that elimination can occur by periplanar trans elimination as well as the usual syn elimination for these systems.

Products 9 and 10 are also 3:1 mixtures of regioisomers. When mixture 9 is oxidized to the sulfone, the vinyl proton of the major isomer is more deshielded, which, along with all other evidence, requires the major isomer to be **9a** and the minor isomer to be **9b**.

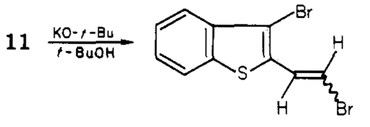

9a


9b

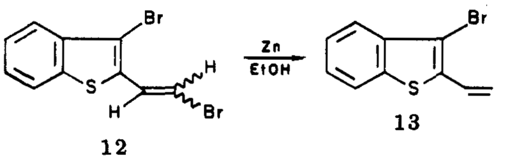
Photoreaction of vinyl bromide and 2,3-dibromobenzo[*b*]thiophene follows a completely different route and yields a single product, 11, which is a substitution product rather than an addition product. This is demonstrated as follows. Reduction of the major adduct from 2,3-dibromobenzo[*b*]thiophene and vinyl bromide with Raney Ni in EtOH at reflux yields predominately 3-bromo-2-ethylbenzo[*b*]thiophene and 2-ethylbenzo[*b*]thiophene; reduction in ethanol at reflux with Zn gives only 3-bromo-2-ethylbenzo[*b*]thiophene (eq 5). Both products have been compared with authentic samples prepared by an alternative route. Treatment of this adduct with potassium *tert*-butoxide in *t*-BuOH gives a mixture of *cis*- and *trans*-1-bromo-2-[3-bromobenzo[*b*]thiophen-2-yl]-ethylene (12, eq 6). The latter, when reduced with Zn in ethanol (eq 7), gives 3-bromo-2-vinylbenzo[*b*]thiophene



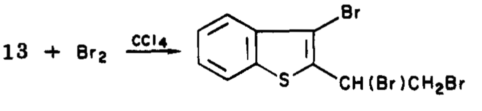
(5)



12 (6)

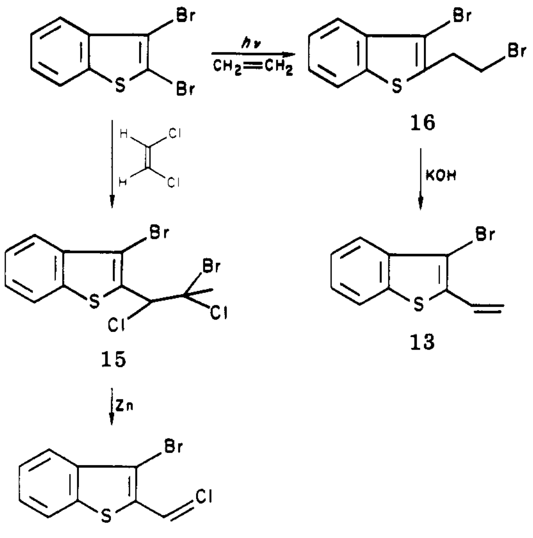


(7)

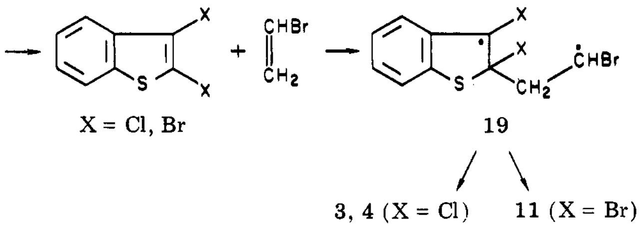


14 (8)

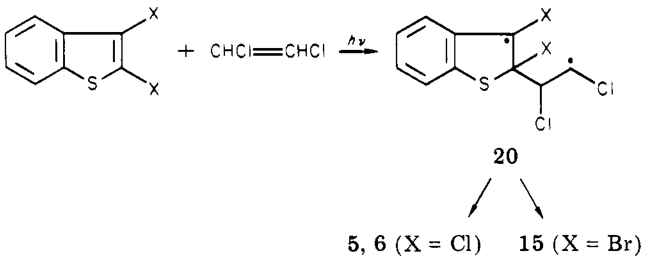
Scheme III



Scheme IV



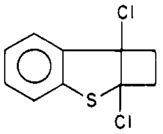
Scheme V



(**13**) which, with bromine in carbon tetrachloride, produces a dibromo adduct, **14**, which was an α,β-dibromoethyl-substituted product and different in spectral properties from the observed photoadduct (eq 8). Addition of bromine to 2-vinylbenzo[*b*]thiophene and 3-vinylbenzo[*b*]thiophene also showed the presence of diastereotopic protons. Thus these results confirm that bromine substitution on the side chain ethyl group is β,β-dibromo rather than α,β-dibromo.

