

## Photochemistry of Benzo[b]thiophenes

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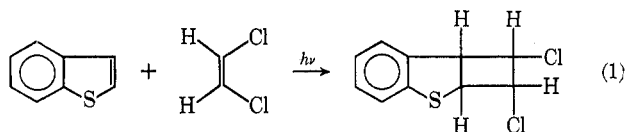
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Addition reactions of haloolefins to benzo[b]thiophene and several of its alkylated derivatives are reported.

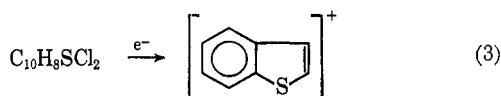
The naphthalene-related coal tar derivative, benzo[b]thiophene, has received little attention from photochemists.<sup>2</sup> Interest in the preparation of unusual fused benzo[b]thiophenes led us to examine sensitized photo-addition reactions to this and related fused heteroaromatic systems. Our results indicate that photo-additions to benzo[b]thiophene and its derivatives provide high yields of cyclobutane adducts.

## Results

Photosensitized addition reactions of haloolefins to linear and cyclic dienes,<sup>3,4</sup> as well as olefins<sup>5,6</sup> produce high yields of 1:1 adducts. Among the major products in these reactions are the cyclobutanes.<sup>7</sup> Using these methods as models, we have found that 1:1 adducts form from the photosensitized addition of *cis*- or *trans*-1,2-dichloroethylene to benzo[b]thiophene. Two major products are separable by vpc (eq 1) and can be isolated in yields as high as 90%.



That the adducts are fused benzo[b]thiophenocyclobutanes is proven by the fact that each is desulfurized and dehalogenated to phenylcyclobutane. Further, the mass spectrum of the adducts includes a parent peak at the *m/e* of the original benzo[b]thiophene (eq 2 and 3),



proving that the benzo[b]thiophene nucleus is undisturbed in the adducts. (The intensity of the benzo[b]thiophene peak in the mass spectrum of the adducts is at least five times larger than the next largest peak.)

- (1) To whom inquiries should be addressed.
- (2) For earlier studies on the photochemistry of benzo[b]thiophene, see W. E. Haines, R. V. Helm, G. L. Cook, and J. S. Ball, *J. Phys. Chem.*, **60**, 549 (1956); W. E. Haines, G. L. Cook, and J. S. Ball, *J. Amer. Chem. Soc.*, **78**, 5213 (1956).
- (3) N. J. Turro and P. D. Bartlett, *J. Org. Chem.*, **30**, 1849 (1965).
- (4) P. D. Bartlett, R. Helgeson, and O. A. Wersel, *Rev. Pure Appl. Chem.*, **16**, 187 (1968).
- (5) W. Metzner and W. Hartmann, *Chem. Ber.*, **101**, 4099 (1968).
- (6) D. Wendisch and W. Metzner, *ibid.*, **101**, 4106 (1968).
- (7) For recent reviews see (a) R. Steinmetz, *Fortschr. Chem. Forsch.*, **7**, 445 (1967); (b) D. R. Arnold in "Advances in Photochemistry," Vol. 6, John Wiley & Sons, Inc., New York, N. Y., 1968, p 301; (c) D. C. Neckers, "Mechanistic Organic Photochemistry," Reinhold Publishing Corp., New York, N. Y., 1967.

We conclude that the products are stereoisomers of 1,2-dichloro-3,4-(2,3-benzo[b]thiopheno)cyclobutane.

Additions of haloolefins to benzo[b]thiophenes appear general. High-yield reactions also occur when alkylated benzo[b]thiophenes are used in place of the unsubstituted derivative. Some examples of additional reactions of haloolefins and heteroaromatic compounds are reported in Table I.

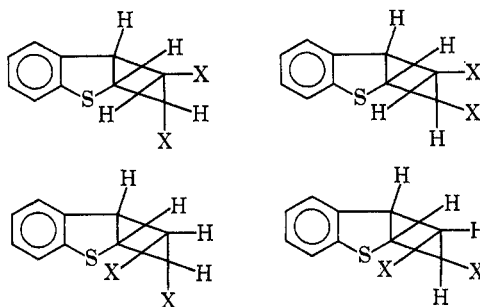
TABLE I

Aromatic compound <sup>a</sup>	Olefin	Products
 A = H; B = H A = D; B = H A = Me; B = H A = Me; B = Me A = H; B = Me A = Cl; B = Cl	 	
 Y = H, Ph <sup>c</sup>	 	

<sup>a</sup> The sensitizer in all cases was benzophenone or acetophenone.

<sup>b</sup> Three 1:1 adducts formed. Because the products were not stable, the reaction was stopped after 1% conversion. <sup>c</sup> In the addition of *cis*-dichloroethylene to 3-phenylthiophene, the major products were a mixture of *m*- and *p*-chlorobiphenyl. These products arise through an apparent 1,4 addition to the phenylthiophene nucleus. More will be reported about this reaction later.

