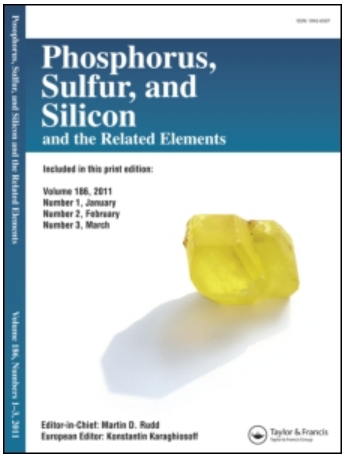

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FRAGMENTATIONS OF BENZO(*b*)THIOPHENES UNDER ELECTRON IMPACT

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FRAGMENTATIONS OF BENZO(*b*)THIOPHENES UNDER ELECTRON IMPACT

by

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Received January 11, 1974

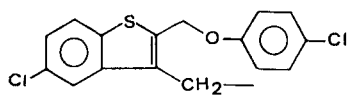
ABSTRACT

Aryloxy, arylmercapto, arylsulfonyl and dialkylamino derivatives of 2,3-dimethylbenzo(*b*)thiophenes exhibit interesting modes of mass spectral fragmentations. Selectivity in relative ease of fragmentation of different functions is noted. Smiles rearrangement is observed in the sulfone derivatives

Very few dialkylbenzo(*b*)thiophenes have been studied for their behavior under electron impact. Among the few that have been studied are 2,5-dimethyl-, 3,6-dimethyl-, 2,7-dimethyl- and 2-propyl 7-methyl benzo(*b*)thiophenes.[1] The predominant mode of fragmentation in all these compounds was the cleavage between the alpha and the beta positions of the side chain. Simple methyl-substituted benzo(*b*)thiophenes undergo ring expansion of either the hetero ring or the benzene ring to the appropriate thiapyran or the tropylium system.[2,3] In another 2,3-dialkylbenzo(*b*)thiophene derivative, a retro Diels-Alder cleavage is observed.[4]

Other than these examples, no derivatives of 2,3-dimethylbenzo(*b*)thiophene appear to have been studied for their behavior under electron impact. We now wish to report additional modes of cleavage exhibited by a number of analogous derivatives. These compounds, **1**, **2**, and **3** originated from a novel Claisen rearrangement we have uncovered.[5] Nucleophilic displacement of the allylic chlorine from **4** using aryloxy anions, secondary amines, and arylmercapto anions readily afforded **1**, **2**, and **3**.

The sulfides **3** were easily oxidized to the corresponding sulfones **5**, using *meta* chloroperbenzoic acid. Owing to the fact that all the above compounds **1**, **2**, **3** and **5** carry the following common unit:



it becomes easier to identify certain modes of fragmentation common to all the four types of compounds. Some of these fragments and pathways are illustrated in the accompanying Schemes I and II.

Fragments corresponding to m/e 321, 286, 250, 194, 159, and 115 are thus fully corroborated from *all* of the compounds studied. Thus, the major pathway for the fragmentation is the cleavage between the alkyl carbons at the 2 and 3 positions and the functional groups attached to them. However, there is observed an interesting variation in the relative ease of cleavage of these functionalities depending on their location. These results are summarized in the accompanying Tables I, II, and III.

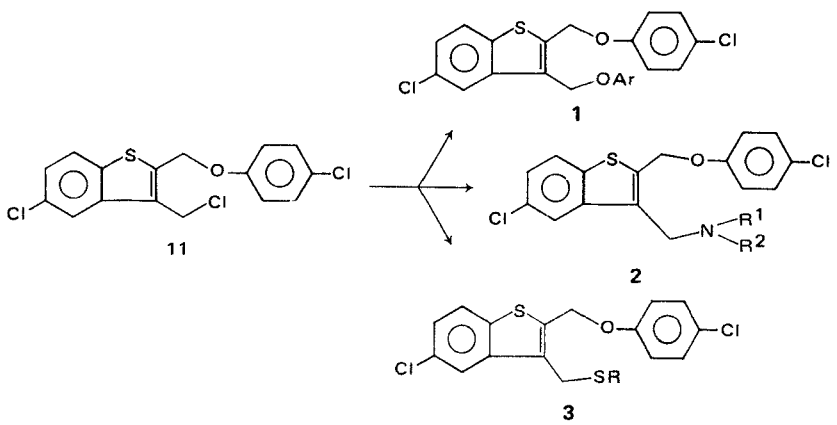
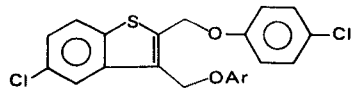
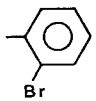
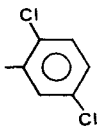
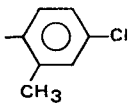
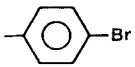
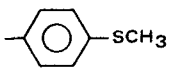
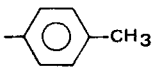


