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Thermolysis of Thiophenedicarboxylic Acid Anhydrides as a Route to Five-Membered Hetarynes¹

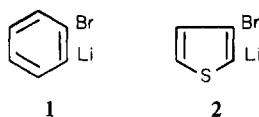
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Contribution from the Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129. Received August 7, 1980

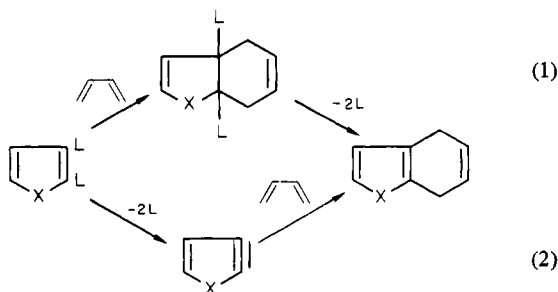
Abstract: Flow vacuum thermolysis (FVT) of the anhydrides of thiophene-2,3- (**5**) and -3,4-dicarboxylic acid (**6**) and of thianaphthene-2,3-dicarboxylic acid (**7**) in the presence of thiophene, 1,3-cyclohexadiene, or benzene gave thianaphthene (**15a**), presumably by aromatization of an intermediate Diels-Alder adduct of the diene traps and the aryne 2,3-didehydrothiophene (**8**). A similar rationale explains the formation of dibenzothiophene from **7** and thiophene, the four monomethylthianaphthenes **22-25** from **5** and cyclopentadiene, 5,6-dimethylthianaphthene (**15f**) from **5** and 2,3-dimethylbutadiene, and a mixture of hydroxythianaphthenes (**15d**) from **5** and furan. The latter reaction also produces a mixture of isomeric cyclopentenothiophenes (**19**) which probably arise by decarbonylation of **15d**. An FVT reaction of **5** with propyne as the trap gave a mixture of allenyl- (**28**) and propynylthiophenes **29** which probably arise by an ene reaction of the trap and the aryne **8**. Decomposition of the anhydrides **5** and **6** in molten anthracene led only to Friedel-Crafts products such as thienylanthracenes **33** and quinones **34** from **5** and **39** and **40** from **6**. The diene reactivity of thiophene **13a** in the gas phase was demonstrated by the formation of naphthalene from its reaction with benzyne generated from the thermolysis of indanetrione and by the formation of indene from **13a** plus cyclopentadiene. Possible, but improbable, interpretations of the FVT results without invoking a five-membered hetaryne intermediate are considered.

Rationale

An analysis² of the abortive attempts^{3,4} to generate five-membered hetarynes suggests that the difficulty arises because, compared to their six-membered analogues, potential five-membered hetaryne precursors are stabilized toward aryne formation and labilized toward nonaryne reactions. A prominent example of the first phenomenon is the relative stability of the *o*-bromolithium compounds **1** and **2** which respectively lose lithium bromide at

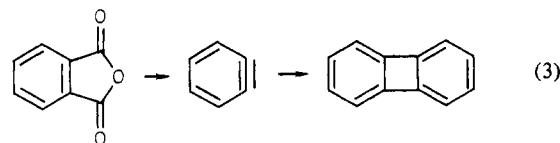


-100 °C to give benzyne⁵ and are stable for prolonged periods at +100 °C.⁶ Among² the nonaryne reactions observed are transhalogenation,⁷ ring opening,⁸ substitution by an addition-elimination process,⁹ and cycloaddition of certain diene traps *prior* to elimination of the ortho-situated leaving groups of the potential aryne precursor (eq 1).⁶ This latter reaction has been particularly

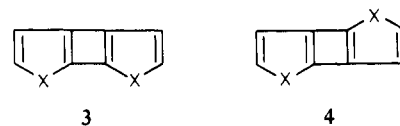


troublesome since the product is the same as that of an elimination-addition process via an aryne intermediate (eq 2) and hence was responsible for many of the false aryne claims in the literature.⁶

Taking these factors into account the best chance for generating a five-membered hetaryne involved selecting a precursor with little tendency to undergo nonaryne reactions and rapidly supplying it with sufficient energy to permit aryne formation to compete with energetically less demanding processes. Flash or flow vacuum thermolysis (FVT)¹⁰ of cyclic anhydrides appeared to meet this need and is well-known as a method for generating six-membered arynes which usually dimerize to biphenylenes in the absence of trapping agents (eq 3).¹¹⁻¹³ Because of the anticipated¹⁴ instability



of the five-membered heterocyclic analogues of biphenylene **3** or **4**, however, their isolation, even under FVT conditions, was



considered problematical, and the use of traps was deemed advisable to provide evidence for aryne intermediacy. The most characteristic traps for this purpose are various conjugated dienes¹⁵ although particularly reactive ones such as cyclopentadienones,^{6,16,17} 1,2,4,5-tetrazines,¹⁸ and isobenzofurans^{17,19}

(1) A preliminary account of a portion of this work has appeared in M. G. Reinecke and J. G. Newsom, *J. Am. Chem. Soc.*, **98**, 3021 (1976).