The position of the substitution in the ethyl function was confirmed as follows: 3-bromo-2-vinylbenzo[*b*]thiophene was synthesized independently and shown to be identical with the product **13** synthesized in two steps from the adduct.

The photochemical addition of 1,2-dichloroethylene and ethylene to 2,3-dibromobenzo[*b*]thiophene also gives linear products under similar experimental conditions. Thus, 2-(β-bromo-α,β-dichloroethyl)-3-bromobenzo[*b*]thiophene (**15**) and 2-(β-bromoethyl)-3-bromobenzo[*b*]thiophene (**16**) were the only isolated products of these reactions. Both reactions are regiospecific, producing only the 2-substituted isomer (Scheme III). Addition of ethylene to 2,3-dichlorobenzo[*b*]thiophene gave the closed cyclic product **18** under identical conditions.



18

Dibromobenzo[*b*]thiophene and dichlorobenzo[*b*]thiophene both produce polymer when irradiated in vinyl bromide in the absence of inhibitor. Benzo[*b*]thiophene produces no polymer under similar conditions. When the addition of ethylene to 2,3-dibromobenzo[*b*]thiophene was performed in 95% EtOH or in acetone containing thiophenol, the major product was 3-bromobenzo[*b*]thiophene. Similarly, 2,3-dichlorobenzo[*b*]thiophene gave 3-chlorobenzo[*b*]thiophene in the presence of thiophenol although in lower yield. This result shows the susceptibility of the C(2)–X bond to cleavage to a free radical which can be trapped if a hydrogen atom donor is present.

The ^{13}C NMR spectra of a number of the benzo[*b*]thiophene adducts are also given in Table I. Although rigorous assignment of ^{13}C absorptions would require a more detailed analysis, two general observations can be made in this system. First, the chlorinated bridgehead carbon atoms appear between δ 130 and 145 and thus confirm closed cyclic structures. Second, the bromine-substituted carbon in the linear products appears between δ 105 and 115 due to the heavy-atom effect of the halogen, thus separating this carbon atom from the aromatic carbon atoms.

Discussion

The three-dimensional full X-ray structures of **3** and **4** confirm, for the first time, that the photochemical addition reaction of halo olefins to benzo[*b*]thiophenes must occur via a biradical intermediate. The addition of vinyl bromide to 2,3-dichlorobenzo[*b*]thiophene is regiospecific, producing only a pair of stereoisomers of one of the two possible adducts while the addition of dichloroethylene to 2,3-dichlorobenzo[*b*]thiophene is also regiospecific, producing only a pair of stereoisomers of one of the two possible adducts. The addition of vinyl bromide to 2,3-dibromobenzo[*b*]thiophene gives only a single linear adduct. These results coupled with the facts that one also obtains poly(vinyl bromide) in the reaction and that radical inhibitor must be added to prevent this suggest that the 2-position of the benzo[*b*]thiophene is the initiating site and that the reaction intermediate is the biradical **19** (Scheme IV). The intermediate can either close to give the adduct as it does in the case of 2,3-dichlorobenzo[*b*]thiophene or it can suffer halogen atom migration to produce the linear addition product.

The addition of 2,3-dichlorobenzo[*b*]thiophene to dichloroethylene occurs with a memory of the original olefin, but not completely so. We believe these results are best interpreted as occurring via an intervening biradical also (**20**, Scheme V), with the ring closure rate being essentially the same as rotation about the formed single bond from the original olefin. Thus closure and rotation compete, and there is some retention of stereochemistry in the adducts. There is also isomerization of the starting olefin during the reaction, but it is impossible to tell whether this isomerization results from energy from the sensitizer or from reversion to starting materials from the biradical intermediate.

Experimental Section

All melting points are taken with a Hoover capillary tube melting point apparatus and are uncorrected. Infrared spectra were taken with a Perkin-Elmer 337 either neat as oils, as KBr disks, or as Nujol mulls. ^{1}H NMR spectra were taken either on a Varian CFT-20 or EM-360 in $CDCl_3$ with Me_4Si as an internal standard. UV spectra were taken on with a Varian 219 recording spectrometer. All analyses are by Spang Microanalytical Laboratories of Eagle Harbor, MI. Commercial samples were all purchased from Aldrich and, when necessary, were purified before use. Irradiations were carried out either with a Hanovia 450-W medium-pressure arc lamp with a Pyrex filter or in a Rayonet reactor equipped with lamps of the proper irradiating wavelength.

General Irradiation Procedure. All solutions were degassed in a nitrogen steam for 15 min at 0 °C and irradiated for 6–24 h. The reaction progress was followed by GLC (5% SE-30, 190 °C), and products were isolated by column chromatography (silica gel, hexanes as the eluant).

