A solution of 1.11 g (0.005 mol) of 2 in 50 ml of methylene chloride was cooled to −40°. To this solution was added dropwise over 10 min, with stirring, a solution of 0.985 g (0.0054 mol) of the acid in 20 ml of ether, while the temperature was maintained below −30°. Stirring was continued for 10 min, and after the addition had been completed, the yellow solid which had slowly separated during the addition was collected and identified as diphenylcyclopropenethione S-oxide hydrogen phthalate (3): yield 1.99 g (96%); mp 95–98°; ir (KBr disk) 1068 cm^{-1} (m, C=S=O^2), 1685 (s, C=O), 1695 (s, C=O), 1842 (m) (cyclopropene C=C stretch[10]), and 3420 (br, OH); λ_{max} (CH$_3$CN) 225 mμ (log ε 4.17), 270 (4.21), 295 (sh, 3.86), 310 (sh, 3.77), 333 (3.89), and 478 (3.37).

Anal. Calcd for C$_{23}$H$_{16}$SO$_5$.^{1}/$_2$H$_2$O: C, 66.81; H, 4.14. Found: C, 66.71; H, 4.27.

The yellow salt was ground into fine particles and added in one portion to a stirred solution of 50 ml of 4% sodium hydrogen carbonate at a temperature of >5°. A reaction ensued with the evolution of carbon dioxide, and 5 was deposited as a bright orange solid, yield 0.8 g (67.1%), mp 40° dec. The product was collected by filtration on a previously cooled apparatus, washed with ice water, and stored and dried in a vacuum desiccator containing pellets of sodium hydroxide.

Further purification was found not to be possible owing to the instability of the product. The microanalytical figures correspond to the inclusion of water in the crystals of this hygroscopic material: ir (CHCl$_3$) 1068 and 1129 cm^{-1} (C=S=O^2); nmr (CDCl$_3$) δ 7.0–8.3 (m, aromatic protons); λ_{max} (CH$_2$Cl$_2$) 248 (sh), 270 (sh), 288, 310, 335, and 430 mμ (sh).

Anal. Calcd for C$_{15}$H$_{10}$SO: C, 75.60; H, 4.23; S, 13.43. Found: C, 73.16; H, 4.42; S, 12.28. Calcd: C:S, 5.63. Found: C:S, 5.96.

The S-oxide decomposed violently when the bulk material was allowed to reach room temperature and gave a polymer with the evolution of sulfur dioxide and hydrogen sulfide, which were detected by their action on acid dichromate paper and moist lead acetate paper, respectively.

Controlled Decomposition of Diphenylcyclopropenethione S-Oxide (1).—The S-oxide was freshly prepared exactly as described previously and decomposed by steam distillation. Hydrogen sulfide and sulfur dioxide were recognized as decomposition products by their characteristic odors and by positive reactions with lead acetate and potassium dichromate papers, respectively. When no more steam-volatile material distilled, the steam distillate (250 ml) was extracted with ether and the ether extract was dried (MgSO$_4$). Evaporation of the solvent afforded an off-white solid, yield 0.083 g (9.4%), mp 60°, unambiguously identified as diphenylacetylene by comparison with an authentic sample (mixture melting point and superimposable infrared spectra). The residue consisted of as yet unidentified high molecular weight material.

Registry No.—1, 23516-87-2; 2, 2570-01-6; 3, 23516-89-4; 5, 12408-01-4.

Correlation of the Reactivity of Thiophene Derivatives[1]

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We have undertaken an investigation of the solvolytic reactivity of a variety of heterocyclic systems. In a recent publication from these laboratories, we have shown[3] that the rates of solvolysis of a variety of

substituted furfuryl alcohol derivatives could be smoothly correlated with σ$^+$ constants. An alternative approach is to examine the possibility that the heterocyclic ring system may be assigned an effective σ$^+$ constant, for itself. Two additional recent studies have pursued this line of endeavor. Hill and Gross have studied the rates of solvolysis of a wide variety of heterocyclic analogs of benzyl acetate,[4] and Taylor has recently examined the pyrolysis of 1-aryl-2-phenylethyl acetates.[5]

It is the purpose of this note to present data on the rates of solvolysis of 1-(2-thienyl)ethyl *p*-nitrobenzoate and 1-(3-thienyl)ethyl *p*-nitrobenzoate and on the acid-catalyzed isomerization of *cis*-2-styrylthiophene, and to examine the correlation of these rates with other types of reactions. The relationship between benzyl systems and aromatic electrophilic substitution has been explored by several groups, including studies by Dewar,[6] Fierens,[7] and Streitwieser.[8] These authors have pointed out that the reactivities of benzyl systems and their analogs are useful probes for the ability of the aromatic moiety to stabilize a positive charge. Further, very good correlations are observed with σ$^+$ substituent constants with a wide variety of reactions.