(2) A comprehensive review of five-membered hetarynes can be found in M. G. Reinecke, "Reactive Intermediates", Vol. 2, R. A. Abramovitch, Ed., Plenum Press, New York, in press.

(3) T. Kauffmann and R. Wirthwein, *Angew. Chem., Int. Ed. Engl.*, **10**, 20 (1971).

(4) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes", Academic Press, New York, 1967, Chapter 6.

(5) H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, **78**, 2217 (1956).

(6) G. Wittig and M. Rings, *Justus Liebigs Ann. Chem.*, **719**, 127 (1968).

(7) H. C. van der Plas, D. A. de Bie, G. Guersten, M. G. Reinecke, and H. W. Adickes, *Recl. Trav. Chim. Pays-Bas*, **93**, 33 (1974).

(8) S. Gronowitz and T. Frejd, *Acta Chem. Scand., Ser. B*, **B30**, 485 (1976).

(9) T. Kauffmann, R. Nurnberg, and K. Udluft, *Chem. Ber.*, **102**, 1177 (1969).

(10) R. F. C. Brown, "Pyrolytic Methods in Organic Chemistry", Academic Press, New York, 1980, Chapter 2.

(11) M. P. Cava, M. J. Mitchell, D. C. DeJongh, and R. Y. Van Fossen, *Tetrahedron Lett.*, 2947 (1966).

(12) E. K. Fields and S. Meyerson, *J. Org. Chem.*, **31**, 3307 (1966).

(13) R. F. C. Brown, D. V. Gardner, J. F. W. McOmie, and R. K. Solly, *Aust. J. Chem.*, **20**, 139 (1967).

(14) T. L. Gilchrist, E. E. Nunn, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1262 (1974); P. J. Garrat, *Pure Appl. Chem.*, **44**, 738 (1975); J. W. Barton and D. J. Lapham, *Tetrahedron Lett.*, 3571 (1979).

(15) Reference 4, p 208ff.

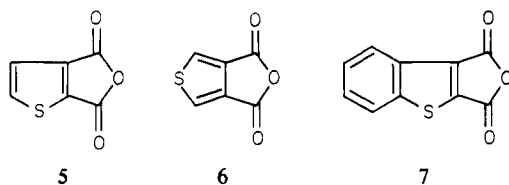
(16) M. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 261 (1965).

Table I. Comparison of Biphenylene Yield on Thermolysis with Relative Intensity (R)^a of Molecular Ion vs. Aryne Ion on Electron Impact

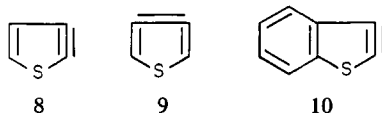
compd	R	% yield of biphenylene
indantrione ^b	3	40
phthalic anhydride ^{b,c}	56 (35)	9 (10–15)
<i>o</i> -sulfolobenzoic anhydride ^b	55	5.5
tetrachlorophthalic anhydride ^c	100	30 ^d
<i>N</i> -methylphthalimide ^b	220	0
tetrabromophthalic anhydride ^c	310	0
5 ^e	48	
6 ^e	44	
7 ^e	104	

^a $R = ([M^+]/[aryne^+]) \times 100$. ^b Reference 13. ^c Reference 11. ^d Octachlorobiphenylene. ^e This work.

which are known to undergo the addition–elimination reaction (eq 1) were avoided. The isomeric thiophene anhydrides **5** and



6 and the benzologue **7** were chosen as the initial precursors to be examined because of their ready availability,^{20,21} because of the prior interest in the corresponding arynes, **8**, **9** and **10**,^{6,22} and

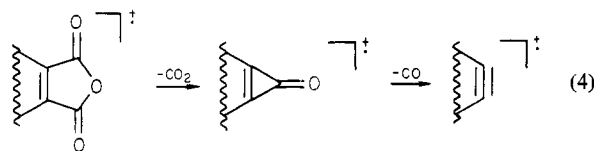


because among the five-membered heterocycles thiophene parallels benzene most closely in its chemistry.²³

Results and Discussion

Mass Spectrometric Studies. While the parallel between thermolytic and mass spectral behavior of a compound is not without exception,²⁴ this relationship has proven useful for predicting the effectiveness of various molecules as aryne precursors.^{11,13} Brown et al. discussed a rough correlation between the relative intensities R of the molecular ion M^+ vs. the putative benzyne ion in the mass spectrum of potential aryne sources and the yield of biphenylene formed on pyrolysis of these compounds presumably by dimerization of the aryne (eq 3). By this criterion the mass spectra of the anhydrides **5**–**7** have R values (Table I) suggesting their suitability as precursors for the arynes **8**–**10**.