TABLE I

2-(*p*-Chlorophenoxymethyl)-3-(aryloxymethyl)-5-chlorobenzo(*b*)thiophene derivatives

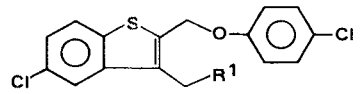


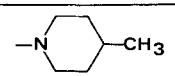
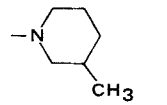
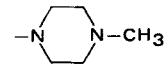
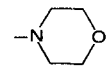
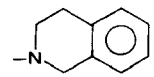
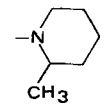
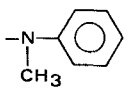
		Loss of substituents carried by											
		2-Methyl				3-Methyl				Both 2- and 3-Methyl			
		20 ev		70 ev		20 ev		70 ev		20 ev		70 ev	
	Ar	$\%\Sigma_{38}$	% Base Peak	$\%\Sigma_{38}$	% Base Peak	$\%\Sigma_{38}$	% Base Peak	$\%\Sigma_{38}$	% Base Peak	$\%\Sigma_{38}$	% Base Peak	$\%\Sigma_{38}$	% Base Peak
1.		6.14	44	3.37	15	13.95	100	7.64	34	13.95	100	22.47	100
2.		3.28	14.5	1.95	7	22.62	100	11.73	42	19.68	87	27.93	100
3.		1.28	5	0.85	3.5	25.71	100	14.32	59	16.71	65	24.27	100
4.		1.81	8	1.10	5	22.68	100	12.76	58	15.19	67	22.00	100
5.		0.74	4.5	0.40	2.0	16.51	100	10.83	54	13.54	82	20.06	100
6.		10.14	64	6.47	28.5	15.85	100	10.26	45	12.99	82	22.70	100

The M/M + 2 ratio for major peaks were calculated and found to agree closely with observed values.

TABLE II

2-(*p*-Chloropenoxymethyl)-3-aminomethyl-5-chlorobenzo(*b*)thiophene derivatives

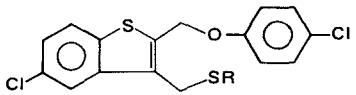


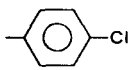
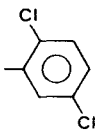
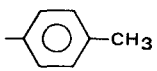
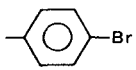
	R′	Loss of substituents carried by: 2-Methyl, 20 ev, %Σ38	2-Methyl, 20 ev, % Base Peak	2-Methyl, 70 ev, %Σ38	2-Methyl, 70 ev, % Base Peak	3-Methyl, 20 ev, %Σ38	3-Methyl, 20 ev, % Base Peak	3-Methyl, 70 ev, %Σ38	3-Methyl, 70 ev, % Base Peak	Both 2- and 3-Methyl, m/e 195, 20 ev, %Σ38	m/e 195, 20 ev, % Base Peak	m/e 195, 70 ev, %Σ38	m/e 195, 70 ev, % Base Peak	m/e 194, 20 ev, %Σ38	m/e 194, 20 ev, % Base Peak	m/e 194, 70 ev, %Σ38	m/e 194, 70 ev, % Base Peak
1.		1.11	4	0.72	4.5	27.78	100	16.09	100	11.53	41.5	14.48	90	1.53	5.5	6.92	43
2.		1.06	4	0.70	4.5	26.40	100	15.64	100	13.20	50	13.60	87	1.72	6.5	6.80	43.5
3.		5.61	52	3.07	28	10.79	100	6.36	58	9.28	86	10.96	100	0.59	5.5	4.27	39
4.		1.43	6	0.91	4	23.92	100	12.95	57	22.25	93	22.73	100	2.27	9.5	7.27	32
5.		0.71	3	0.42	2	23.84	100	12.56	60	19.55	82	20.94	100	2.26	9.5	6.28	30
6.		1.45	5.5	0.76	5.5	26.36	100	12.12	87	12.39	47	13.93	100	3.95	15	7.52	54
7.		0.82	3	0.44	4	27.51	100	11.12	100	8.25	30	8.11	73	3.71	13.5	8.45	76
8.		2.13	9.5	1.34	6.5	11.89	53	6.38	31	22.44	100	20.58	100	5.61	25	10.50	51

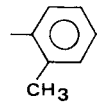
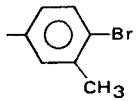
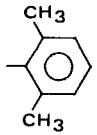
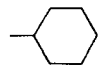
The M/M + 2 ratio for major peaks were calculated and found to agree closely with the observed values.