Ruling out the existence of *trans* ring-fused products,<sup>8</sup> four stereoisomers can be formed from the addition of symmetrical olefins to benzo[b]thiophene and its derivatives.



(8) H. Weitkamp and F. Korte, *Chem. Ber., Suppl.*, **7**, 75 (1966).

Since the addition products from 2,3-dimethylbenzo[b]thiophene and dichloroethylenes gave the simplest nmr spectra, we chose to investigate this system in detail. All four stereoisomers are observed in the additions of dichloroethylene to 2,3-dimethylbenzo[b]thiophene. Three of the products can be separated in pure form, while the fourth product constitutes less than 2% of the total adduct yield. We obtained the distribution of products from the addition of *cis*- or *trans*-1,2-dichloroethylene to 2,3-dimethylbenzo[b]thiophene shown in Table II.

TABLE II  
ADDITION OF DICHLOROOLEFINS TO  
2,3-DIMETHYLBENZO[b]THIOPHENE

Isomer	<i>cis</i> , %	<i>trans</i> , %
1	1	1
2	40	60
3	47	27
4	11	12

1 *cis,endo*      2 *trans*  
3 *cis,exo*      4 *trans*

Structures are assigned on the basis of the following evidence. (A) Sensitized additions of *cis*- and *trans*-dichloroethylenes to indene take place with *cis* products being predominant in the case of the *cis*-dichloroethylene addition and *trans* product being predominant in *trans*-dichloroethylene addition.<sup>4</sup> Therefore, compound 3 is probably an adduct with the two chlorines *cis*, compound 2 an adduct with two chlorines *trans*. Minor product 4 cannot be assigned on this basis. (B) The coupling constants of cyclobutane hydrogens have been shown generally to be larger for compounds where the hydrogens are *cis* to one another than where the hydrogens are *trans*; *i.e.*,  $J_{cis}/J_{trans} > 1.0$ . Thus the AB coupling constant for compound 3 should be larger than for compound 2, as is observed (Table III).

The complete structures 2 and 3 are proposed. Further evidence that these structures are correctly assigned derives from the observation that the chemical shifts of the methyl groups differ the most in 2. The *cis* chlorine-methyl relationship of the methyl attached to the thioether carbon results in a maximum downfield shift of the methyl hydrogens. The minimum effect should result from the relationship of the other chlorine and methyl.

When the relationship of the 3-methyl group to chlorine is made *cis* (3), this chemical-shift difference decreases. Compound 4 is the other *trans* isomer, and compound 1 the other *cis,endo* isomer based on arguments like those above.

TABLE III  
NMR SPECTRA OF ADDUCTS FROM *cis*-1,2-DICHLOROETHYLENE  
AND 2,3-DIMETHYLBENZO[b]THIOPHENE

Compd	System	Nmr data <sup>a</sup>	
		$J_{AB}$	Chemical shift
2	AB	$J_{AB} = 7.0$ cps	Me-2 1.64
		$H_A$ 4.70	Me-3 1.43
		$H_B$ 4.90	Aryl 7.13
3	AB	$J_{AB} = 8.5$ cps	Me-2 1.58
		$H_A$ 4.25	Me-3 1.52
		$H_B$ 4.38	Aryl 7.13
4	AB	$J_{AB} = 9$ cps	Me-2 1.56
		$H_A$ 4.17	Me-3 1.38
		$H_B$ 4.40	Aryl 7.16

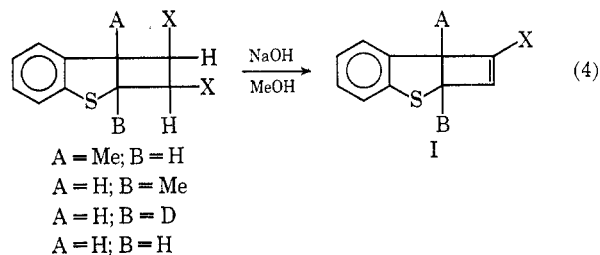
<sup>a</sup> Chemical shifts given in parts per million.

The results of a comparison of the product distributions to the case of indene additions are given in Table IV.

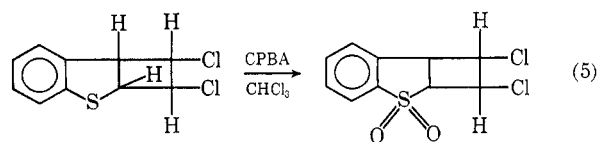
Structure assignment in the additions of haloolefins to less highly substituted benzo[b]thiophenes are based on the nmr spectra reported in Table V as well as by dehydrohalogenation experiments. ABC systems are observed in all the stereoisomers separated from 2- and 3-methylbenzo[b]thiophene, while four-proton systems are observed with the addition products from benzo[b]thiophene itself. The distribution of products is reported in Table VI.<sup>9</sup>