In addition to the molecular and aryne ions, the mass spectra display peaks at $M - CO_2$ (base peak) but not at $M - CO$ (Table II), typical of many aromatic cyclic anhydrides^{11,25} and indicating a sequential loss of CO_2 and then CO from the molecular ion as shown in eq 4. Except for the usual thiophene and thianaphthene



- (17) K. Rasheed, *Tetrahedron*, **22**, 2957 (1966).
 (18) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **6**, 16 (1967).
 (19) G. Wittig and E. R. Wilson, *Chem. Ber.*, **98**, 451 (1965); ref 4, p 291.
 (20) M. G. Reinecke, J. G. Newsom, and K. A. Almquist, *Synthesis*, 327 (1980).
 (21) D. H. W. MacDowell and J. C. Wisowaty, *J. Org. Chem.*, **37**, 1712 (1972).
 (22) M. G. Reinecke and H. W. Adickes, *J. Am. Chem. Soc.*, **90**, 511 (1968).
 (23) S. Gronowitz, *Adv. Heterocycl. Chem.*, **1**, 1 (1963).
 (24) R. C. Dougherty, *Top. Curr. Chem.*, **45**, 93 (1974).
 (25) F. W. McLafferty and R. S. Gohlke, *Anal. Chem.*, **31**, 2076 (1959).

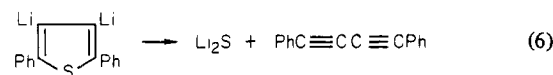
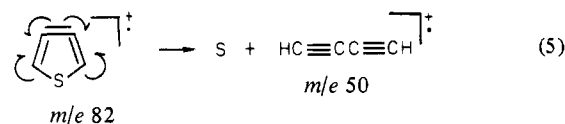
Table II. Mass Spectra of Thiophene Anhydrides

fragment	rel ion intens		
	5	6	7
M	27	23	55
$M - CO_2$	100	100	100
$M - CO_2, -CO$	56	54	53
$M - CO_2, -CO, -S$		40	

Table III. FVT of Thiophene-2,3-dicarboxylic Acid Anhydride (**5**) with Various Trapping Agents

trap	products	% yields
thiophene (13a)	thianaphthene (15a)	59
	sulfur	?
1,3-cyclohexadiene (13b)	thianaphthene (15a)	14
benzene (13c)	thianaphthene (15a)	17
	2- and 3-phenylthiophene	<1
	dithienylbenzene	<1
furan (13d)	cyclopentenothiophenes (19)	8
	hydroxythianaphthenes (15d)	1
cyclopentadiene (13e)	4-methylthianaphthene (22)	6.8
	7-methylthianaphthene (23)	5.8
	5-methylthianaphthene (24)	0.5
	6-methylthianaphthene (25)	0.5
2,3-dimethylbutadiene (13f)	5,6-dimethylthianaphthene (15f)	13
propyne	allenylthiophene (28) and propynylthiophene (29)	9

fragmentations,²⁶ the only other significant peak is one at m/e 50 for the 3,4-anhydride **6**, corresponding to loss of $CO_2 + CO + S$ from the molecular ion. It is tempting to speculate that this species arises from the cation radical of the 3,4-aryne (**9**) as indicated in eq 5, a process which shows some analogy to the ring opening of 2,5-diphenyl-3,4-dilithiothiophene (eq 6),⁶ a typical nonaryne reaction of β -lithiothiophenes.⁸



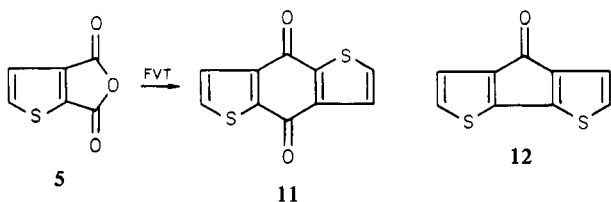
Thermolysis Studies of Thiophene-2,3-dicarboxylic Acid Anhydride (5**).** Although there are no prior reports of the thermolysis of the anhydride **5**, the corresponding diacid has been known for sometime to decompose at 270 °C with charring, gas evolution, and the production of a white sublimate (**5?**).²⁷ A preliminary examination of the thermal stability of the anhydride **5** indicated 73% decomposition after 2.5 h in a sealed tube at 270 °C with the formation of a shiny, brittle, black polymer, carbon dioxide (35%), and a yellow crystalline product (24%) which, by comparison with an authentic sample,²⁸ proved to be identical with the thiophene analogue of anthraquinone (**11**).²¹