TABLE III

2-(*p*-Chlorophenoxymethyl)-3-(aryl, alkyl or cycloalkyl)-thiomethyl-5-chlorobenzo(*b*)thiophene derivatives



		Loss of substituents carried by											
		2-Methyl				3-Methyl				Both 2- and 3-Methyl			
		20 ev		70 ev		20 ev		70 ev		20 ev		70 ev	
	R	$\%\Sigma_{38}$	% Base Peak	$\%\Sigma_{38}$	% Base Peak	$\%\Sigma_{38}$	% Base Peak	$\%\Sigma_{38}$	% Base Peak	$\%\Sigma_{38}$	% Base Peak	$\%\Sigma_{38}$	% Base Peak
1		26.90	100	14.50	66.5	2.02	7.5	1.41	6.5	15.60	58	21.80	100
2.		21.88	94	12.08	50	1.05	4.5	0.84	3.5	17.22	74	24.15	100
3.		32.41	100	18.67	100	2.92	9	1.96	10.5	10.05	31	15.87	85
4.		15.56	73	8.07	40	1.91	9	1.31	6.5	13.33	62.5	20.18	100

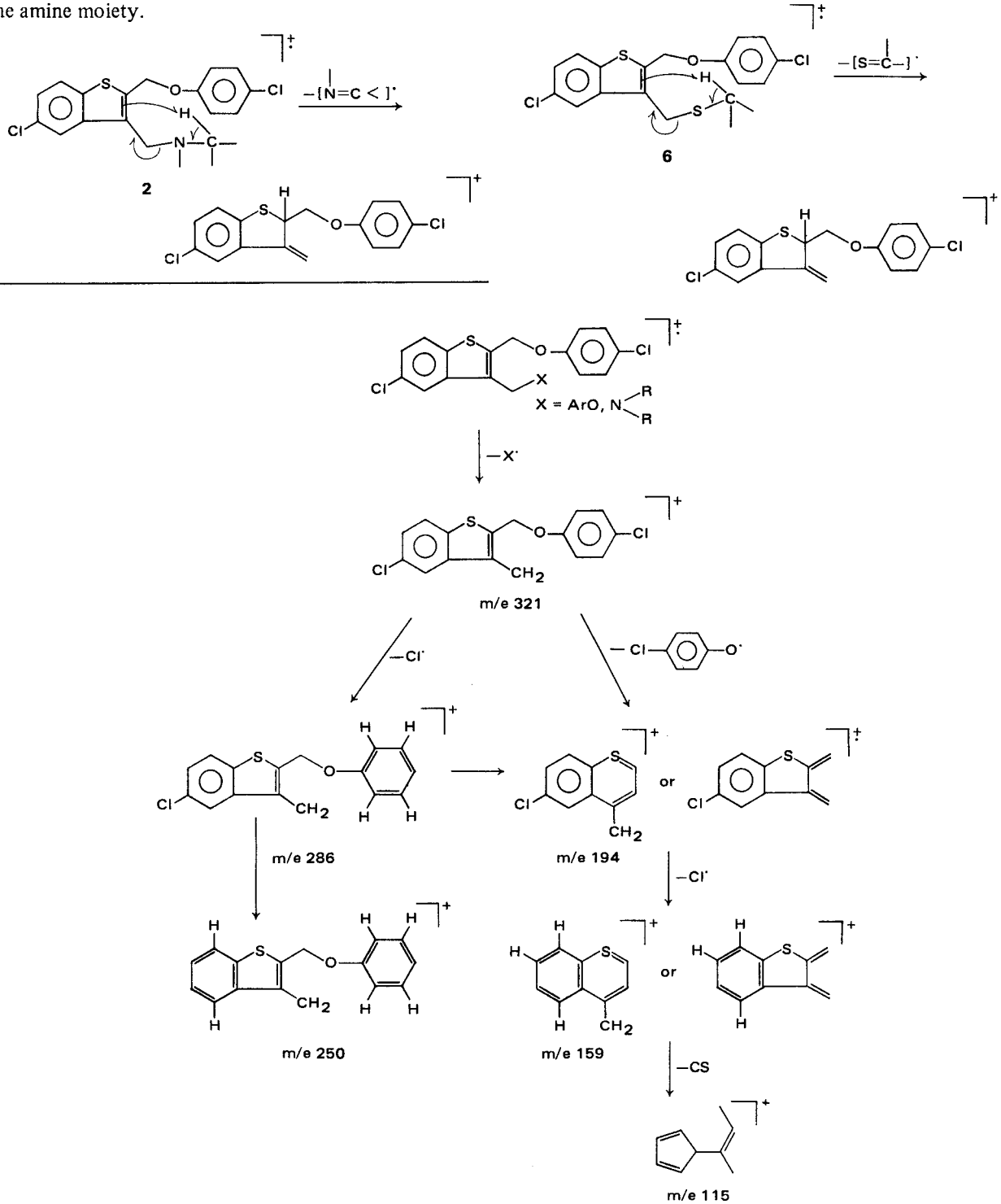
5.		35.34	100	18.99	100	1.59	4.5	2.09	11	11.31	32	17.09	90
6.		15.08	72	7.43	43	1.99	9.5	1.30	7.5	12.15	58	17.29	100
7.		28.61	100	13.30	80	2.86	10	1.66	10	10.30	36	16.62	100
8.*		9.84	75	4.26	47	7.87	60	3.45	38	12.33	94	8.80	97
9.*	$-CH_2CH_2CH_3$	14.94	41.5	7.45	24	4.50	12.5	2.33	7.5	36.01	100	31.03	100
10.*	$-CH_2CH_2CH_2CH_3$	14.47	41	7.23	23.5	4.94	14	2.62	8.5	35.30	100	30.78	100

The M/M + 2 ratio for major peaks were calculated and found to agree closely with observed values.