Our new data are summarized in Tables I and II.

Table I
Rate of Solvolysis of Substituted Ethyl *p*-Nitrobenzoates in 80% Ethanol

Compound	Temp, °C	k, sec^{-1}
1-(2-Thienyl)ethyl	25.00	2.27 ± 0.04 × 10^{-6}
p-nitrobenzoate	45.00	2.61 ± 0.05 × 10^{-5}
1-(3-Thienyl)ethyl		
p-nitrobenzoate	75.00	9.7 ± 0.25 × 10^{-6}
1-(*p*-Anisyl)ethyl	45.00	2.30 × 10^{-5}
p-nitrobenzoate^a	75.00	5.02 × 10^{-4}

^{a} From ref 3.

Table II
Rate of Isomerization of *cis*-1-Aryl-2-Phenylethenes in Aqueous Sulfuric Acid

Compound	H$_2$SO$_4$, wt %	H_0	k_{obsd}, sec^{-1}
cis-2-Styrylthiophene	51.6	−3.60	4.0 × 10^{-3}
cis-4-Methoxystilbene^a	51.6	−3.60	4.6 × 10^{-3}

^{a} Interpolated from D. S. Noyce, D. R. Hartter, and F. B. Miles, *J. Amer. Chem. Soc.*, **90**, 4633 (1968).

The solvolysis rate of 1-(2-thienyl)ethyl *p*-nitrobenzoate is very similar to that of 1-(*p*-anisyl)ethyl *p*-nitrobenzoate.[3] The reduced reactivity of 1-(3-thienyl)ethyl *p*-nitrobenzoate is reminiscent of the reduced reactivity of the 3 position in detritiation of thiophene studied by Melander and Olsson[9] and the protodesilylation of thiophene derivatives, studied by Eaborn and his coworkers.[10]

(1) Supported in part by grants from the National Science Foundation (GP-1572 and GP-6133X).

(2) National Institutes of Health Predoctoral Fellow, 1966–1968 (GM-32822).

(3) D. S. Noyce and G. V. Kaiser, *J. Org. Chem.*, **34**, 1008 (1969).

(4) E. A. Hill and M. L. Gross, Abstracts of papers, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, p O-170.

(5) R. Taylor, *J. Chem. Soc.*, B, 1397 (1968).

(6) M. J. S. Dewar and R. J. Sampson, *ibid.*, 2946 (1957).

(7) M. Planchen, P. J. C. Fierens, and R. H. Martin, *Helv. Chim. Acta*, **42**, 517 (1959).

(8) *Cf.* A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, p 370.

(9) K. Halvorson and L. Melander, *Ark. Kemi*, **8**, 29 (1956); B. Ortman and S. Olsson, *ibid.*, **15**, 275 (1960).

(10) C. Eaborn and J. A. Sperry, *J. Chem. Soc.*, 4921 (1961); F. B. Deans and C. Eaborn, *ibid.*, 2299 (1959).

To examine the relationship of this information to that for a variety of other reactions of thiophene derivatives we have collected the relevant data in Table III. If a single substituent constant will sat-

<div style="text-align:center">TABLE III</div>
<div style="text-align:center">RELATIVE REACTIVITY OF THIOPHENE DERIVATIVES</div>

1. Electrophilic Substitution Reactions

Reaction	ρ^a	Log $(k_2/k_{Ph})^b$	Log $(k_3/k_{Ph})^c$	Ref
A. Bromination	−12.1	9.70		*d, e*
B. Chlorination	−10.0	7.11		*d, f*
C. Protodetritiation	−8.5	7.38	4.27	*g, h*
D. Protodeboronation	−5.2	5.93	3.85	*i, j*
E. Iododeboronation	−4.76	3.99	2.84	*k*
	−4.59	3.68		*l*
F. Protodesilylation	−4.78	3.70	2.06	*l*
G. Mercuration	−4.00	4.9		See text
H. Protodemercuration	−2.44	3.23		See text
I. Nitration	−6.5	1.7–2.9		See text