Photocycloaddition of 2,3-Dichlorobenzo[*b*]thiophene to Vinyl Bromide. Preparation and separation of **3** and **4** was done according to the procedures of Neckers and Wagenaar.[2]

Cycloaddition of 1,2-Dichloroethylene to 2,3-Dichlorobenzo[*b*]thiophene. 2,3-Dichlorobenzo[*b*]thiophene[14] (3.1 g, 0.015 mol) and 0.9 g of benzophenone were dissolved in 150 mL of 1,2-dichloroethylene, purged with N_2, and irradiated fro 23 h with a Hanovia 450-W medium-pressure mercury lamp. After removal of 1,2-dichloroethylene, chromatography gave first the starting material and then the cycloadducts (1.67 g, 37%) as a mixture of isomers, mp 92–94.5 °C.

Isomer 5 (cis): ^{1}H NMR δ 4.78 (1 H J = 9 Hz) 4.33 (1 H J = 9 Hz), 7.0–7.6 (4 H, m, aromatic).

Isomer 6 (trans): ^{1}H NMR δ 4.77 (1 H, J = 8.2 Hz), 4.46 (1 H, J = 8.2 Hz) 7.0–7.5 (m, 4 H, aromatic); UV λ_{max} 296 nm (ϵ 641), 242 (5990), 224 (8170); mass spectrum, m/e (relative intensity) 298 (M^+, 6.4), 263 (–Cl, 2.5), 228 (–2Cl, 12.8), 202 (–CHClCHCl, 100). Anal. Calcd for $C_{10}H_6Cl_4$: C, 40.03; H, 2.02; Cl, 47.27; S, 10.69. Found: C, 39.89; H, 2.02; Cl, 47.19; S, 10.78.

Elimination Using KOH in Methanol. 1,5,6,7-Tetrachloro-2-thia-3,4-benzobicyclo[3.2.0]-3-heptenes (200 mg, 0.67 mmol) **5** and **6** in 20 mL of MeOH were treated with excess powdered KOH. The reaction proceeded rapidly and was finished within 15 min. After evaporation of the MeOH, the residue was partitioned between ether and water, and the ether layer was washed with water until neutral. Preparative TLC with hexanes gave two bands. Band 1 was 1,5,6-trichloro-2-thia-3,4-benzobicyclo[3.2.0]-3,6-heptadiene (**9**; 101 mg, 0.383 mmol, 57.5%) as an inseparable mixture of isomers in approximately a 3:1 ratio: mp 74–76 °C; ^{1}H NMR δ 6.02 (s, 1 H, isomer a), 6.10 (s, 1 H, isomer b), 6.97–7.58 (m, 4 H, aromatic); IR 1580 (w), 1460 cm^{-1} (w); UV ($CHCl_3$) λ_{max} 291 nm (ϵ 1700), 298 (1650); mass spectrum, m/e (relative intensity) 262 (M^+, 49), 227 (–Cl, 100), 202 (–CHCCl, 20), 192 (–2Cl, 75), 183 (–SCCl, 47). Band 2 contained 1,5-dichloro-6-methoxy-2-thia-3,4-benzobicyclo[3.2.0]-3,6-heptadiene (**10**; 35 mg, 0.136 mmol, 20.3%; oil) as an inseparable mixture of positional isomers in 4:1 ratio: ^{1}H NMR (isomer a) δ 3.62 (s, 3 H), 5.98 (s, 1 H); ^{1}H NMR (isomer b) δ 3.46 (s, 3 H), 6.10 (s, 1 H), 7.0–7.63 (m, 4 H, aromatic); IR 1580 (w) 1450 cm^{-1} (w); mass spectrum, m/e (relative intensity) 258 (M^+, 46), 243 (–CH_3, 82), 228 (–CH_2O, 26), 223 (–Cl, 100).

Elimination with KOH in EtOH. When MeOH was replaced with EtOH in the reaction above, an ethoxy-substituted product was formed in approximately 25% yield, as well as the previously reported eliminated product: NMR δ 1.3 (t, 3 H) 3.86 (q, 2 H, 8–11 lines) 5.94 (s, 1 H) 7.06–7.18, 7.37–7.50 (m, 4 H, aromatic).

Oxidation with *m*-Perchlorobenzoic Acid. To **9** (200 mg, 0.76 mmol) in 10 mL of $CHCl_3$ was added 326 mg (1.90 mmol) of MCPBA. After the mixture was refluxed overnight, it was extracted three times with 1 N NaOH, washed with water until neutral, and dried over $MgSO_4$. The sulfone (178 mg, 0.605 mmol, 80%) was recrystallized from petroleum ether–CCl_4 mixed solvent: mp 154–156 °C; ^{1}H NMR δ 6.67 (s, 1 H), 7.67 (m, 4 H aromatic); IR 1630 (w), 1615 (s), 1475 (w), 1450 (m), 1380 (m), 1330 cm^{-1} (s); UV (EtOH) 221 nm (ϵ 6800), 258 (257), 264 (427), 269 (565), 287 (487); MS, m/e (relative intensity) 294 (M^+, 2.2), 259 (–Cl, 67), 230 (–SO_2, 60), 183 (–SO_2CCl, 68), 160 (–SO_2Cl_2, 100). Anal. Calcd for $C_{10}H_5Cl_3O_2S$: C, 40.63; H, 1.71; Cl, 35.99; S, 10.85. Found: C, 40.76; H, 1.76; C, 35.97; S, 10.85.