* For compound 8–10, loss of substituents carried by 3-methyl is indicated by m/e 320 instead of m/e 321 and loss of substituents carried by both 2- and 3-methyl is indicated by m/e 195 instead of m/e 194 (vide discussion, page 6 and 7).

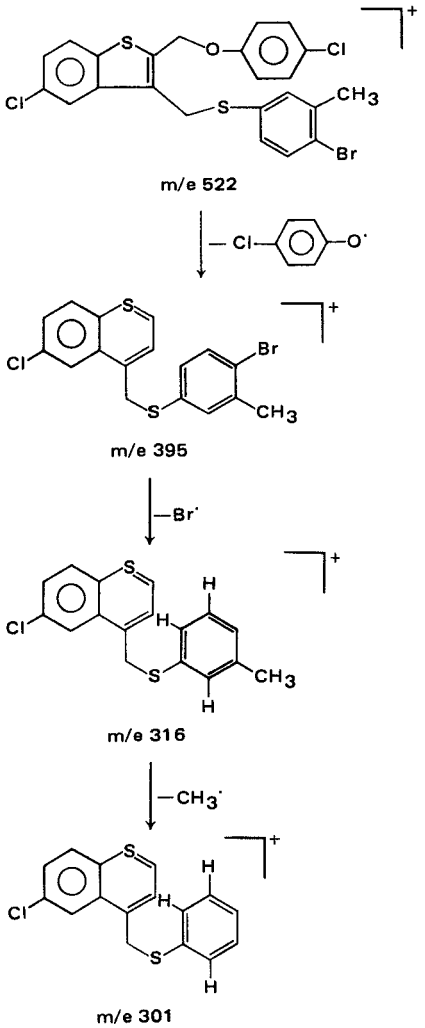
In addition to the above feature, one also observes a McLafferty-like rearrangement in the case of the aminomethyl derivatives, **2**. Consequently, the fragment corresponding to 194 becomes 195 with the gain of a hydrogen from the alkyl group attached to the amine moiety.

The same rearrangement is also observed in the case of alkyl sulfides of the following type, **6**.



SCHEME I

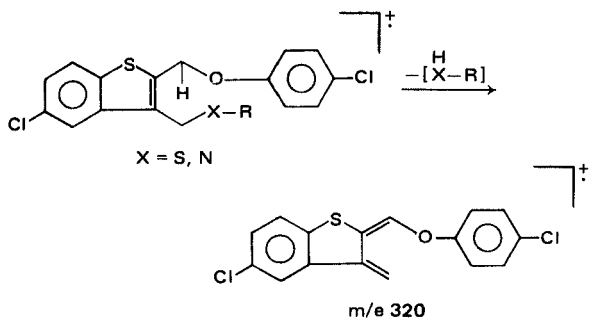
All the transitions indicated by arrowheads are supported by metastable peak correlations. The structural representations for the fragments are tentative and based on mechanistic analogies. Alternative formulations are also conceivable.



SCHEME II

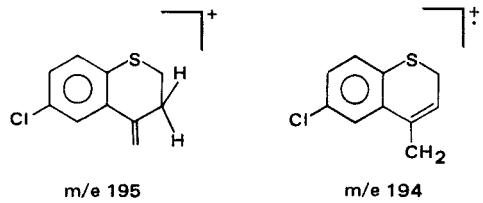
All the transitions indicated by arrowheads are supported by metastable peak correlations.

A different mode of McLafferty-like rearrangement is also possible in which a hydrogen is gained by the leaving group on the 3-methyl side chain. This is illustrated below:

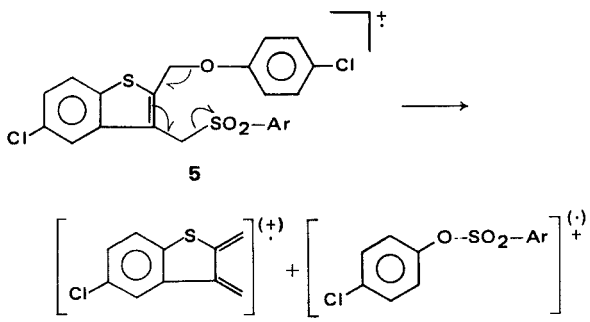


This is indeed observed as a significant fragment in all cases involving the aliphatic sulfides and amines. (See Table II and III.)

