change at the α position by a factor of ca. 10^3.[16] Epimerization of *cis*- or *trans*-2,3-dimethyl-2-phenylthiirane 1,1-dioxide is unlikely, since *cis*-2,3-dimethylthiirane 1,1-dioxide, which has an acidic proton of a comparable type, does not epimerize under these conditions.[13]

(16) D. A. Schexnayder, Ph.D. Dissertation, Northwestern University, June 1968.

(17) This result is more definitive than the rough kinetic studies of the decomposition of the unstable thiirane 1,1-dioxides themselves.[3] Furthermore, reexamination of the earlier data[3] makes us doubtful as to the reality of the small accelerations in rates observed with increasing methoxide concentration. Our present view is that the decomposition of thiirane 1,1-dioxides is *not* accelerated by low concentrations of bases.

(18) The rate constant k_{-1} probably refers in actual practice to solvent exchange rather than protonation, since the rate-limiting step in these exchanges is probably solvent exchange.[10] Corrections for statistical factors and isotope effects need also to be made, but the 100-fold figure should be of the right order of magnitude.

(19) F. G. Bordwell, D. D. Phillips, and J. M. Williams, Jr., *J. Amer. Chem. Soc.*, **90**, 426 (1968).

(20) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, pp 254–255.

(21) L. A. Paquette, *Accounts Chem. Res.*, **1**, 209 (1968). It is true that this carbanion (labeled **24** in the paper) may be formed faster than that leading to the trans thiirane 1,1-dioxide (**25**) because of a lower rotational barrier, but it is also true that **24** will revert faster to its rotamer (I). There is no reason to believe, then, that the equilibrium concentration of **24** will be higher than that of **25** for this reason, as was assumed.

(22) F. G. Bordwell, B. B. Jarvis, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, **90**, 5298 (1968).

(23) It is assumed that the relative equilibrium concentrations of cis and trans 2,3-, 2,2,3-, and 2,2,3,3-substituted thiirane 1,1-dioxides will not differ greatly from those of the corresponding cis and trans alkenes. This assumption is supported by the formation of a near-equilibrium concentration of *cis*- and *trans*-2-butene from *cis*-2,3-dimethylthiirane 1,1-dioxide when equilibration is effected with *t*-BuOK-*t*-BuOH,[13] and by the formation of only *trans*-stilbene from *cis*-2,3-diphenylthiirane 1,1-dioxide when equilibration is effected with NaOMe-MeOH.[3]

(24) Nmr spectra were determined on a Varian A-60 spectrometer (60 MHz). Infrared spectra were run on a Beckman IR-5 spectrophotometer in KBr disks. Analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

(25) Compound **11** was formed to the exclusion of $PhCHBrSO_2CH(CH_3)Ph$. Data obtained in these experiments indicate that free-radical brominations α to the sulfone group are effective when the hydrogen atom being replaced is both benzylic and tertiary. In fact, it was found previously that simple benzyl and allyl sulfones do not undergo free-radical bromination under comparable conditions.[26]

(26) See H. J. Baker, W. Steven, and N. Dost, *Recl. Trav. Chim. Pays-Bas*, **67**, 451 (1948); *Chem. Abstr.*, **43**, 559 (1949).

(27) M. D. Wolfinger, Ph.D. Dissertation, Northwestern University, June 1968, p 240.

Concerning Driving Forces for 1,3-Elimination Reactions. Dehydrohalogenation of 1-Halo-2-thia-2,3-dihydrophenalene 2,2-Dioxides in a Ramberg-Bäcklund Reaction

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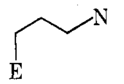
Data obtained for the reaction of 1-bromo-2-thia-2,3-dihydrophenalene 2,2-dioxide (8) with NaOMe and MeOH, including deuterium exchange, kinetic order, kinetic salt effects, and kinetic activation parameters, are shown to be remarkably similar to data obtained under similar conditions in a study of an open-chain analog, $PhCHBrSO_2CH_2Ph$ (9). The evidence points to a two-stage (carbanion) mechanism for 8, despite the presence of a geometry that would appear to favor a one-stage (concerted) mechanism. It is concluded that the concerted mechanism for 1,3-elimination has relatively little driving force.