3-Bromo-2-(β,β-dibromoethyl)benzo[*b*]thiophene (11). 2,3-Dibromobenzo[*b*]thiophene (1 g, 3.4 mmol), 100 mg of benzophenone, and 200 mg of 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide were dissolved in 65 mL of vinyl bromide and irradiated for 5.5 h at –22 °C. Chromatography gave starting material, followed by **11**: 610 mg (1.5 mmol, 45% yield); mp 68–70 °C; ^{1}H NMR δ 4.00 (d, 2 H, J = 6.8 Hz), 5.89 (t, 1 H, J = 6.8 Hz), 7.2–7.9 (m, 4 H, aromatic); mass spectrum, m/e (relative intensity) 396 (M^+, 10), 316 (–HBr, 4), 238 (–2Br, 23), 225 (–$CHBr_2$, 100); UV (EtOH) 304 nm (ϵ 4600), 294 (4300), 275 (8700), 268 (8300); ^{13}C NMR δ 137.44, 133.62, 125.55, 125.03, 123.10, 122.16, 109.33, 44.95 (t), 51.80 (d). Anal. Calcd for $C_{10}H_7Br_3S$: C, 30.10; H, 1.77; Br, 60.09; S, 8.04. Found: C, 30.11; H, 1.72; Br, 60.01; S, 8.08.

3-Bromo-2-(β-bromo-α,β-dichloroethyl)benzo[*b*]thiophene (15). 2,3-Dibromobenzo[*b*]thiophene (1.0, 3.4 mmol), benzophenone (100 mg), and 60 mL of 1,2-dichloroethylene were irradiated for 24 h at 25 °C. After starting material, **15** (376 mg, 0.97 mmol, 28% yield; mp 50–53 °C) and **17** (~20 mg, 0.07 mmol) were isolated. For **15**: ^{1}H NMR δ 5.80–6.13 (m, 2 H), 7.18–7.83 (m, 4 H, aromatic); mass spectrum, m/e (relative intensity) 386 (M^+, 6), 307 (–Br, 6), 306 (–HBr, 8), 272 (–Br, –Cl, 88), 259 (–CHClBr, 52), 228 (–2Br, 31), 158 (–2Br, –2Cl, 100); UV (EtOH) 309 nm (ϵ 4800), 298 (5300), 278 (11 000), 233 (18 800); ^{13}C NMR δ 136.93, 135.28, 126.82, 125.59, 122.00, 122.64, 111.00, 73.26, 62.47, 60.08, 51.45. Anal. Calcd for $C_{10}H_6Br_2Cl_2S$: C, 30.88; H, 1.55; Br, 41.09; Cl, 18.23; S, 8.24. Found: C, 30.70; H, 1.42; Br, 40.87; S, 8.18.

3-Bromo-2-(β-bromoethyl)benzo[*b*]thiophene (16). 2,3-Dibromobenzo[*b*]thiophene (1.0 g, 3.4 mmol) and benzophenone (100 mg) in 60 mL acetone were cooled to –22 °C, and ethylene was bubbled through. Irradiation for 16 h gave **16**: 290 mg (0.906 mmol, 26% yield); mp 27–30 °C; ^{1}H NMR δ 3.47 (AA′BB′, 4 H), 7.1–7.8 (m, 4 H, aromatic); mass spectrum, m/e (relative intensity) 318 (M^+, 30), 239 (–Br, 17), 238 (–HBr, 7), 225 (–CH_2Br, 100), 160 (–2Br, 40), 146 (–CH_2Br, Br, 15); UV ($CHCl_3$) 302 nm (ϵ 6000), 294 (5300), 274 (9100), 266 (9500); ^{13}C NMR δ 138.08, 137.36, 136.13, 125.35, 125.12, 123.01, 122.34, 107.53, 33.36, 29.90. Anal. Calcd for $C_{10}H_8Br_2S$: C, 37.52; H, 2.52; Br, 49.94; S, 10.02. Found: C, 37.62; H, 2.39; Br, 49.83; S, 10.00.

Addition of Ethylene to 2,3-Dichlorobenzo[*b*]thiophene. 2,3-Dichlorobenzo[*b*]thiophene (1.0 g, 4.95 mmol) and benzophenone (100 mg) in 60 mL of acetone were cooled to –22 °C, and ethylene was bubbled through. Irradiation for 6.5 h gave 375 mg (1.63 mmol) of **18** which matched an authentic sample: ^{13}C NMR δ 140.51, 139.49, 130.07, 126.05, 125.85, 121.77, 82.12, 80.11, 39.83, 37.83.