There is a distinct preference for the loss of the *para* chlorophenoxy group in the case of the amino and sulfide derivatives. Indeed, in the case of the sulfides, at 20 ev, M-127 (loss of the aryloxy group) is the base peak in every instance although at 70 ev, loss of both the side chain groups leads to formation of fragments of m/e 194 and 195.

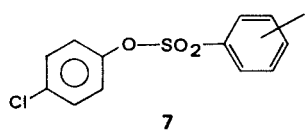


There is another intriguing pathway possible for the formation of the fragment of m/e 194. This involves a direct interaction of the following type:



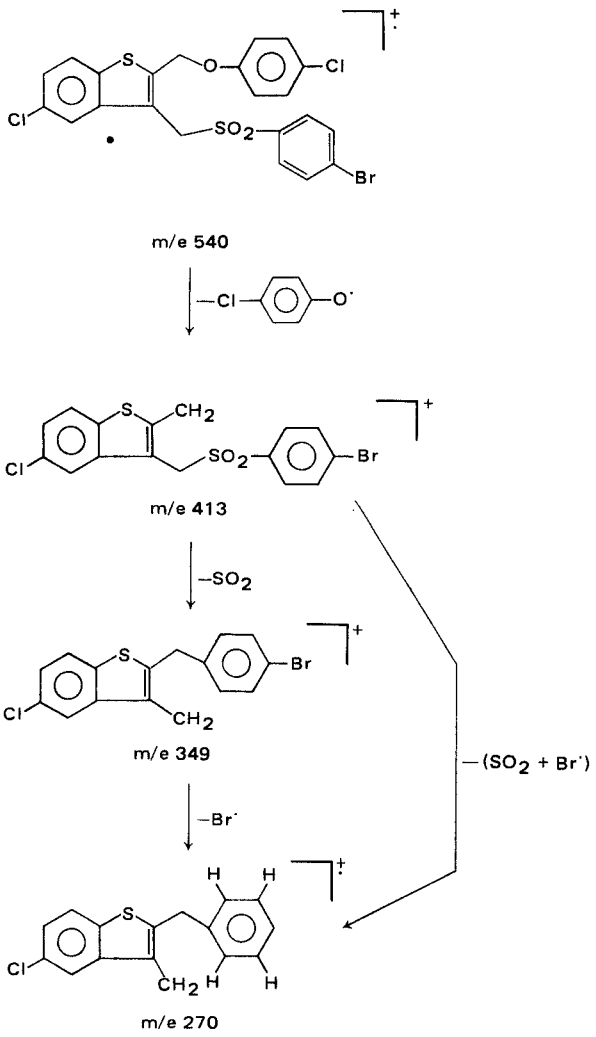
We have indeed observed such a pathway in a related study.[6]

However, despite the favorably enforced cis geometry of the double bond in the benzothiophene, sulfones, **5**, do not show any evidence for concerted elimination of fragments corresponding to the aryl arenesulfonates, **7**.



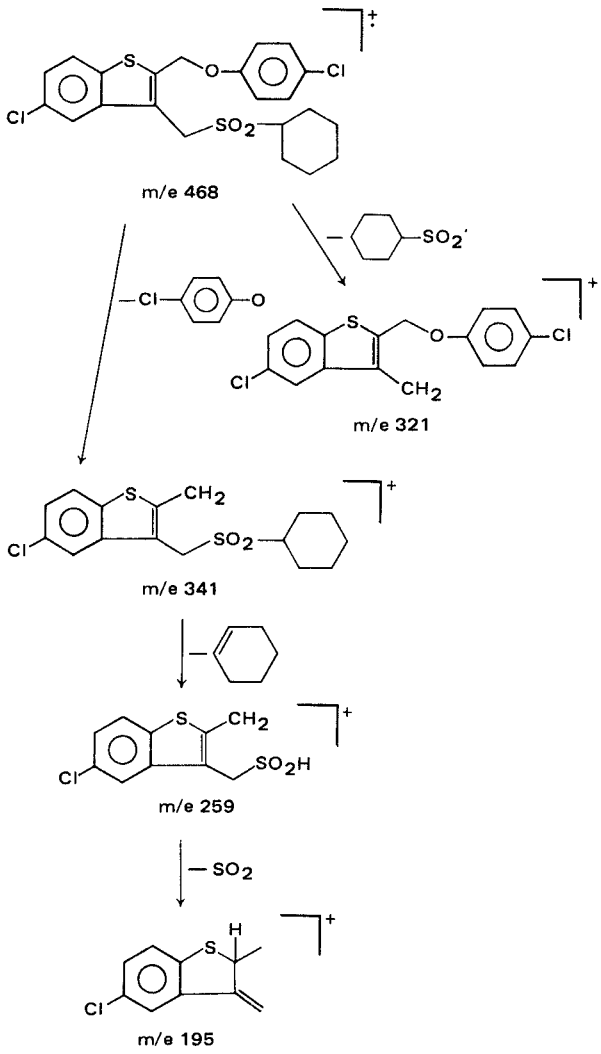
This observation, although puzzling at first sight, finds a rationale in a totally different mode of fragmentation—*viz.* the Smiles rearrangement.