The stereochemistry of two-stage 1,3-elimination reactions involving carbanion intermediates is dictated primarily by the necessity of inversion at the nucleofugal center (N).[1] In acyclic systems this requires removal of the electrofugal atom or group (E) from either conformation 1 (exo-sickle) or conformation 2 (W). Concerted 1,3-elimination reactions could also presumably utilize transition states with geometries corresponding to 1, 2, or one of three other possibilities (endo-S, apo-S, or U).[2]



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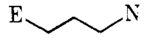

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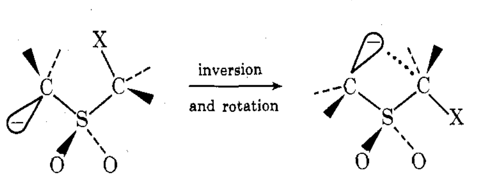
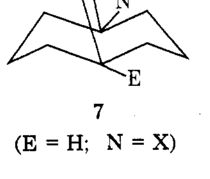
1,3-Dehydrobromination of $PhCH(Me)SO_2CBr(Me)Ph$ (3)[3] and 1,3-debromination of $PhCHBrSO_2CHBrPh$ (4)[1] have been found to involve carbanion intermediates and to prefer overall W geometry (2). Here the preference of W over exo-S geometry is believed to be dictated by preferred deprotonation (of 3) or removal of Br^+ (from 4) from a conformation in which these electrofugal atoms are flanked by the two oxygen atoms of the sulfonyl group.[1,3] The resulting carbanion (*e.g.*, 5) is prevented for steric reasons from effecting ring closure. The transition state required for ring closure is 6 wherein carbanion 5 has inverted its configuration and rotation has occurred around the O_2S–CX bond so as to permit inversion of configuration when the nucleofugal group X departs.[1] (Rotation around O_2S–C^- would give the wrong stereochemical result: a barrier to this rotation is assumed.)

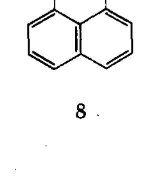


5 6

If this representation of the reaction is correct, one would expect 1,3-eliminations of this type to be particularly facile in cyclic analogs such as 1-halo-9-thiabicyclo[3.3.1]nonane 1,1-dioxides (7), where the E and N atoms are fixed in the W configuration and the E atom is flanked by the oxygen atoms of the sulfonyl group, or 1-



7
(E = H; N = X)



8

Table I
Rate Data for the 1,3-Elimination Reaction of 1-Bromo-2-thia-2,3-dihydrophenalene 2,2-Dioxide (8, X = Br)[a–c]

Runs	Temp, °C	[CH_3ONa]	k_{obsd}, sec^{-1}	k_2, M^{-1} sec^{-1}
3	25.0	2.36×10^{-1}	2.63×10^{-3}	1.12×10^{-2}
1	25.0	2.48×10^{-1}	2.73×10^{-3}	1.10×10^{-2}
2	25.0	1.24×10^{-1}	1.04×10^{-3}	0.85×10^{-2}
3	25.0	1.18×10^{-1}	1.05×10^{-3}	0.89×10^{-2}
2	25.0	1.06×10^{-1}	0.98×10^{-3}	0.92×10^{-2}
3	35.0	1.18×10^{-1}	4.34×10^{-3}	3.62×10^{-2}
2	34.9	5.90×10^{-2}	1.95×10^{-3}	3.30×10^{-2}
2	34.9	5.90×20^{-2} [d]	1.73×10^{-3}	2.94×10^{-2}
2	43.0	5.90×10^{-2}	5.76×10^{-3}	0.98×10^{-1}
2	42.5	5.90×10^{-2} [d]	5.00×10^{-3}	0.85×10^{-1}
3	42.5	1.18×10^{-1}	1.30×10^{-2}	1.10×10^{-1}