#### Chemical Reactions of the Addition Products—

The adducts of *cis* and *trans* dihaloolefins and benzo[b]thiophenes easily lose 1 mol of HCl in refluxing methanolic NaOH. The products isolated (yields averaged *ca.* 60%) were the corresponding cyclobutenes. The nmr spectra of the isomeric mixtures confirmed that the elimination went in the direction shown in eq 4, and I was the major isomer in all cases examined. As might be expected, rapid dehydrohalogenation occurs for those isomers with *trans* HCl stereochemistry, while the *trans*-dihalocyclobutenes were recovered even after 24-hr reaction with methanolic NaOH. There was no tendency for any of the adducts to lose a second mole of HCl under the conditions of the experiment, and in all cases the products were thermally stable at 60°.<sup>10</sup>



*m*-Chloroperbenzoic acid smoothly oxidized the saturated adducts to the sulfone (eq 5).



(9) For leading references concerning the nmr spectra of halogenated cyclobutenes, see ref 4 and (a) R. Steinmetz, W. Hartmann, and G. O. Schenk, *Chem. Ber.*, **98**, 3854 (1965); (b) J. K. Williams, D. W. Wiley, and B. C. McKusick, *J. Amer. Chem. Soc.*, **84**, 2210 (1962); (c) P. D. Bartlett, L. K. Montgomery, and B. Seidel, *ibid.*, **86**, 604 (1964).

(10) Thermal rearrangements of these molecules do occur at higher temperatures: J. H. Dopfer and D. C. Neckers, *Tetrahedron Lett.*, 2913 (1969).

TABLE IV

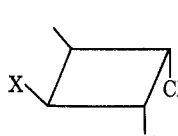
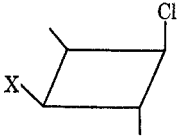
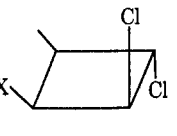
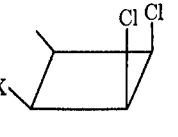
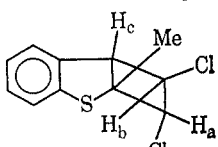
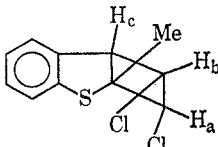
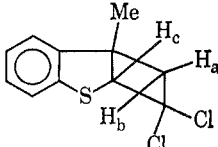
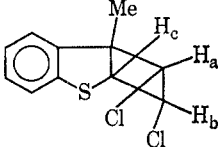
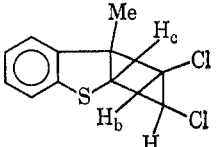
				
	<i>cis</i> -Dichloroethylene			
Indene	53	13	30	4
2,3-Dimethylbenzo[ <i>b</i> ]thiophene	47	40	11	1
	<i>trans</i> -Dichloroethylene			
Indene	16	20	59	5
2,3-Dimethylbenzo[ <i>b</i> ]thiophene	27	60	12	1

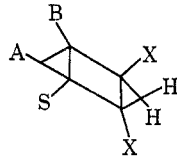
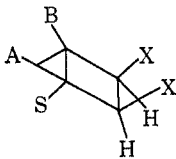
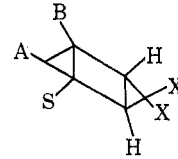
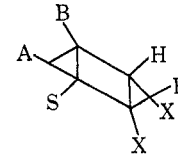
TABLE V

NMR SPECTRA OF HALOOLEFIN ADDUCTS TO BENZO[*b*]THIOPHENES

Compd	Registry no.	Nmr data <sup>a</sup>
	23735-57-1	H <sub>a</sub> , H <sub>b</sub> , and H <sub>c</sub> form a complex ABC pattern. H <sub>a</sub> is a four-peak multiplet centered at 3.60 ppm. H <sub>b</sub> and H <sub>c</sub> fall together at 4.35 ppm.
	23735-58-2	H <sub>a</sub> , H <sub>b</sub> , and H <sub>c</sub> form an ABC pattern at 4.20-4.60 ppm.
	23735-59-3	H <sub>a</sub> , H <sub>b</sub> , and H <sub>c</sub> form a complex ABX system. H <sub>c</sub> is a broad doublet centered at 3.60 ppm. H <sub>a</sub> and H <sub>b</sub> fall together as three doublets (AX and AB) at 4.00, 4.21, and 4.33 ppm, respectively.
	23735-60-6	H <sub>a</sub> , H <sub>b</sub> , and H <sub>c</sub> form an ABX system. H <sub>a</sub> 3.96 ppm H <sub>c</sub> 4.40 ppm H <sub>b</sub> multiplet at 4.60-4.80 ppm
	23735-61-7	ABC system, complex coupling 4.52-4.70 ppm

<sup>a</sup> See Table III, footnote a.