The preferential loss of the *para* chlorophenoxy unit from the sulfide leads to an intriguing Smiles rearrangement in the case of the analogous sulfones, **5**. In every instance, here again the 2-aryloxy group is lost in greater relative abundance, although the resulting fragment no longer forms the base peak. This is a consequence of a facile rearrangement of such a fragment into an ion that readily loses SO_2. This process is observed in every example studied except in those cases where the sulfone is attached to an aliphatic or alicyclic group (propyl, butyl, cyclohexyl). Metastable peak correlations distinctly identify these transformations as outlined in the accompanying Scheme III.



SCHEME IIIa

All the transitions indicated by arrowheads are supported by metastable peak correlations.



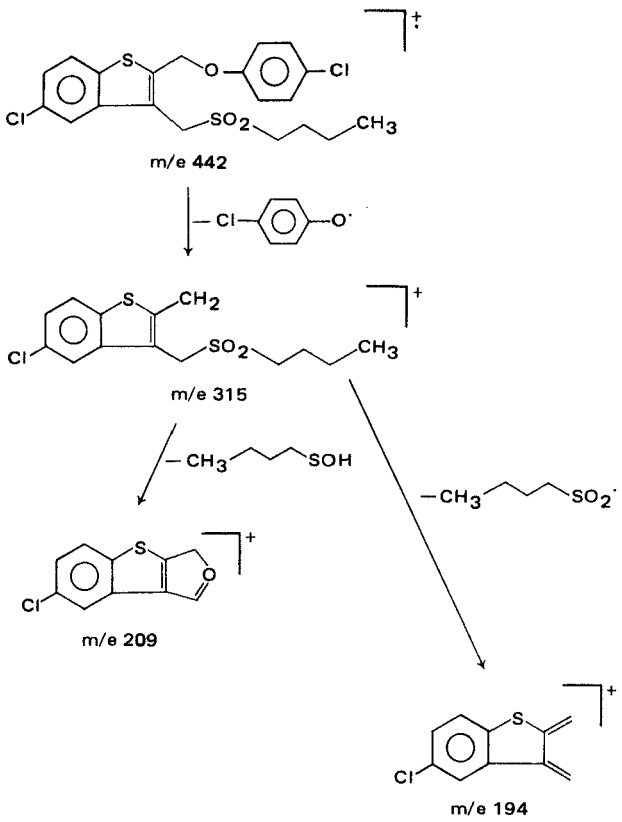
SCHEME IIIb

All the transitions indicated by arrowheads are supported by metastable peak correlations.

Intriguingly, there is no loss of SO_2 from the molecular ion itself, and the elimination of SO_2 *follows* the loss of the *para* chlorophenoxy function. That the loss of the SO_2 is triggered by the initial cleavage and loss of the aryloxy group is amply confirmed by the total absence of SO_2 loss in the case of the aliphatic or alicyclic sulfones mentioned above. The results are summarized in Table IV.

To our knowledge, there appears to be no report in the literature of such a Smiles rearrangement in benzo(*b*)thiophene derivatives under electron impact. Nor is there any information in related heterocycles like the benzofuran and indoles. Our own studies on these latter systems will be reported in a subsequent publication, utilizing a novel indole synthesis we have recently achieved.[7]

In summary, this study adds an interesting McLafferty-like rearrangement and a Smiles rearrangement to the previously reported modes of fragmentation in benzothiophene derivatives under electron impact. Additionally, a changing pattern in relative ease of cleavage of sidechain functions in such benzo(*b*)thiophenes is also noted. This feature is dependent upon the nature of the function attached to the 3-methyl group of the benzo(*b*)thiophene.



SCHEME IIIc

All the transitions indicated by arrowheads are supported by metastable peak correlations.

Experimental Section

Mass spectra were secured on a Hitachi Perkin Elmer RMU-6E mass spectrometer, at electron energies 70 and 20 ev. It was found that variation of the sample heater temperature had very little effect on the spectra. Computer calculations were conducted at the University of Idaho computer center utilizing a modified published program.[8]

Other spectral data were collected as follows: (a) nmr; Varian A-60; $CDCl_3$; TMS = 0 ppm. Melting points were taken on a Thomas-Hoover capillary melting point apparatus with an ordinary thermometer and were not corrected. Microanalyses were performed by the microanalysis laboratory of this department. All compounds in this study gave satisfactory spectral and analytical data.

The 2,3-diaryloxymethylbenzo(*b*)thiophene derivatives and 2-aryloxymethyl-3-aminomethylbenzo(*b*)thiophene derivatives were synthesized according to our earlier published procedure.[9] 2-(*p*-Chlorophenoxymethyl)-3-(*N*-methyl-*N*-phenylaminomethyl)-5-chlorobenzo(*b*)-thiophene, mp 121° was additionally synthesized.[9]

Anal. Calcd. for $C_{23}H_{19}Cl_2NOS$: C, 64.48; H, 4.47; N 3.27. Found: C, 64.50; H, 4.43; N, 3.14.