[a] Correlation coefficients for all runs were at least 0.999. [b] In no case did rate constants (which were averaged) differ by more than 5% from the mean value. [c] E_a = 25.5 kcal/mol^{-1} and ΔS^* = 16 eu (r = 0.9999) from reactions involving 0.118 *M* sodium methoxide. [d] This solution was 0.064 *M* in $LiClO_4$.

Table II
Rate Data for the 1,3-Elimination Reaction of $C_6H_5CHBrSO_2CH_2C_6H_5$ (9)

Runs	Temp, °C	[CH_3ONa]	k_{obsd}, sec^{-1}	k_2, M^{-1} sec^{-1}
2	25.0	1.24×10^{-1}	1.17×10^{-2}	9.4×10^{-2}
2	25.0	4.97×10^{-2}	3.80×10^{-3}	7.6×10^{-2}
2	25.0	4.97×10^{-2} [a]	3.23×10^{-4}	6.5×10^{-2}
	25.0	1.55×10^{-2} [b]		7.5×10^{-2}

[a] This solution was 0.093 *M* in $LiClO_4$. [b] Taken from F. G. Bordwell and J. M. Williams, Jr., *J. Amer. Chem. Soc.*, **90,** 435 (1968).

halo-2-thia-2,3-dihydrophenalene 2,2-dioxides (8), where this geometry is either preferred or easily attained.

Recent studies have indeed shown that 7 and 8 do undergo Ramberg–Bäcklund type reactions. Reaction of 7 (X = Br) with sodium *tert*-pentoxide in tetraglyme at 70° for 1 hr gave an 81% yield of $\Delta^{1,5}$-bicyclo[3.3.0]octane,[4] and a 75% yield was obtained from 7 (X = Cl) when treated with aqueous potassium hydroxide at 100° for 48 hr.[5] Also, the parent sulfone 8 (X = H) is readily converted to acenaphthylene by reaction with KOH–CCl_4 under conditions where the evidence points to the chloro sulfone (8, X = Cl) as the intermediate.[6] Since the favored W geometry is readily available to 8, it seemed likely that proton removal, inversion at that carbon atom, and intramolecular displacement of X (with inversion) would all occur in a single transition state (concerted mechanism). The concerted mechanism would be expected to be preferred in this instance, since the conformation of the ground state is already constricted, which should lead to a more positive entropy of activation than for the acyclic analog. We therefore decided to study the Ramberg–Bäcklund reaction of 8 as a model for the concerted mechanism.

Results

The desired α-halo sulfones (8, X = Br or Cl) were prepared by halogenating the corresponding sulfide followed by oxidation. The four benzylic protons of the parent sulfone appear as a singlet in the nmr spectrum. Since examination of molecular models indicates that the ring containing the sulfone bridge is puckered, the nmr data suggest that ring inversion is rapid on the nmr time scale. The nmr spectra of the halo sulfones 8 show a large downfield shift (1 ppm) of one of the methylene protons relative to the other, indicating that the system is mobile, allowing considerable 1,3-diaxial interaction between one of the methylene protons and the halogen.

Reaction of 8 (X = Br or Cl) with sodium methoxide in methanol gave acenaphthylene in high yield, and as the only detectable product. Treatment of 8 (X = Br or Cl) with NaOMe–MeOD gave dideuterioacenaphthylene. Recovery of the bromo sulfone from a run after about 1 half-life showed that the α and α′ protons had been completely exchanged by deuterium.