2. Side-Chain Carbonium Ion Reactions

Reaction	ρ^a	Log $(k_2/k_{Ph})^b$	Log $(k_3/k_{Ph})^c$	Ref
J. Solvolysis of 1-arylethyl *p*-nitrobenzoate	−6.0	4.8	3.0	*m*
K. Isomerization of *cis*-1-aryl-2-phenylethene	−3.3	2.55		*m*
L. Rearrangement of arylpropenylcarbinol	−2.9	1.7		*n*
M. Pyrolysis of 1-aryl-2-phenylethyl acetate	−0.66	0.52	0.25	*g*
N. Ir frequency of acetylarene				See text

a ρ for named reaction with substituted benzenes.   *b* Rate for 2-thienyl system relative to benzene.   *c* Rate for 3-thienyl system relative to benzene.   *d* L. W. Stock and F. W. Baker, *J. Amer. Chem. Soc.*, **84**, 1661 (1962).   *e* P. Linda and G. Marino, *Chem. Commun.*, 499 (1967).   *f* G. Marino, *Tetrahedron*, **21**, 843 (1965).   *g* Reference 5.   *h* Reference 9.   *i* K. V. Nahabedian and H. G. Kuivila, *J. Amer. Chem. Soc.*, **83**, 2167 (1961).   *j* R. D. Brown, A. S. Buchanan, and A. A. Humffray, *Aust. J. Chem.*, **18**, 1521 (1965).   *k* R. D. Brown, A. S. Buchanan, and A. A. Humffray, *ibid.*, **18**, 1527 (1965).   *l* Reference 10.   *m* This study.   *n* E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1097 (1947); E. A. Braude and J. S. Fawcett, *ibid.*, 4158 (1952).

isfactorily correlate all of the information, then eq 1 should hold, (where ρ is that for the benzene family)

$$\log k_{thiophene} - \log k_{benzene} = \rho \cdot \sigma^+ \tag{1}$$

for a series of compounds with the substituting group in both the 2 and the 3 position. A plot of the data from Table III is given in Figure 1.

Data for many electrophilic aromatic substitution reactions, including bromination (A), chlorination (B), protodetritiation (C), iododeboronation (E), and protodesilylation (F) are satisfactorily correlated with a single substituent constant for the 2-thienyl moiety. Protodeboronation deviates substantially, and Taylor[5] has suggested that this datum may be in error. Additionally, carbonium ion reactions in the side chain correlate satisfactorily, with the exception of the data for the infrared carbonyl stretching frequency reported by Traylor and Ware[11] which predicts a σ^+ value clearly inconsistent with the rest of the information discussed here.

Data for some other reactions do not correlate at all well, and there appear to be some good reasons for this. Nitration by nitric acid–perchloric acid has

(11) T. G. Traylor and J. C. Ware, *J. Amer. Chem. Soc.*, **89**, 2304 (1967).
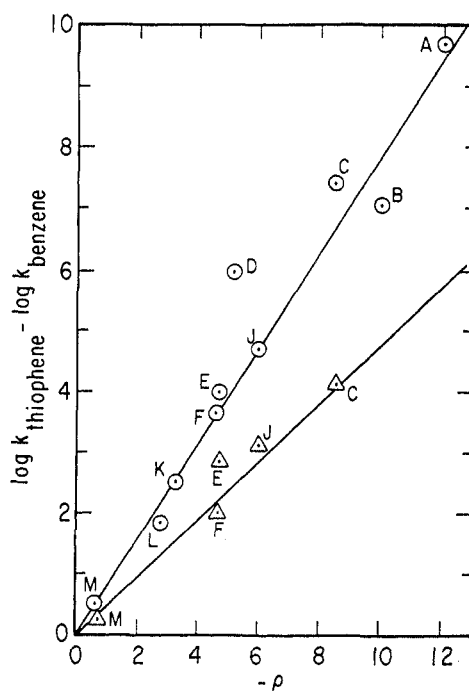

Figure 1.—Correlation of thiophene reactivity with electrophilic reactions in benzene: ⊙, 2-substituted thiophenes; △, 3-substituted thiophenes.

been examined recently by Coombes, Moodie, and Schofield.[12] They have concluded that nitration of thiophene is encounter controlled. Thus the reactivity of thiophene, reported as 50 or 150 times benzene in two solvent systems, is not a true measure of relative reactivity.[12] Similar reservations apply to the reported ratio of 850 for nitration in acetic acid–acetic anhydride.[13]

Taylor[5] has presented the arguments for excluding the demercuration by hydrochloric acid[14] from any correlation, because of the well-known coordination propensities of mercury. Similar considerations are likely to apply to the mercuration by mercuric acetate in acetic acid.[15]

In addition to these tabulated reactions, it is apparent that acetylation, for which there is fragmentary information, would correlate well, as thiophene is reported[16] to have nearly the same reactivity as anisole.