TABLE VI

					
		A	B	C	D
		A, %	B, %	C, %	D, %
A = Me	<i>cis</i> -1,2-Dichloroethylene	12	46	12	48
B = H					
A = Me	<i>trans</i> -1,2-Dichloroethylene	54	21	54	23
B = H					
A = H	<i>cis</i> -1,2-Dichloroethylene	...	47	30	23
B = Me					
A = H	<i>trans</i> -1,2-Dichloroethylene	...	16	41	42
B = Me					

Loss of molecular chlorine occurs with Zn and amyl alcohol (bp 130°). At lower temperatures (e.g., MeOH or EtOH at reflux), loss of chlorine was exceedingly slow. One hydrocarbon product was isolated from the loss of molecular chlorine by the adducts benzo[b]thiophene, but it was not monomeric and appeared to be a combination of the adduct minus Cl<sub>2</sub>. Experiments with more active dehalogenating agents designed for use at room temperature are currently in progress.

### Discussion

Addition reactions of the type reported represent facile entries into substituted dihydrobenzo[b]thiophene systems.<sup>11</sup> Several observations bear on the mechanism of the reaction. First, although benzophenone ( $E_t = 69.2$  kcal/mol) and acetophenone ( $E_t = 73.3$  kcal/mol) sensitize the addition of *cis*- and *trans*-1,2-dichloroethylene to 2,3-dimethylbenzo[b]thiophene, anthraquinone ( $E_t = 62$  kcal/mol) and 2-acetonaphthone ( $E_t = 58.9$  kcal/mol) do not. Second, the uv spectrum of benzo[b]thiophene is essentially the same in *cis*-1,2-dichloroethylene, *trans*-1,2-dichloroethylene, and cyclohexane. Third, although the extent of *cis*-*trans* isomerization of the haloolefin is limited in all reactions (less than 10%), extensive dimerization of the haloolefin takes place in competition with the addition to the heteroaromatic compound.<sup>12</sup> Finally, the reactions are, at least in part, stereospecific.

As in similar systems<sup>3,4</sup> it appears that sensitized formation of the benzo[b]thiophene triplet state is the initial photochemical act involved in the addition. Acetophenone and benzophenone both have triplet energies which make transfer to benzo[b]thiophene ( $E_t = 68.9$  kcal/mol)<sup>13</sup> allowed. Anthraquinone and phenanthrene, with triplet energies below 68.9 kcal/mol but above that of the haloolefins (62 kcal/mol), do not sensitize the reaction. The same can be said for 2-acetonaphthone ( $E_t = 58.9$  kcal/mol), although the actual role of this molecule as a sensitizer is still not clear.

The reaction of benzo[b]thiophene and *cis*-dichloroethylene occurs also in the absence of sensitizer. Although this reaction is *ca.* 90% less efficient than the sensitized process, the adduct distribution is virtually identical with the benzophenone sensitized case.

Two facts remain to explain at this point. (A) Why are dimers of the haloolefins observed? (B) Why is the reaction stereoselective?

Dimers of the haloolefin probably derive from the transfer of energy to the haloolefin in competition with the other energy-transfer process, involving the heteroaromatic compound. Although we cannot preclude the photolytic dissociation of the cyclobutane products to an excited haloolefin, followed then by dimerization,

(11) Sensitized additions of maleic anhydride and its derivatives to thiophene were reported some years ago: G. O. Schenck, W. Hartmann, and R. Steinmetz, *Chem. Ber.*, **96**, 498 (1963). Recently, R. M. Kellogg and H. Wynberg [*Tetrahedron Lett.*, 5895 (1968)] reported intercepting the excited singlet state of 2-phenylthiophene by its addition to piperylene. The dimerization of benzo[b]thiophene 1,1-dioxide also represents examples of the sort of reaction reported above in heteroaromatic sulfur systems.

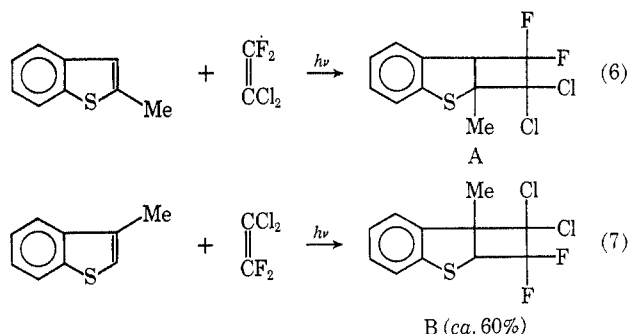
(12) Two major dimers are isolated by vpc. These dimers both have the same molecular weight and analyze for C<sub>8</sub>H<sub>6</sub>Cl<sub>4</sub>. Nevertheless, the nmr, infrared, and mass spectra of the molecules indicate that they are linear alkenes rather than cyclobutanes. More will be reported on this observation later.

(13) R. C. Heckman, *J. Mol. Spectrosc.*, **2**, 27 (1958).

this process is deemed unlikely in view of the high yields of adducts actually isolated.