Excellent first-order plots were obtained from spectrophotometric rate measurements made under pseudo-first-order conditions. Small increases in second-order rate constants were observed with increasing concentrations of sodium methoxide (Table I). Surprisingly enough, the rate constants *decreased* slightly, but significantly, in the presence of lithium perchlorate. Examination of the rates for the reaction of sodium methoxide in methanol with and without added lithium perchlorate for $PhCH_2SO_2CHBrPh$ (9), an open-chain analog of 8, revealed comparable effects (Table II).

Data were also obtained for chloride 8 at 25° (k_2 = 0.93, 0.93, and 0.93 × 10^{-4} M^{-1} sec^{-1} with 0.248 *M* NaOMe) and 39.7° (k_2 = 0.93, 1.00, and 1.09 × 10^{-3} M^{-1} sec^{-1} with 0.248 *M* NaOMe; 0.83, 0.83, and 0.71 × 10^{-3} M^{-1} sec^{-1} with 0.124 *M* NaOMe); E_a = 30.3 kcal/mol for the runs with 0.248 *M* base.

Discussion

It is significant that the rate data accumulated for the 1-halo-2-thia-2,3-dihydrophenalene 2,2-dioxide system (8) bear a remarkable resemblance to the data obtained for a open-chain analog, $PhCHXSO_2CH_2Ph$ (9).[7] In each instance methoxide-catalyzed deuterium exchange is much faster than intramolecular nucleophilic displacement to form the thiirane 1,1-dioxide ring. Both reactions show slight increases in rate constants for alkene formation with increasing methoxide concentrations and slight decreases in these rate constants with increasing lithium perchlorate concentration (Tables I and II). Both reactions exhibit large k^{Br}/k^{Cl} leaving group effects (121 at 25° for 8 and 280 for 9). The overall rate of alkene formation from 9 (X = Br) is *ca.* 11 times faster at 25° than that from 8 (X = Br), but the activation parameters are the same within the experimental error of the measurements (E_a = 25.5 kcal/mol and ΔS^* = 16 eu at 25° for 8 as compared to 25 kcal/mol and 17 eu at 25° for 9). The data point strongly to reaction of 8 and 9 by similar mechanisms. For 9, numerous lines of evidence point to (1) reversible carbanion formation as the initial step, (2) rate-limiting intramolecular nucleophilic displacement to form a thiirane 1,1-dioxide as the second step, and (3) rapid thermal decomposition of the thiirane dioxide to an alkene as the third step.[7-9] There appears to be every reason to accept this mechanism also for the Ramberg–Bäcklund reaction of 8.

Table III
Methoxide Ion Induced 1,3-Eliminations and Deuterium Exchange of 2-Thia-2,3-dihydrophenalene 2,2-Dioxides (8)

Compd	Quantity, mmol	MeO$^-$, mmol	ρ solvent (ml)	Reaction time	Product
8 (X = Br)	0.50	3.7	MeOH (15)	12 hr	AN-H_2[a]
8	0.26	3.7	MeOD (10)	4 hr	AN-d_2[a]
8	0.09	0.18	MeOD (4)	50 sec	**1c-d$_3$**[b]
8 (X = Cl)	0.45	2.1	MeOD (10)	36 hr	AN-d_2[a]

[a] AN-H_2 is acenaphthylene. [b] Characterized by ir, nmr, and melting point.

where one might have expected bond making to aid bond breaking in a concerted fashion.[16] The conclusion concerning the rarity of the one-stage mechanism for 1,3-eliminations is supported in a general way by evidence that in similar reactions where two bonds are formed and two bonds are broken, such as S$_N$2′ reactions[8] and 1,2-elimination reactions,[17] two-stage mechanisms are much more common than one-stage mechanisms. Aside from the entropy factor mentioned previously, the most important factor dictating the preference for the two-stage mechanism in these reactions is probably the greater degree to which solvation forces can be utilized in providing the energy necessary for rehybridization of the two carbon atoms and in the cleavage of the C–X bond. In addition to these factors, the one-stage mechanism has a particular handicap in 1,3-eliminations in that a highly strained three-membered ring is being formed. As a result the amount of energy released during formation of the new C–C bond in a 1,3-elimination is appreciably less, for example, than during formation of the new C=C bond in a 1,2-elimination. This makes the concerted mechanism less attractive in a 1,3- than in a 1,2-elimination process.