Addition of Ethylene in 95% EtOH. 2,3-Dibromobenzo[*b*]thiophene (1.0 g, 3.4 mmol) and 100 mg of benzophenone in 60 mL 95% EtOH were irradiated 6.6 h at 350 nm and –22 °C. GLC showed 12% 3-bromobenzo[*b*]thiophene and 7% **11**.

Addition of Ethylene in the Presence of Thiophenol. 2,3-Dibromobenzo[*b*]thiophene (1.0 g, 3.4 mmol), 100 mg of benzophenone, and 0.51 g of thiophenol in 60 mL of acetone were irradiated 6.6 h at 350 nm and –22 °C. This gave 52% 3-bromobenzothiophene and <1% **11**. 2,3-Dichlorobenzo[*b*]thiophene (1.0 g, 4.95 mmol), 100 mg of benzophenone, and 0.54 g of thiophenol in 60 mL of acetone were irradiated 6.6 h at 350 nm and –22 °C and gave 36% 3-chlorobenzo[*b*]thiophene and 3.5% **18**.

Irradiation of Benzo[*b*]thiophenes in Vinyl Bromide. Benzo[*b*]thiophene (75.4 mg, 0.563 mmol) and 16 mg of benzophenone in 10 mL of vinyl bromide when irradiated for 1 h at 0 °C resulted in a clear solution with no apparent polymer being formed.

2,3-Dichlorobenzo[*b*]thiophene (113.4 mg, 0.561 mmol) when irradiated as above gave an opaque suspension containing poly(vinyl bromide).

2,3-Dibromobenzo[*b*]thiophene (159.0, 0.548 mmol) when irradiated as above gave an opaque suspension containing poly(vinyl bromide).

Base-Catalyzed Elimination of 11. Potassium *tert*-butoxide in *tert*-butyl alcohol was added dropwise to a solution of 450 mg

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[14] Cherry, W. H.; Davies, W.; Ennis, B. C.; Porter, Q. N. *Aust. J. Chem.* **1967**, *20*, 313.

[15] For a more detailed analysis of substituted benzo[*b*]thiophene ^{13}C NMR see: Geneste, P.; Olive, J. L.; Ung, S. N.; El Amoud El Faghi, M. *J. Org. Chem.* **1979**, *44*, 2887.

(1.13 mmol) **11** in 50 mL of benzene, and the reaction progress was followed by GLC (5% SE-30 Chrom W, 210 °C). The resulting solution was neutralized and dried over $MgSO_4$, and the solvent was evaporated to give 217 mg (0.682 mmol, 60% yield) of crude product **12**. The product was recrystallized from EtOH: mp 105.5–107 °C; ^1H NMR δ 6.78 (d, J = 14.2 Hz, trans), 6.55 (d, J = 8.2 Hz, cis), 7.2–7.9 (m, 5 H, vinyl, aromatic); IR 1600 cm^{-1}; mass spectrum, *m/e* (relative intensity) 316 (M^+, 47), 237 (–Br, 34), 158 (–2Br, 100); ^{13}C NMR δ 138.07, 136.41, 134.27, 129.48, 126.30, 125.32, 123.37, 122.16, 110.06, 108.29. Anal. Calcd for $C_{10}H_6Br_2S$: C, 37.76; H, 1.90; Br, 50.25; S, 10.08. Found: C, 37.82; H, 1.81; Br, 50.35; S, 10.12.

Elimination of 16. Treatment with *t*-BuOK/*t*-BuOH in benzene gave a 95% crude yield of 3-bromo-2-vinylbenzo[*b*]thiophene identified by comparison with an authentic sample.

Zinc Dihalogenation of 15. Refluxing **15** (28 mg) with 180 mg of Zn in 2 mL of 95% EtOH for 1.25 h gave 2-chloro-1-(3-bromobenzo[*b*]thiophenyl)ethylene: ^1H NMR δ 6.55 (d, 1 H, J = 13 Hz, trans), 6.23 (d, 1 H, J = 8 Hz, cis), 7.2–7.8 (m, 5 H, vinyl, aromatic); IR 1600 cm^{-1}; mass spectrum, *m/e* (relative intensity) 272, (M^+, 100), 237 (–Cl, 19), 193 (–Br, 23), 158 (–Br, Cl, 100); UV (EtOH) 307 nm (ϵ 21 000), 296 (19 900), 264 (9700), 257 (10 000), 233 (12 100). Anal. Calcd for $C_{10}H_6BrClS$: C, 43.90; H, 2.21; Br, 29.21; Cl, 12.96; S, 11.72. Found: C, 43.83; H, 2.10; Br, 29.14; S, 11.56.

3-Bromo-2-vinylbenzo[*b*]thiophene. From 12. Zinc (1 g) was added to a solution of 105 mg of **12** in 5 mL of dimethoxyethene, and the mixture was refluxed for 19 h. Filtration and evaporation gave a product, **13**, which was heat sensitive: ^1H NMR (ABX system) δ 5.40 (H_A, J_{AX} = 11.0 Hz), 5.72 (H_B, J_{BX} = 17.5 Hz), 7.09 (H_X, J_{AX} = 11.0 Hz, J_{BX} = 17.5 Hz), 7.2–6.8 (m, 4 H, aromatic); IR 1620 cm^{-1}; UV ($CHCl_3$) λ_{max} 302 nm (ϵ 17 500), 292 (16 000), 266 (8400), 258 (8800).