Stereoselectivity in the addition reactions may result from the fact that the additions are conducted in two different solvents. On the other hand, it may be that the adducts, even though they "recognize" the fact that they come from different dihaloolefins, still form from rotationally equilibrated diradical intermediates.<sup>14</sup> The high reactivity of benzo[b]thiophene in electrophilic substitution reactions<sup>15-17</sup> suggests that the excited state might react with electropositive olefins rapidly also.

An interesting correlative observation concerning the mechanism of the sensitized cycloaddition reactions derives from the addition of 1,1-dichloro-2,2-difluoroethylene to benzo[b]thiophenes. These additions suggest that product control depends, at least in part, on the stability of the intermediate biradical. Thus 2-methylbenzo[b]thiophene gives adduct A exclusively (eq 6), while 3-methylbenzo[b]thiophene gives adduct B



in major proportions (eq 7). Thus, as in the case of additions of haloolefins to indene, the adducts formed recognize at least partially which haloolefins they come from. Yet additions of unsymmetrical olefins point to a stepwise addition process. Experiments designed to resolve the mechanistic aspects of the problem are currently in progress.

Dehydrohalogenation of the adducts leads to the 2 isomers predicted in every case. The structures of the stereoisomeric cyclobutenes follow from their nmr spectra. One may predict that the major isomer probably forms *via* the transition state shown below, because the abstracted hydrogen at position a is less hindered than its counterpart b next to sulfur. Presumably the olefin II would also be less hindered than

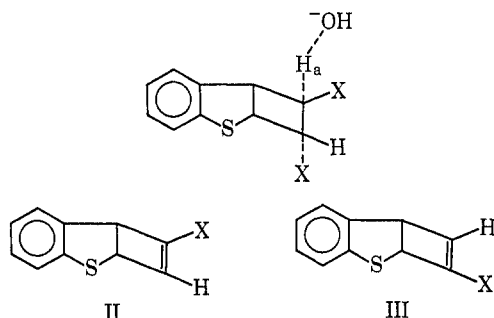
(14) W. L. Dilling, T. E. Tabor, and F. P. Boer, *J. Amer. Chem. Soc.*, **92**, 1399 (1970).

(15) See, e.g., C. A. VanderWerf, "Acids, Bases and the Chemistry of the Covalent Bond," Reinhold Publishing Corp., New York, N. Y., 1963.

(16) That dicyanoethylene is sufficiently reactive to capture the excited singlet state of acetone, for example, was recently demonstrated: N. J. Turro, P. Wriede, J. C. Dalton, D. Arnold, and A. Glück, *J. Amer. Chem. Soc.*, **89**, 3950 (1967).

(17) (a) Significant in this regard is the observation that most olefins which add to photoexcited aromatics are electron poor at the olefinic carbon. Thus dicyanoethylene, maleic anhydride, maleimide, etc., add most easily. See e.g., E. Ciganek, *ibid.*, **89**, 1458 (1967); (b) E. A. Hill and J. D. Roberts, *ibid.*, **89**, 2047 (1967). (c) For systems related to those we report, see ref 4 and 5 and J. S. Swenton and A. J. Krubsack, *ibid.*, **91**, 786 (1969).

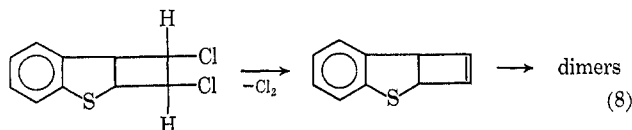
its counterpart III, because chlorine-sulfur interactions are minimized.



That dehydrohalogenation leads to the cyclobutenes shown rather than ring-opened or rearranged products derives from several observations.

First, the methyl-group absorbances in the nmr spectrum in all cases approximate those in the initially formed adducts, thus suggesting that they are attached to a nonolefinic carbon. Second, mass spectra of the adducts contain predominant peaks at the parent benzo[b]thiophene. Finally, cycloadducts formed from 2-deuteriobenzo[b]thiophene and *cis*-dichloroethylene gave the expected two singlets in the cyclobutene region (vinyl and allyl) of the nmr spectrum after treatment with methanolic sodium hydroxide (see Experimental Section).

Dehalogenation of the cyclic adducts is more difficult than the corresponding reactions in related systems. When two halogens finally are extricated from the molecule, the temperature of the reaction medium is too high for the olefin to survive and dimeric materials form, probably by ring-opening rearrangement and Diels-Alder coupling. Although a peak at *m/e* 128 was predominant in the mass spectrum, peaks above 160



were also present, thus indicating higher molecular weight materials (eq 8) which easily decompose to form naphthalene. Ring opening and dimerization of benzo[b]thiophene are indicated.