Table IV
Nmr Data for 2-Thia-2,3-dihydrophenalene Derivatives[a]

Compd	Methylene	Methine	Aromatic
8 (X = H)	4.60 (s, 4 H)		~7.7 (m, 6 H)
8 (X = Br)	4.43 (d, d, J = 16, 3 Hz, 1 H) 5.42 (d, J = 16 Hz, 1 H)	6.03 (d, J = 3 Hz, 1 H)	~7.7 (m, 6 H)
8 (X = Cl)	4.45 (d, d, J = 16, 3 Hz, 1 H) 5.32 (d, J = 16 Hz, 1 H)	5.93 (d, J = 3 Hz, 1 H)	~7.7 (m, 6 H)
10[b]	4.00 (s, 4 H)		~7.4 (m, 6 H)

[a] Chemical shifts are reported in δ units downfield from tetramethylsilane as internal standard. [b] Mp 95–97° (lit.[19] mp 102°).

Table V
Melting Points and Carbon–Hydrogen Analyses for 2-Thia-2,3-dihydrophenalene 2,2-Dioxides[a]

Compd[b]	Mp, °C	Molecular formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
8 (X = H)	244–245	$C_{12}H_{10}SO_2$	66.03	4.62	65.83	4.55
8 (X = Br)	197–198	$C_{12}H_9BrSO_2$	48.50	3.05	47.83	2.99
8 (X = Cl)	167–168	$C_{12}H_9ClSO_2$	56.80	3.57	56.76	3.70

[a] The characteristic ir absorptions at 7.6 and 8.9 μ were observed for the sulfones; crystallized from dichloromethane–hexane.

The failure of 8 to take advantage of the concerted pathway indicates that the concerted mechanism can provide but little driving force in this instance. Apparently stepwise ionic processes, wherein maximum advantage can be taken of solvation forces, provide a lower energy pathway.[13]

The present evidence indicates that, even under what appear to be the most favorable circumstances for a concerted pathway, the Ramberg–Bäcklund reaction occurs by a two-stage rather than a one-stage mechanism. Previously we surveyed the stereochemical evidence that has accumulated with regard to 1,3-elimination reactions and concluded that concerted 1,3-eliminations are rare, if they exist at all.[1,15] This conclusion was based on the premise that, if the one-stage mechanism is favored energetically, examples where a high degree of stereoselectivity is observed should be common and one preferred stereochemical pathway would be likely to emerge. Instead, many 1,3-eliminations exhibit little or no selectivity, and no one stereochemical pathway has emerged as dominant. One example of U geometry being preferred to endo-S has been found,[2] but in most instances the preferred geometry is either exo-S or W. These latter geometries are those expected for two-stage pathways. To this evidence we now add the failure of a driving force to emerge in an example

Experimental Section

Nmr spectra were determined on a Varian T-60 spectrometer (60 MHz). Chemical shifts are reported in δ units (parts per million downfield from TMS) and were determined in chloroform-d solution. Infrared spectra were run on a Beckman IR-5 spectrophotometer in KBr disks. Analyses were performed by Micro-Tech Laboratories, Skokie, Ill. Melting points are uncorrected.

Preparation of Sulfones. Chlorination (and bromination) of 2-thia-2,3-dihydrophenalene (10) was carried out according to the procedure of Tuleen.[18] The crude halo sulfides were oxidized to sulfones (8) with *m*-chloroperoxybenzoic acid (MCPBA). The isolated yields of **8b** (X = Cl) 52 and **8c** (X = Br) were 52 and 59%, respectively. The known sulfone **8a** (X = H) was obtained from **10** in 64% yield upon oxidation of the latter with MCPBA.