Synthesis of 2-Aryloxymethyl-3-arylthiomethylbenzo(*b*)-thiophene (3)

2-(*p*-Chlorophenoxymethyl)-3-chloromethyl-5-chlorobenzo(*b*)thiophene (4) was synthesized according to our earlier published procedure.[9] It was found that the Claisen rearrangement of 4-(*p*-chlorophenyl)-1-(*p*-chlorophenoxy)sulfinylbut-2-yne to the corresponding ketol was complete within 30 minutes and the allylic conversion of the ketol to 2-(*p*-chlorophenoxymethyl)-3-chloromethylbenzo(*b*)thiophene (4) was complete in one hour as an improvement on our earlier published procedure.[5,9]

Condensation of 2-(*p*-chlorophenoxymethyl)-3-chloromethyl-5-chlorobenzo(*b*)thiophene (4) with aryl and alkyl mercaptans

The aryl thiolate was prepared under nitrogen by stirring appropriate thiophenol (0.011 mol) with potassium hydroxide (0.01 mol) in tetrahydrofuran (THF, 20 ml) for 3 hours. To this solution of 2-(*p*-chlorophenoxymethyl)-3-chloromethyl-5-chlorobenzo(*b*) thiophene (0.01 mol, 3.58 g) in tetrahydrofuran (40 ml) was added slowly with stirring at 25° and the stirring was continued for 12 hours more. The alkyl mercaptans were condensed with 11 by stirring a mixture of alkyl mercaptan (0.011 mol), potassium hydroxide (0.01 mol) and compound 4 (0.01 mol, 3.58 g) in dimethylformamide (DMF, 60 ml) for 12 hrs. The compounds thus obtained are listed in Table V.

Oxidation of sulfide derivatives of Table V to the corresponding sulfone derivatives

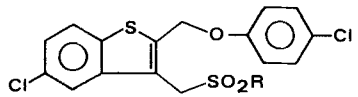
The appropriate sulfide (0.005 mol) was refluxed with 85% *m*-chloroperbenzoic acid (2 equiv., 0.01 mol, 2 g) in chloroform (180 ml) for 6 hours. The reaction mixture was cooled and more chloroform (300 ml) was added. The chloroform solution was washed with 5% NaOH solution (once), with water (three times), and was dried (Na_2SO_4). Removal of solvent gave a white solid which was recrystallized from chloroform/petroleum pentane (30–60°). The sulfone derivatives thus obtained are listed in Table VI.

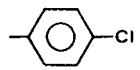
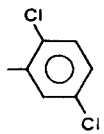
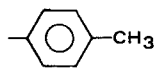
Acknowledgments

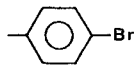
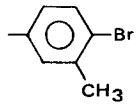
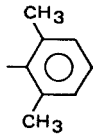
We deeply appreciate the very generous assistance of Mr. Doug McIntosh in securing the numerous mass spectra recorded in the course of this study. It is a pleasure to acknowledge Mr. Dallas K. Bates for assistance in procuring and modifying the program for computer plotting of all the spectra utilized in the present study. Our grateful thanks are due to Professors C. D. Hurd and Peter Brown for their helpful comments.

TABLE IV

2-(*p*-Chlorophenoxymethyl)-3-(aryl or alkyl or cycloalkyl)sulfonyimethyl-5-chlorobenzo(*b*)thiophene derivatives



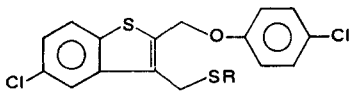
		Loss of substituents carried by						Smiles rearrangement		
		2-Methyl		3-Methyl		Both 2- and 3-methyl		Loss of sulfur dioxide		
		20 ev	70 ev	20 ev	70 ev	20 ev	70 ev	20 ev	70 ev	
	R	%Σ_{38} / % Base Peak	%Σ_{38} / % Base Peak	%Σ_{38} / % Base Peak	%Σ_{38} / % Base Peak	%Σ_{38} / % Base Peak	%Σ_{38} / % Base Peak	%Σ_{38} / % Base Peak	%Σ_{38} / % Base Peak	m/e (due to)
1.		14.60 85	6.58 26.5	1.63 9.5	0.99 4	17.18 100	24,81 100	9.45 55	6.70 27	305 (P-127-SO_2)
2.		9.40 51	2.70 10	4.61 25	2.70 10	18.45 100	26.95 100	4.98 27	3.23 12	339 (P-127-SO_2)
3.		17.36 100	6.57 35	1.73 10	1.13 6	10.42 60	18.76 100	17.36 100	11.25 60	285 (P-127-SO_2)