### Experimental Section

All melting points are uncorrected. Infrared spectra were taken in carbon tetrachloride using a Perkin-Elmer Infracord 137, and nmr spectra were taken (10% in CCl<sub>4</sub>) using a Varian A-60 spectrometer. Reference is to tetramethylsilane. Mass spectra were recorded on an A.E.I.-MS 9 equipped with an A-700 Model F & M vpc with thermal conductivity detectors. Analyses were performed by Mr. W. Hazenberg and his associates of one of these laboratories.

**Starting Materials.**—Benzo[b]thiophene, *cis*-dichloroethylene, *trans*-dichloroethylene, benzophenone, acetophenone, and 2-acetonaphthone were commercial materials purified when necessary by conventional methods. 2-Methylbenzo[b]thiophene, mp 48.5–51° (lit.<sup>18</sup> mp 51–52°), was prepared by the reaction of 2-benzo[b]thienyllithium with dimethyl sulfate. 3-Methylbenzo[b]thiophene was prepared by conventional methods<sup>19</sup> and was the gift of Mr. H. Luth.

**Preparation of 2-Deuteriobenzo[b]thiophene.**—2-Benzo[b]thienyllithium was prepared from 6.5 g (0.05 mol) of benzo[b]-

thiophene and 0.075 mol of *n*-butyllithium by adding the lithium reagent in ether to a solution of the benzo[b]thiophene in 50 ml of ether. After the color changed to orange-red (20 min), an excess of D<sub>2</sub>O (15 ml) was carefully added. The ether layer was removed and the product was dried and distilled. The product was shown to be almost completely deuterated by nmr.

**Preparation of 2,3-Dimethylbenzo[b]thiophene.**—3-Methylbenzo[b]thiophene (6.5 g, 0.05 mol) was lithiated by the addition of 70 ml of an 0.8 *N* solution of *n*-butyllithium to a solution of the benzo[b]thiophene in 125 ml of anhydrous ether. After the color of the solution changed, 12.0 g (0.1 mol) of dimethyl sulfate was added carefully. The reaction mixture spurted vigorously during the addition and a white solid (Li<sub>2</sub>SO<sub>4</sub>) gradually formed.

After all the lithium adduct was discharged, 100 ml of ethanol and 0.2 g of sodium metal were added to the mixture. The solution was brought to reflux and the excess ether was removed. Then the mixture was refluxed for 40 min more and the solution was allowed to stand at room temperature overnight.

A 400-ml portion of warm water was subsequently added to dissolve the lithium salts and the mixture was extracted with ether. A 5.85-g sample of crude 2,3-dimethylbenzo[b]thiophene (purity >95%, yield 85%) was obtained after removal of the ether: nmr δ 2.18 (s, 3 H), 2.36 (s, 3 H), and 6.95–7.60 ppm (m, 4 H).

*Anal.* Calcd for C<sub>10</sub>H<sub>10</sub>S: C, 74.14; H, 6.22; S, 19.79; mol wt, 162. Found: C, 73.72; H, 6.22; S, 19.82; mol wt, 162 (mass spectrum).

**General Irradiation Procedures.**—Irradiations were carried out using a Hanau S-81 or a Hanovia 450-W medium-pressure mercury arc lamp and an immersion well. Yields were somewhat higher when a Pyrex immersion well was used, but use of a quartz well had little or no effect on product compositions. For synthetic purposes, most reactions were run on a 150-ml scale using the haloolefin as the solvent. A 3–4-g sample of the benzo[b]thiophene, 1.0 g of the sensitizer, and 100–150 g of the haloolefin were irradiated for periods ranging from 12 to 48 hr. Longer periods of irradiation did not improve the yields much because, by this time, the reaction mixtures were usually brown and contained several outstanding internal filters which prevented further reaction.

After irradiation, the solvent was removed on a rotary evaporator and the products were separated from the sensitizer and residual tars using thick layer chromatography. A 2-mm layer of silica gel (Merck PF 254) was prepared and activated at 110° for 1 hr. *Ca.* 1 g of the crude products was added to the plate (20 × 100 cm) and the elution was carried out using a 50:50 mixture of pentane-CH<sub>2</sub>Cl<sub>2</sub>. This procedure separated the sensitizer but did not separate the isomeric products from each other or from excess starting materials.

The products were removed from the silica gel by stirring for 2 hr with a large excess of methanol and then evaporating the methanol. Dissolved silica gel had to be removed by taking the oil up in methylene chloride or chloroform, drying over sodium or magnesium sulfate, filtering, and evaporating the solvent.

Separating of the isomeric products could be effected using gas chromatography. Generally better separation occurred using a Carbowax 20 M column, at temperatures of 150–200°. GE-SE30 columns were used for some preparative purposes.

Slightly higher yields of adducts could be obtained when the irradiations were carried out in benzene. In a typical experiment, 3.0 g of 2-methylbenzo[b]thiophene, 0.4 g of benzophenone, and 100 ml of 1,2-dichloroethylene in 250 ml of benzene gave >90% yield after purification by column chromatography on silica gel with CCl<sub>4</sub> as the eluting solvent.