With the above reservations in mind, generally satisfactory correlation of a wide variety of reactions involving electron-deficient intermediates may be achieved with a σ^+ constant for the 2-thienyl group of −0.80, and for the 3-thienyl group of −0.47.

In summary, it might be mentioned that the electronic nature of the thiophene ring shows a dual characteristic. In the original Hammett (σ) sense, the thiophene ring is somewhat electron withdrawing, as evidenced by the fact that thiophene-2-carboxylic acid is a stronger acid than benzoic acid.[17] It thus appears that the difference between σ and σ^+ for the

(12) R. G. Coombes, R. B. Moodie, and K. Schofield, *J. Chem. Soc., B*, 800 (1968); J. G. Hoggett, R. B. Moodie, and K. Schofield, *ibid.*, 1 (1969).

(13) E. Imoto and R. Motoyama, *Kogyu Kagaku Zasshi*, **55**, 305 (1952).

(14) R. D. Brown, A. S. Buchanan, and A. A. Humffray, *Aust. J. Chem.*, **18**, 1513 (1965).

(15) R. Motoyama, S. Nishimura, E. Imoto, Y. Murakami, K. Hari, and J. Ogawa, *Nippon Kagaku Zasshi*, **78** 962 (1957).

(16) P. Linda and G. Marino, *Tetrahedron*, **23**, 1739 (1967).

(17) W. Ostwald, *Z. Phys. Chem.*, **3**, 369 (1889).

thiophene ring is substantially larger than for the simple substituents on the benzene ring.

Experimental Section[18]

Preparation of Materials.—2-Acetylthiophene was reduced with sodium borohydride to afford 1-(2-thienyl)ethanol, which was converted into 1-(2-thienyl)ethyl *p*-nitrobenzoate, mp 64.5–65.8° from 20:1 hexane–ethyl acetate, using *p*-nitrobenzoyl chloride and pyridine.

Anal. Calcd for $C_{13}H_{11}NO_4S$: C, 56.31; H, 4.00; N, 5.05; S, 11.56. Found: C, 56.33; H, 4.24; N, 5.06; S, 11.50.

1-(3-Thienyl)ethanol.—The procedure of Gronowitz[19] for the preparation of 3-thienyllithium was followed. To this reagent at −70°, a solution of acetaldehyde in ether was added. The mixture was allowed to warm to room temperature and was worked up in the usual manner. There was obtained 65% 1-(3-thienyl)ethanol, bp 102–105° (15 mm). The ir spectrum and nmr spectrum were consistent. Conversion into the ester was accomplished in the usual manner to give 1-(3-thienyl)ethyl *p*-nitrobenzoate, colorless needles from hexane–ethyl acetate (20:1), mp 54.0–54.5°.

Anal. Found: C, 56.49; H, 3.99.

cis-2-Styrylthiophene.—Condensation of thiophene-2-carboxaldehyde with phenylacetic acid afforded α-phenyl-β-(2-thienyl)-acrylic acid, mp 190–191.5° (lit.[20] mp 188.5–190°). Decarboxylation with copper and quinoline[21] afforded a mixture from which a small amount of the *trans* isomer crystallized. The remaining oil was separated by glpc over 20% SE-30 on 60–80 mesh Chromosorb, at 180°. The early fraction was *cis*-2-styrylthiophene. The spectral characteristics showed the absence of *trans* olefinic absorption in the ir and an uv spectrum distinct from that of authentic *trans*-2-styrylthiophene.

Anal. Calcd for $C_{12}H_{10}S$: C, 77.38; H, 5.41; S, 17.21. Found: C, 77.06; H, 5.42; S, 17.21.

Kinetic Methods.—The procedures for the solvolysis rate measurements have been described.[3] The rate of the acid-catalyzed isomerization was followed by uv spectrometry, using procedures like those described previously.[22]

Registry No.—1-(2-Thienyl)ethyl *p*-nitrobenzoate, 23516-71-4; 1-(3-thienyl)ethyl *p*-nitrobenzoate, 23516-72-5; *cis*-2-styrylthiophene, 23516-73-6.