Product Studies. The halo sulfones **8b** and **8c** were allowed to react with excess sodium methoxide in methanol or methanol-d_1. The product, acenaphthylene, was identified by its ultraviolet and nmr spectra and melting point. See Table III for a summary of representative product study experiments, and Tables IV and V for data supporting structures of substrates used in kinetic studies.

Kinetic Method. See previous reports from this laboratory for the spectrophotometric determination of rates.[7] The appearance of acenaphthylene was measured at 320 mμ, and the rates were followed through at least 5 half-lives.

Acknowledgment. This work was supported by the National Science Foundation (GP-29539X).

Registry No.—8 (X = H), 29376-61-2; 8 (X = Br), 51392-61-1; 8 (X = Cl), 51392-62-2; 9, 19217-59-5; 10, 203-85-0.

References and Notes

(1) For pertinent references and a discussion see F. G. Bordwell and B. B. Jarvis, *J. Amer. Chem. Soc.*, **95**, 3585 (1973).

(2) A. Nickon and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **89**, 3914 (1967).

(3) F. G. Bordwell, E. Doomes, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, **92**, 2581 (1970).

(4) E. J. Corey and E. Block, *J. Org. Chem.*, **34**, 1233 (1969).

(5) L. A. Paquette and R. W. Houser, *J. Amer. Chem. Soc.*, **91**, 3870 (1969).

(6) C. A. Meyers, A. M. Malte, and W. S. Matthews, *J. Amer. Chem. Soc.*, **91**, 7510 (1969).

(7) F. G. Bordwell and J. M. Williams, Jr., *J. Amer. Chem. Soc.*, **90**, 435 (1968).

(8) F. G. Bordwell, *Accounts Chem. Res.*, **3**, 281 (1970).

(9) The evidence indicates that this is the most common mechanism,[10] but that sometimes deuterium exchange and thiirane dioxide formation are competitive:[11] one example is known where thiirane dioxide decomposition is rate limiting.[3,12]

(10) F. G. Bordwell and M. D. Wolfinger, *J. Org. Chem.*, **39**, 2521 (1974).

(11) F. G. Bordwell and J. B. O'Dwyer, *J. Org. Chem.*, **39**, 2519 (1974).

(12) F. G. Bordwell and E. Doomes, *J. Org. Chem.*, **39**, 2526 (1974).

(13) One could also argue that the axial proton **8** is removed preferentially because this allows maximum overlap with the naphthalene ring (stereoelectronic control). The evidence that stereoelectronic control provides much in the way of driving force for deprotonation is also slight, however.[14]

(14) F. G. Bordwell and R. G. Scamehorn, *J. Amer. Chem. Soc.*, **90**, 6749 (1968).

(15) For an example where superficial examination of a Ramberg-Bäcklund reaction suggested a concerted mechanism, but more careful examination revealed a two-stage mechanism; see ref 11.

(16) A driving force has failed to emerge in a 1,2-elimination where one might have been expected; see F. G. Bordwell, D. A. R. Happer, and G. D. Cooper, *Tetrahedron Lett.*, 2759 (1972).

(17) F. G. Bordwell, *Accounts Chem. Res.*, **5**, 374 (1972).

(18) D. L. Tuleen, *J. Org. Chem.*, **32**, 4006 (1967).

(19) R. H. Schlessinger and I. S. Ponticello, *J. Amer. Chem. Soc.*, **89**, 3614 (1967).