**Addition of Benzo[b]thiophene to *cis*-Dichloroethylene.**—From 2.0 g of benzo[b]thiophene, 200 g of *cis*-dichloroethylene, and 500 mg of acetophenone was obtained 2.0 g (60%) of crude adduct.

*Anal.* Calcd for C<sub>10</sub>H<sub>8</sub>Cl<sub>2</sub>S: C, 51.96; H, 3.49; Cl, 30.67; S, 13.88; mol wt, 230. Found: C, 52.06; H, 3.44; Cl, 30.82; S, 13.74; mol wt, 230 (mass spectrum).

**Addition of 2-Methylbenzo[b]thiophene to *cis*-Dichloroethylene.**—From 3.0 g of 2-methylbenzo[b]thiophene, 1.0 g of benzophenone, and 200 g of *cis*-dichloroethylene was obtained *ca.* 1.5 g (*ca.* 50%) of crude adducts.

*Anal.* Calcd for C<sub>11</sub>H<sub>10</sub>Cl<sub>2</sub>S: C, 53.88; H, 4.11; Cl, 28.92; S, 13.08; mol wt, 244. Found: C, 53.84; H, 4.18; Cl, 28.36; S, 12.92; mol wt, 244 (mass spectrum).

**Addition of 3-Methylbenzo[b]thiophene to *cis*-Dichloroethylene.**—From 2.5 g of 3-methylbenzo[b]thiophene, 1.25 g of

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(19) E. G. G. Werner, *Rec. Trav. Chim. Pays-Bas*, **68**, 509 (1949).

benzophenone, and 200 g of *cis*-dichloroethylene was obtained *ca.* 1.5 g (50%) of crude adducts.

*Anal.* Calcd for  $C_{11}H_{10}Cl_2S$ : C, 53.88; H, 4.11; Cl, 28.92; S, 13.08; mol wt, 244. Found for isomer 1: C, 54.33; H, 4.18; S, 13.18; mol wt, 244 (mass spectrum). Found for isomer 2: C, 54.19; H, 4.19; Cl, 28.55; S, 13.29; mol wt, 244 (mass spectrum).

**Addition of 2,3-Dimethylbenzo[b]thiophene to *cis*-Dichloroethylene.**—A 5.0-g sample of 2,3-dimethylbenzo[b]thiophene, 2.0 g of benzophenone, and 150 g of *cis*-dichloroethylene gave *ca.* 3.0 g (50%) of crude product.

*Anal.* Calcd for  $C_{12}H_{12}Cl_2S$ : C, 55.61; H, 4.67; Cl, 27.36; S, 12.37; mol wt, 258. Found: C, 55.70; H, 4.56; Cl, 27.00; S, 12.44; mol wt, 258 (mass spectrum).

**Addition of 1,1-Dichloro-2,2-difluoroethylene.**—An 800-mg sample of the benzo[b]thiophene, 200 mg of acetophenone, and 5 g of 1,1,2,2-dichlorodifluoroethylene were sealed, under vacuum, in a Pyrex tube. After 16-hr irradiation, the tube was opened and the low-boiling materials were removed. The products were separated as before *via* thick layer chromatography and finally collected from a 5% Carbowax 20 M column thermostated at 150°.

The mass spectra of the adducts indicated them to be 1:1 addition products, and they were similar, in every respect, to those formed from benzo[b]thiophene and 1,2-dichloroethylene. The nmr spectra of the adducts, reported below, were used to assign structure.

**Raney Nickel Desulfurization. Crude Adducts from Benzo[b]thiophene and *cis*-Dichloroethylene.**—Raney nickel (10 g) was prepared in the usual fashion<sup>20</sup> and washed several times with water. When the pH became approximately neutral, the material was considered suitable for use and transferred to a 500-ml, round-bottom flask which was equipped with a stirrer, a condenser, and a dropping funnel. A 400-mg sample of the combined adducts in 200 ml of absolute ethanol was added and the mixture was refluxed for 12 hr. At the end of this period the Raney nickel was removed by filtration and the solvent was dried and evaporated.

The major component of the fraction remaining was a material with a cumene-like odor. Collection of this product from a GE-SE 30 column at 190° produced phenylcyclobutane: mass spectrum *m/e* (rel intensity) 132 (100), 116 (20), 115 (27), 105 (96), 104 (100), 103 (95), 91 (55), 78 (75), and 77 (60); nmr<sup>21</sup>  $\delta$  1.65–2.62 (m, 6 H), 3.15–3.70 (m, 1 H), and 7.12 ppm (s, 5 H); mol wt, 132 (mass spectrum).

**Oxidation to the Sulfone. General Procedure.**—A 2-g sample of the adduct from 2-methylbenzo[b]thiophene and 1,2-dichloroethylene and 3.5 g of *m*-chloroperbenzoic acid were dissolved in 60 ml of  $CHCl_3$ . An instant warming of the solution took place, after which the mixture was refluxed for 12 hr.