3-Bromo-2-vinylbenzo[*b*]thiophene. 2-(β-Hydroxyethyl)benzo[*b*]thiophene (2.0 g, 0.0112 mol) was treated with excess bromine to give, after quenching with Na_2SO_3, washing, solvent evaporation, and recrystallization from EtOH, 2.55 g (9.96 mmol, 89%) of 3-bromo-2-(β-hydroxyethyl)benzo[*b*]thiophene: mp 67–69 °C; ^1H NMR δ 3.04 (t, 2 H), 3.39 (s, 1 H), 3.76 (t, 2 H), 7.0–7.7, (m, 4 H, aromatic). 3-Bromo-2-(β-hydroxyethyl)benzo[*b*]thiophene (1.5 g, 5.89 mmol) and 328 mg of powdered KOH were heated with a flame at 2 mmHg, and **13** distilled as a result; 27 mg (0.113 mmol, 1.9% yield).

Zinc Reduction of 11. Zinc (1.0 g) and **11** (150 mg, 0.376 mmol) in 5 mL of EtOH were refluxed 2 h to give, after filtration and column chromatography, of 3-bromo-2-ethylbenzo[*b*]thiophene: 73 mg (0.30 mmol, 80% yield); ^{13}C NMR δ 138.63, 137.09, 124.91, 124.72, 122.64, 122.34, 105.21, 23.60, 14.71.

Raney Nickel Reduction of 11. Raney Ni (3 mL, ~1.8 g) and **11** (500 mg, 1.24 mmol) in 20 mL of 95% EtOH was refluxed 15 h to give, after filtration and column chromatography, 40.1 mg (0.167 mmol) of 3-bromo-2-ethylbenzo[*b*]thiophene (13%) and 61.9 mg (.377 mmol) 2-ethylbenzo[*b*]thiophene (30%). ^{13}C NMR (2-ethylbenzo[*b*]thiophene) δ 140.37, 139.35, 126.21, 124.06, 123.39, 122.74, 122.14, 119.73, 24.12 (t), 15.41 (q).

Bromination of 3-Bromo-2-vinylbenzo[*b*]thiophene. A small sample of **13** in $CDCl_3$ was placed in an NMR tube and bromine added. The NMR showed diastereotopic protons in the product. ^1H NMR δ 4.03 (d, 1 H, J = 9 Hz), 4.06 (d, 1 H, J = 7 Hz), 5.77 (AB, 1 H, J = 7, 9 Hz), 7.1–7.8 (m, 4 H aromatic).

Bromination of 2-Vinylbenzo[*b*]thiophene. Bromine was added dropwise to a solution of 200 mg (1.25 mmol) 2-vinylbenzothiophene in 10 mL of CCl_4. When the solution did not decolorize it was quenched with Na_2SO_3, washed, and dried to give crude crystals of 2-(α,β-dibromoethyl)benzo[*b*]thiophene: 390 mg (1.22 mol, 97%); mp 97–98 °C; ^1H NMR δ 3.96 (d, 1 H, J = 9 Hz), 3.98 (d, 1 H, J = 7 Hz), 5.41 (AB, 1 H, J = 7, 9 Hz), 7.1–7.8 (m, 5 H, aromatic); mass spectrum, *m/e* (relative intensity) 318 (M^+, 6), 239 (–Br, 5), 238 (–HBr, 5); ^{13}C NMR δ 142.92, 139.90, 138.73, 125.32, 124.75, 124.33, 124.15, 122.56, 45.94, 35.53. Anal. Calcd for $C_{10}H_8S\ Br_2$: C, 37.52; H, 2.52; Br, 49.94; S, 10.02. Found: C, 37.54; H, 2.43; Br, 49.77; S, 10.04.

Bromination of 3-Vinylbenzo[*b*]thiophene. 3-Vinylbenzo[*b*]thiophene (150 mg, 0.94 mmol) was treated as above to give 184 mg (0.58 mmol) of 3-(α,β-dibromoethyl)benzo[*b*]thiophene: 184 mg (0.58 mmol, 62% yield); ^1H NMR δ 4.01 (d, 1 H, J = 7 Hz), 4.04 (d, 1 H, J = 8 Hz), 5.74 (t, 1 H, J = 7, 8 Hz), 7.05–7.9 (m, 8 H, aromatic); ^{13}C NMR δ 104.51, 136.64, 132.59, 125.66, 124.93, 124.35, 122.99, 122.00, 44.11 (d), 33.48 (t).