4.		8.52	50	3.84	16	2.22	13	1.44	6	17.05	100	23.98	100	13.38	78.5	9.35	39	270 (P-127-SO_2—Br)
5.		13.09	76	5.60	26	3.79	22	2.47	11.5	13.44	78	21.53	100	17.23	100	11.41	53	285 (P-127-SO_2)
6.		8.15	49	3.32	16	2.66	16	1.66	8	13.31	80	20.73	100	16.63	100	10.36	50	284 (P-127-SO_2—Br)
7.		3.83	25	1.43	7.5	9.19	60	4.48	23.5	15.31	100	19.05	100	13.78	90	8.29	43.5	299 (F-127-SO_2)
8.		19.04	100	7.16	48	2.86	15	1.56	10.5	10.19	53.5	14.91	100	0.19	1.0	0.15	1.0	277 (P-127-SO_2)
9.	$-CH_2CH_2CH_3$	27.15	100	14.44	53	1.90	7	1.36	5	22.40	82.5	27.25	100	0	0	0	0	
10.	$-CH_2CH_2CH_2CH_3$	26.60	100	14.32	66	1.60	6	1.19	5.5	18.88	71	21.69	100	0	0	0	0	

The M/M + 2 ratio for major peaks were calculated and found to agree closely with observed values.

TABLE V

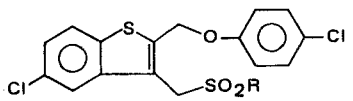
2-(*p*-Chlorophenoxymethyl)-3-(aryl, alkyl or cycloalkyl)-thiomethyl-5-chlorobenzo(*b*)thiophene derivatives



	R	MP (°C)	% Yield	Molecular formula	Analysis % Calcd. C	Calcd. H	Found C	Found H
1.	*o*-Cresyl	137	82	$C_{23}H_{18}Cl_2OS_2$	62.02	4.04	62.09	4.08
2.	*p*-Bromophenyl	137-38	86	$C_{22}H_{15}BrCl_2OS_2$	51.76	2.94	51.67	2.98
3.	*p*-Chlorophenyl	131	85	$C_{22}H_{15}Cl_3OS_2$	56.71	3.22	56.74	3.20
4.	4-Bromo-3-methylphenyl	155-56	84	$C_{23}H_{17}BrCl_2OS_2$	52.67	3.24	52.48	3.24
5.	2,5-Dichlorophenyl	152	83	$C_{22}H_{14}Cl_4OS_2$	52.80	2.80	52.55	2.84
6.	2,6-Dimethylphenyl	157	84	$C_{24}H_{20}Cl_2OS_2$	62.74	4.35	62.64	4.38
7.	*n*-Propyl	96-97	81	$C_{19}H_{18}Cl_2OS_2$	57.43	4.54	57.51	4.59
8.	*n*-Butyl	93-94	80.5	$C_{20}H_{20}Cl_2OS_2$	58.40	4.86	58.70	4.90
9.	Cyclohexyl	124-25	82.5	$C_{22}H_{22}Cl_2OS_2$	60.41	5.03	60.43	5.05
10.	*p*-Cresyl	107	88.4	$C_{23}H_{18}Cl_2OS_2$	62.02	4.04	62.28	4.10

TABLE VI

2-(*p*-Chlorophenoxymethyl)-3-(aryl, alkyl or cycloalkyl)sulfonylmethyl-5-chlorobenzo(*b*)thiophene derivatives



	R	MP (°C)	% Yield	Molecular Formula	Analysis Calc. C	Calc. H	Found C	Found H
1.	*o*-Cresyl	210	83	$C_{23}H_{18}Cl_2O_3S_2$	57.86	3.77	58.01	3.73
2.	*p*-Bromophenyl	213 (d)	85	$C_{22}H_{15}BrCl_2O_3S_2$	48.71	2.76	48.49	2.71
3.	*p*-Chlorophenyl	201	88	$C_{22}H_{15}Cl_3O_3S_2$	53.06	3.01	53.01	2.96
4.	4-Bromo-3-methylphenyl	190	85	$C_{23}H_{17}BrCl_2O_3S_2$	49.64	3.06	49.59	3.26
5.	2,5-Dichlorophenyl	214 (d)	88.8	$C_{22}H_{14}Cl_4O_3S_2$	49.62	2.63	49.60	2.59
6.	2,6-Dimethylphenyl	193	89	$C_{24}H_{20}Cl_2O_3S_2$	58.65	4.07	58.97	4.10
7.	*n*-Propyl	201	89	$C_{19}H_{18}Cl_2O_3S_2$	53.15	4.19	52.86	4.18
8.	*n*-Butyl	194	85.5	$C_{20}H_{20}Cl_2O_3S_2$	54.17	4.51	53.88	4.58
9.	Cyclohexyl	242	86	$C_{22}H_{22}Cl_2O_3S_2$	56.29	4.69	56.26	4.65
10.	*p*-Cresyl	165-7	86	$C_{23}H_{18}Cl_2O_3S_2$	57.86	3.77	57.63	3.71

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