(18) Melting points and boiling points are uncorrected. Analyses were performed by the Microanalytical Laboratory of The Department of Chemistry, University of California.

(19) S. Gronowitz, *Ark. Kemi,* **8**, 441 (1955).

(20) G. M. Badger, J. A. Elix, and G. E. Lewis, *Aust. J. Chem.,* **19**, 1243 (1966).

(21) R. E. Buckles and N. G. Wheeler, *Org. Syn.,* **33**, 88 (1953).

(22) D. S. Noyce, D. R. Hartter, and F. B. Miles, *J. Amer. Chem. Soc.,* **90**, 4633 (1968).

### The Reaction of 4-Methylmercaptocyclohexene with Hydrogen Iodide

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It has recently been shown that activation of the double bond of the monoadduct of 1,5-cyclooctadiene and methanesulfenyl chloride toward a second molecule of the sulfenyl chloride practically precludes isolation of the monoadduct even when the diolefin is initially present in tenfold excess.[1] To account for this effect, transannular activation of the double bond by the

(1) W. H. Mueller, *J. Amer. Chem. Soc.,* **91**, 1223 (1969).

methylmercapto group forming a 9-methyl-9-thiabicyclo[4.2.1]nonanesulfonium ion (I) was invoked and subsequently verified by its isolation.

Y = SR or H
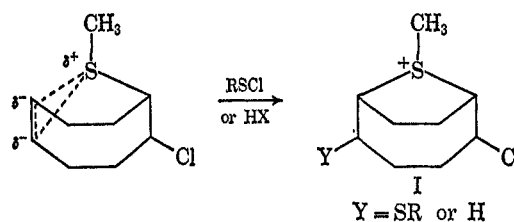
To test the limits of such transannular interactions, the behavior of 1,4-cyclohexadiene under similar conditions was studied. The difference between the two cases was signaled by the observation that, unlike 1,5-cyclooctadiene, the six-membered-ring analog readily affords a monoadduct with methanesulfenyl chloride. A diadduct can subsequently be prepared which is identical with the product of 1,4-cyclohexadiene and 2 mol of the sulfenyl chloride in one step. Contrary to the finding with the eight-membered-ring diene, it could be demonstrated that the remaining double bond of the monoadduct (sans the chlorine atom) is somewhat *deactivated* toward attack of a second methanesulfenyl chloride in competition with cyclohexene.[2] This deactivation may arise from adverse steric effects of the methylmercapto group which may effectively limit the corridors of approach of an incoming group and thereby hinder addition. These ostensibly contradicting observations may result from subtle differences in geometry between the two monoadducts (evident in their molecular models).[3] Also, in contrast with the results of 1,5-cyclooctadiene, the presently formed diadduct is covalent, and, as expected, indications are that it is a mixture of isomeric dimethylmercaptodichlorocyclohexanes.

Participation of the 4-methylmercapto group was, however, clearly evident in the reaction of 4-methylmercaptocyclohexene with hydrogen iodide. In methylene chloride, a white precipitate which proved to be 7-methyl-7-thiabicyclo[2.2.1]heptanesulfonium iodide (II) was isolated. This substance was identical in all respects with the compound reported by Corey and Block which results from addition of methyl iodide to 7-thiabicyclo[2.2.1]heptane.[4]
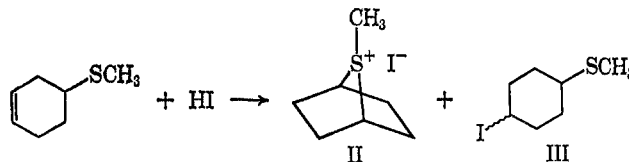
An oil containing predominantly *cis*- and *trans*-4-methylmercaptoiodocyclohexane (III) could be isolated from the mother liquors.[5] The structural assignment

(2) The disappearance under competitive conditions of 4-methylmercaptocyclohexene and cyclohexene in the presence of methanesulfenyl chloride was followed by gc. It was found that the latter is consumed 1.17 times as fast as the former.

(3) One alternative rationale for this deactivation involves a fast and reversible attack of electrophiles upon the sulfur atom. The adverse effect can then be both steric and electronic in origin.

(4) E. J. Corey and E. Block, *J. Org. Chem.,* **31**, 1663 (1966).

(5) Although this mixture showed but a single sharp –SCH₃ signal in the nmr (in several solvents), gc indicated three products of composition 42:7.5:50.5. The minor isomer is believed to be 3-methylmercaptoiodocyclohexane, the major isomers III.