X-ray Crystal Structure Determinations. Crystal Data for 3. $BrCl_2SC_{10}H_7$, mol wt 310.04 g mol^{-1}, monoclinic $P2_1/n$, a = 8.415 (3) Å, b = 11.466 (5) Å, c = 11.742 (11) Å, β = 96.70 (6)°, V = 1125.16 Å^3, ρ_{calcd} = 1.83 g cm^{-3}, Z = 4, μ = 39.95 cm^{-1} (Mo Kα, λ = 0.710 34 Å).

An irregular-shaped crystal of approximate dimensions 0.2 × 0.2 × 0.3 mm was mounted on the end of a glass fiber with epoxy glue and attached to a standard goniometer head. The crystal was aligned on a four-circle X-ray diffractometer from which four preliminary ω-oscillation photographs were taken at various ϕ settings. The approximate positions of 12 reflections were selected from these photographs and used as input into an automatic indexing program.[16] The resulting reduced cell and reduced cell scalars indicated monoclinic symmetry. Observed layer spacings from three axial ω-oscillation photographs were within experimental error of those predicted for this cell.

Accurate unit cell parameters were obtained by a least-squares fit to $\pm 2\theta$ values of 16 independent high-angle reflections on a previously aligned four-circle diffractometer at room temperature by using graphite-monochromated Mo Kα radiation.

Collection and Reduction of X-ray Intensity Data for 3. Data was collected at room temperature by using a fully automated four-circle X-ray diffractometer designed and built in the Ames Laboratory and interfaced to a PDP-15 computer in a real-time mode.[17] All data within a sphere of $2\theta \leq 50°$ (4771 reflections) in the hkl, $\bar{h}k\bar{l}$, $\bar{h}\bar{k}l$, and hkl octants were measured by using an ω-step-scan procedure.

As a general check on the electronic and crystal stability, the intensities of three standard reflections were remeasured every 75 reflections. These standard reflections were not observed to vary significantly throughout the data collection period.

The space group was uniquely identified as $P2_1/n$ by systematic absences in the raw data occurring when $k = 2n + 1$ for the $0k0$ reflections and $h + l = 2n + 1$ for the $h0l$ reflections.

The intensity data were corrected for Lorentz and polarization effects. Absorption corrections were made[18] (μ = 39.95 cm^{-1}) where the maximum and minimum transmission factors were 0.995 and 0.355, respectively. The estimated variance in each intensity was calculated by eq 9, where C_T and C_B represent the total and

$$\sigma_I^2 = C_T + K_T C_B + (0.03C_T)^2 + (0.03C_B)^2 \tag{9}$$

background counts, K_T is a counting time constant, and the factor of 0.03 represents an estimate of nonstatistical errors.

Equivalent data were averaged, yielding 3406 observed ($I_o \geq 3\sigma I_o$) reflections of which 1664 were considered independent. Reflection 002 was omitted from the data reduction and the data averaging procedures because of counting rate errors associated with its very large intensity. The 1664 independent reflections were retained for use in the structural solution and refinement.

Crystal Data for 4. $BrCl_2SC_{10}H_7$, mol wt 310.04 g mol^{-1}, monoclinic $P2_1/n$, a = 8.380 (11) Å, b = 19.320 (11) Å, c = 7.455 (5) Å, β = 111.45 (5)°, V = 1123.40 Å^3, ρ_{calcd} = 1.83 g cm^{-3}, Z = 4, μ = 39.95 cm^{-1} (Mo, Kα, λ = 0.710 34 Å).

A square crystal of approximate dimensions 0.10 × 0.25 × 0.25 mm was mounted on the end of a glass fiber with Elmer's Glue-All, due to adverse reaction with organic-based glues, and attached to a standard goniometer head. Indexing was carried out as described above. Slow reaction at the interface between the glue and the crystal resulted in the loss of the crystal before absorption correction data could be obtained. Accurate unit cell parameters were estimated via an average of 16 retuned values from the data collection period.

Collection and Reduction of X-ray Intensity Data for 4. All data were collected as described above within a sphere of $2\theta < 50°$ (4771 reflections) in the hkl, $\bar{h}\bar{k}l$, $\bar{h}k\bar{l}$, and $h\bar{k}\bar{l}$ octants and were measured by using an ω-step-scan procedure. Considerable decay (~54%) in the integrated intensities of the standard reflections was observed throughout the data collection period.

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Examination of the raw data revealed systematic extinctions of the type $0k0$ when $k = 2n + 1$ and $h0l$ when $h + l = 2n + 1$ which uniquely identified the space group as $P2_1/n$.

The intensity data were corrected as described earlier. Absorption corrections were not made due to sudden loss of the crystal; the maximum and minimum transmission factors were estimated at 0.67 and 0.40, respectively.

Equivalent data were averaged, yielding 3791 observed ($I_o > 3\sigma I_o$) reflections of which 1505 were considered independent, and subsequently retained for use in the structural solution and refinement.