After reaction, the chloroform solution was extracted three times with 50 ml of 1 *N* sodium hydroxide, washed twice with 100 ml of water, and dried over sodium sulfate.

After the chloroform had been removed, the crude sulfone was recrystallized from cyclohexane, and carbon tetrachloride yielded 48% of the isomeric sulfones, mp 125–128°, 132–136°.

**Base-Catalyzed Elimination Reactions. General Procedure.**—A 1.00-g sample of the mixture of adducts from benzo[b]thiophene and *cis*-dichloroethylene was treated with 1.0 g of NaOH in 4.0 g of MeOH. The material was stirred at reflux for 30 min and then 5 ml of excess methanol was added and the material was refluxed for an additional 12 hr. An extensive precipitate (sodium chloride) formed on the bottom of the flask. The product, a sweet-smelling, slightly yellow liquid, was separated by evaporating all the excess methanol. The crude product was dissolved in chloroform and filtered to remove the excess sodium

chloride. The dehydrohalogenated isomer was separated from residual starting material by preparative vpc on a 5% 4-ft Carbowax 20 M column thermostated at 180°.

The nmr spectrum of the major isolated adduct (>90%) showed a vinyl singlet, as well as a pair of doublets (AB), and was consistent with the assigned structure:  $\delta$  7.04 (s, 4 H, aryl), 4.81 and 4.59 (two d, 2 H, AB), and 6.00 ppm (s, 1 H, cyclobutene); mass spectrum ratio 3.2:1 [M/(M + 2)].

*Anal.* Calcd for  $C_{10}H_7ClS$ : mol wt, 194. Found: mol wt, 194 (mass spectrum).

Deuteration of the benzo[b]thiophene at the 2 position produced adducts which, following base-catalyzed elimination as above, had a change in the nmr spectrum:<sup>8,22,23</sup> the AB doublet collapsed to a singlet at 5.58 ppm. Thus the lower field portion of the AB doublet comes from the proton at the 3 position in the original benzo[b]thiophene, as would be expected from electro-negativity arguments.

**Dehydrohalogenation of the 2-Methylbenzo[b]thiophene Adducts.**—A procedure similar to that outlined above was employed. After preparative vpc two isomers (85:15) were separated as a mixture and the nmr spectra of the materials were obtained: major isomer  $\delta$  7.07 (s, 4 H), 5.89 (s, 1 H), 4.09 (s, 1 H), and 1.78 ppm (s, 3 H); minor isomer  $\delta$  7.06 (s), 6.01 (d), 4.22 (d,  $J = 1.5$  cps), and 1.78 ppm (s). The singlets for the major isomer were really a very weakly coupled doublet ( $J < 1$  cps).

*Anal.* Calcd for  $C_{11}H_9ClS$ : mol wt, 208. Found: mol wt, 208 (mass spectrum).

**3-Methylbenzo[b]thiophene Adducts.**—A procedure similar to that described above was used. Two adducts were separated as a mixture by preparative vpc and their nmr spectra follow: major isomer  $\delta$  7.03 (s, 4 H), 6.00 (s, 1 H), 4.36 (s, 1 H), and 1.68 ppm (s, 3 H); minor isomer  $\delta$  7.02, 5.76, 4.12, and 1.67 ppm.

**Dehalogenation of the Adducts from Benzo[b]thiophene and *cis*-Dichloroethylene.**—A 160-mg sample (0.7 mmol) of the combined adducts from benzo[b]thiophene and *cis*-dichloroethylene was refluxed over 2.0 g of zinc powder which had been washed three times with a 5% ammonium chloride solution and three times with water in *n*-amyl alcohol (bp 137°) to which a crystal of anhydrous zinc chloride had been added. After 24 hr, the zinc products were filtered and the solvent was partially removed by distillation at reduced pressure.

Direct injection from the vpc (GE SE-30, 10% 150°) into the mass spectrometer revealed a single component of molecular weight 220 which showed no molecular ion but whose most intense peak was *m/e* 128 (naphthalene).

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(22) It is significant that another isomer appeared when this dehydrohalogenated product was injected into the mass spectrometer using vpc injection techniques. This isomer, although very minor, had the same molecular weight as the dehydrohalogenation product but a much greater peak at  $M - 32$ . We attribute this peak to the corresponding naphthalene.

(23) During the elimination reaction, *ca.* 35% exchange of H for D occurred at the 2 position of the dehydrohalogenated product. This suggests that even in the bridgehead system shown, some significant basicity of the position  $\alpha$  to the sulfur atom exists.

(20) See, *e.g.*, A. I. Vogel, "Practical Organic Chemistry" Longmans Green, and Co., Ltd., London, 1962, p 821.

(21) J. W. Wilt, L. L. Mavavetz, and J. F. Zawadyki, *J. Org. Chem.*, **31**, 3018 (1966).