When the anhydride **5** was sublimed through an internally heated FVT apparatus¹⁰ with a nitrogen sweep (see Experimental Section) at approximately 500 °C, considerable charring took place and the quinone **11** was once again isolated along with a fluorenone analogue, tentatively identified as **12** from its spectral properties. FVT reactions in the presence of potential aryne traps (Table III) sometimes also gave trace quantities of the quinone **11** and the fluorenone **12** if the rate of sublimation of the anhydride **5** through

(26) Q. N. Porter and J. Baldas, "Mass Spectrometry of Heterocyclic Compounds" Wiley-Interscience, New York, 1971, p 243 ff.

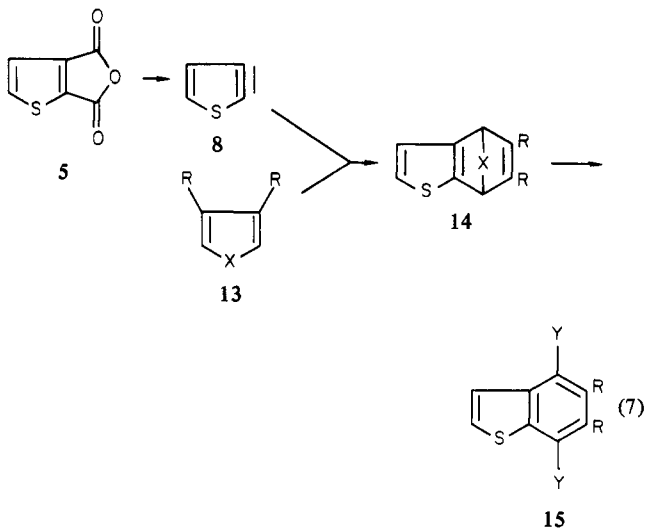
(27) M. Gerlach, *Justus Liebigs Ann. Chem.*, **267**, 145 (1892).

(28) We wish to express our gratitude to Professor MacDowell for supplying this authentic sample.



the reaction zone was too rapid. In all these experiments, however, the extent of charring was greatly diminished with attendant improvement of the material balance.

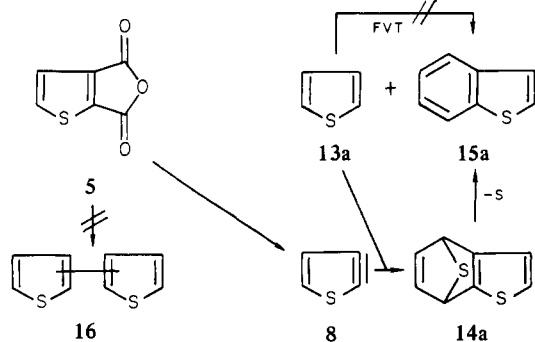
The majority of reactions summarized in Table III can be rationalized according to eq 7 as involving trapping of the in-



	X	R	Y
a	S	H	H
b	CH ₂ CH ₂	H	H
c	CH=CH	H	H
d	O	H	H, OH
e	CH ₂	H	H, CH ₃
f	H, H	CH ₃	H

intermediate arylene **8** in a Diels–Alder reaction with dienes (**13**) to give an unisolated adduct **14** which undergoes secondary transformations, leading to the isolated thianaphthenes (**15**). The basis for this claim as well as the arylene origin of products not covered by the above generalization will be discussed before possible nonaryne interpretations of the results are considered.