Structural Solution and Refinement. The position of the bromine atom in 3 was obtained from an analysis of a standard sharpened three-dimensional Patterson map. The positions of the remaining nonhydrogen atoms were determined by successive structure factor[19] and electron density map calculations.[20]

The positions of the bromine, sulfur, and chlorine atoms in 4 were obtained from an analysis of a sharpened three-dimensional Patterson map by using superposition techniques.[21] The positions of the remaining nonhydrogen atoms were determined by successive structure factor and electron density map calculations.

The hydrogen positions were calculated with the C–H bond distance set to 1.05 Å. The isotropic thermal parameters for hydrogens were fixed at 4.0 Å^2.

The aromatic positional and anisotropic thermal parameters for the nonhydrogen atoms were refined initially by block-matrix and finally by full-matrix least-squares procedures,[19] minimizing the function $\sum w||F_o| - |F_c||^2$, where $w = 1/\sigma F^2$, to a conventional residual index of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.045$ and a weighted residual index of $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.059$ for 3. For 4, $R = 0.071$ (0.058 for reflections limited to $2\theta \le 45°$) and a weighted residual index of $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.080$ (0.070 for reflections limited to $2\theta \le 45°$).

The final positional and thermal parameters for 3 are listed in Tables II and III, respectively, while bond lengths and bond angles are listed in Tables IV and V, respectively (see supplementary material). An ORTEP[22] drawing of the molecule is given in Figure 2. The least squares planes are given in Table VI.

The final positional and thermal parameters for 4 are listed in Tables VII and VIII, respectively, while bond lengths and bond angles are listed in Tables IX and X, respectively (see supplementary material). An ORTEP drawing of the molecule is given in Figure 3. The least-squares planes are given in Table XI.

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Registry No. **3**, 85268-50-4; **4**, 85317-25-5; **5**, 85268-51-5; **6**, 85317-26-6; **7**, 78514-41-7; **8**, 85282-17-3; **9a**, 85268-52-6; **9b**, 85268-54-8; **10a**, 85268-55-9; **10b**, 85268-56-0; **11**, 85282-18-4; (*cis*)-**12**, 85268-57-1; (*trans*)-**12**, 85268-58-2; **13**, 85268-59-3; **14**, 85268-60-6; **15**, 85268-61-7; **16**, 85282-19-5; **17**, 85268-62-8; **18**, 78514-42-8; 2,3-dichlorobenzo[*b*]thiophene, 5323-97-7; vinyl bromide, 593-60-2; (*cis*)-1,2-dichloroethylene, 156-59-2; (*trans*)-1,2-dichloroethylene, 156-60-5; **9a** sulfone, 85268-53-7; 3-bromo-2-ethylbenzo[*b*]thiophene, 64860-32-8; 2-ethylbenzo[*b*]thiophene, 1196-81-2; 2-vinylbenzo[*b*]thiophene, 78646-50-1; 2-(α,β-dibromoethyl)benzo[*b*]thiophene, 85268-63-9; 3-vinylbenzo[*b*]thiophene, 6889-73-2; 3-(α,β-dibromoethyl)benzo[*b*]thiophene, 85268-64-0; ethylene, 74-85-1.

Supplementary Material Available: Tables II–XI containing final positional and thermal parameters, bond distances, bond angles, and least-squares planes for 3 and 4 (10 pages). Ordering information is given on any current masthead page.

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[21] Calculations were carried out on a VAX 11/780 computer. Positions of the heavier atoms were obtained by using the superposition program SUPR (Hubbard, C. R.; Babich, M. W.; Jacobson, R. A.). Structure factor calculations and least-squares refinements were done by using the block matrix/full matrix program ALLS (Lapp, R. L.; Jacobson, R. A.). Fourier series calculations were done by using the program FOUR (Powell, D. R.; Jacobson, R. A.), and for molecular drawings the program ORTEP (Johnson, C. K.) was used. Scattering factors, modified for the real and imaginary parts of anomalous dispersion, were taken from: "International Tables for X-ray Crystallography"; Vol. IV.

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Direct Photolysis of 1-Halo-1-hexynes. Lack of Ionic Behavior

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Direct photolyses at >200 nm of 1-bromo- and 1-iodo-1-hexynes were performed in polar and nonpolar solvents. Only radical-derived products were obtained even in polar solvents, contrary to the previously reported ionic photochemical behavior of alkyl and vinyl halides. The results are discussed from an energy point of view; the ionization potential of the initially formed organic radical well accounts for the obvious difference in photobehavior between alkynyl and alkyl or vinyl halides.

It had been generally believed that direct irradiation of organic halides leads to homolytic cleavage of the C–X bond and the subsequent formation of radical-derived products.[1] Recent investigations by Kropp et al.[2] and Taniguchi et al.[3] have, however, clearly shown that, upon irradiation in a polar solvent, alkyl and vinyl halides, particularly iodides, exhibit ionic behavior as well as radical behavior. The ionic behavior upon photolysis is reasonably understood by assuming initial homolytic cleavage of the

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