Ion Radicals. XXIX. Reaction of Thianthrene Cation Radical Perchlorate with Some Benzene Derivatives[1,2]

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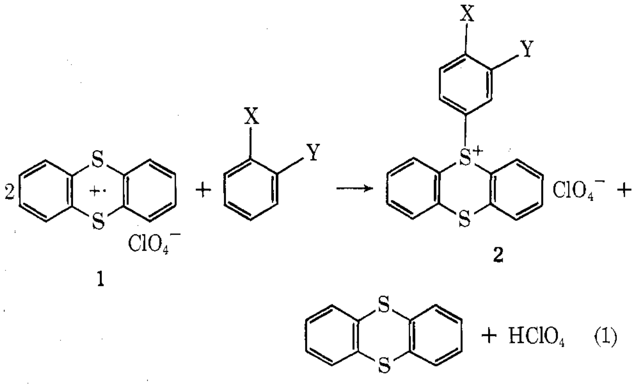
Thianthrene cation radical perchlorate ($Th\cdot^+ClO_4^-$, 1) reacted in acetonitrile solution with acetanilide, phenol, *o*-chlorophenol, *o*-*tert*-butylphenol, and *N,N*-dimethylaniline to give 5-arylthianthrenium perchlorates ($ThAr^-ClO_4^-$) in which bonding is presumed to have occurred at the aryl position para to the functional group. Excellent yields were obtained, except in the case of *N,N*-dimethylaniline, which also underwent oxidative dimerization to *N,N,N′,N′*-tetramethylbenzidine. Thianthrene (Th) was formed along with the formation of the 5-arylthianthrenium perchlorates, according to the anticipated stoichiometry $2Th\cdot^+ + ArH \rightarrow Th + ThAr^+ + H^+$. Reaction of 1 with hydrazobenzene caused both oxidation to azobenzene and rearrangement (by concurrently formed acid) to benzidine monoperchlorate. Kinetics of reaction of 1 with phenol and acetanilide in acetonitrile were followed by use of the Durrum-Gibson stopped-flow spectrophotometer. Kinetics of reaction with anisole were reexamined by the same technique, allowing in each case the use of $[1]_0$ in the range 10^{-6}–10^{-5} *M*. Reactions were second order in $Th\cdot^+$ and inverse order in thianthrene. Difficulties with a mechanism of reaction involving the thianthrene dication, formed in the first-stage disproportionation of the thianthrene cation radical, are discussed. No other suitable mechanism is found.

Results and Discussion

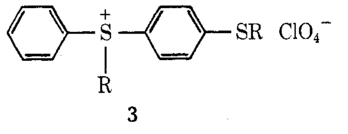
Products. The substitution reactions of organic cation radicals with aromatic substrates are not well explored. Anodic dimerizations, particularly of aromatic amines and phenols, are well known,[5] but we exclude them from the class of substitution reactions we have in mind. An earlier report[6] showed that thianthrene cation radical perchlorate (1) reacted with anisole to form 5-(*p*-anisyl)thianthrenium perchlorate (**2a**) according to the stoichiometry of eq 1. Compounds of this class are not well known. They may be formed in some cases (*e.g.*, X = Y = H) by reaction of thianthrene oxide with the aromatic and aluminum chloride.[6,7] Recently, analogous examples (3) have been made by the anodic dimerization of the sulfides C_6H_5SR (R = phenyl and alkyl).[8] We have now found that reaction of 1 with acetanilide and three phenols occurs very readily in good yield according to eq 1. Reaction with *N,N*-dimethylaniline also occurred, but in poorer yield (21%), being overshadowed by oxidative dimerization to *N,N,N′,N′*-tetramethylbenzidine (TMB) and the latter's oxidation to the corresponding cation radical ($TMB\cdot^+$). Reaction of 1 with hydrazobenzene led not only to the formation of thianthrene and azobenzene but also to benzidine; benzidine rearrangement must without doubt have occurred from the acid liberated in the redox reaction.



1

2

	a	b	c	d	e	f	g
X	OMe	NHAc	OH	OH	OH	NMe_2	NH_2
Y	H	H	H	Cl	*t*-Bu	H	H



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Kinetics and Mechanism. In the earlier report the reaction of 1 with anisole was found to be second order in