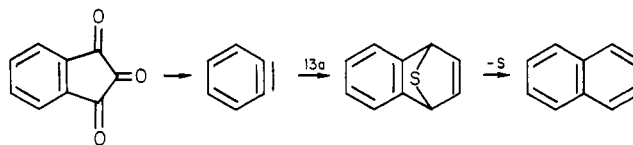
The FVT of **5** with thiophene (**13a**) as a trap produces sulfur as the only other identifiable product besides thianaphthene (**15a**). The absence of bithienyls (**16**) is particularly significant in that



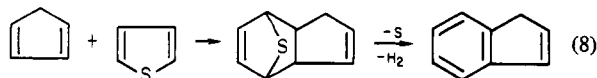
it suggests that thianaphthene (**15a**) does not arise from a secondary pyrolysis of thiophene (**13a**), a reaction that has been well studied and demonstrated under a variety of conditions to give bithienyls (**16**) as major products.^{29,30} This hypothesis was

confirmed for the FVT conditions as well by the almost total lack of reaction when the thiophene (**13a**) alone was passed through the FVT apparatus. No thianaphthene (**15a**) was found and only a trace (<0.2%) of bithienyls (**16**). The formation of thianaphthene (**15a**) must therefore involve the reaction of thiophene (**13a**) with the anhydride (**5**) or some species derived from it as in eq 7.

This sequence is supported by several analogies for each of the two steps of the proposed mechanism. The latter step (**14a** → **15a**) is a thermal extrusion of sulfur³¹ from the type of intermediate (**14a**) which has never been fully characterized but is often invoked in the formation of benzenoid compounds.^{32,33} The first step (**13a** + **8** → **14a**) involves a Diels–Alder reaction between an aryne (**8**) and thiophene (**13a**) acting as a diene. Although thiophene (**13a**) was considered for many years to lack diene reactivity,³⁴ it has now been shown to react with a variety of dieneophiles such as activated alkynes,³³ polyhalobenzenes,³⁵ and, in spite of an early report to the contrary,³⁶ benzyne itself not only in the gas phase³⁰ but in solution as well.³⁷ Two further examples of thiophene (**13a**) diene reactivity were observed under FVT conditions. In the first, benzyne, generated by the decarbonylation of indanetrione,³⁸ reacted with thiophene (**13a**) to give naphthalene in 9% yield, presumably via the cycloaddition–extrusion sequence



The second example was discovered while trying to explain some minor products from the FVT of the anhydride **5** in the presence of cyclopentadiene (vide infra). Whereas the FVT of cyclopentadiene alone forms no indene, this compound is produced in 10% yield from a mixture of cyclopentadiene and thiophene (**13a**) most probably by the cycloaddition–extrusion–dehydrogenation sequence shown in eq 8.



Support for the sequence in eq 7 in the reactions with cyclohexadiene (**13b**) and benzene (**13c**) as traps rests on precedents for the Diels–Alder reactions of these compounds with other arynes^{39,40} and on the known retro-Diels–Alder⁴¹ loss of ethylene⁴² or acetylene,⁴⁰ from adducts analogous to (**14b**) and (**14c**). The benzene reaction also yields trace amounts (<1%) of a dithienylbenzene as well as 2- and 3-phenylthiophene perhaps from formal insertion reactions⁴³ of the arylene **8** into benzene. The possibility that these products are a source of the thianaphthene (**15a**) is considered unlikely on the basis of failure to observe this

(30) E. K. Fields and S. Meyerson, *Chem. Commun.*, 708 (1966).

(31) B. P. Stark and A. J. Duke, "Extrusion Reactions", Pergamon Press, Oxford, 1967, Chapter 6.

(32) T. J. Barton, M. D. Martz, and R. G. Zika, *J. Org. Chem.*, **37**, 552 (1972).

(33) R. Helder and H. Wynberg, *Tetrahedron Lett.*, 605 (1972); H. J. Kuhn and K. Gollnick, *Chem. Ber.*, **106**, 674 (1973); K. Kobayashi and K. Mutai, *Chem. Lett.*, 1149 (1977).

(34) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **5**, 211 (1966).

(35) D. D. Callander, P. L. Coe, J. C. Tatlow, and A. J. Utt, *Tetrahedron*, **25**, 25 (1969); S. Hayashi and N. Ishikawa, *Nippon Kagaku Zasshi*, **91**, 1000 (1970); S. Hayashi and N. Ishikawa, *Yuki Gosei Kagaku Kyokaiishi*, **28**, 533 (1970); *Chem. Abst.*, **73**, 4524c (1970); P. L. Coe, G. M. Pearl, and J. C. Tatlow, *J. Chem. Soc. C*, 604 (1971).

(36) D. D. Callander, P. L. Coe, and J. C. Tatlow, *Chem. Commun.*, 143 (1966).

(37) D. Del Mazza and M. G. Reinecke, *Heterocycles*, **14**, 647 (1980).

(38) R. F. C. Brown and R. K. Solly, *Aust. J. Chem.*, **19**, 1045 (1966).

(39) H. E. Simmons, *J. Am. Chem. Soc.*, **83**, 1657 (1961).

(40) L. Friedman and D. F. Lindow, *J. Am. Chem. Soc.*, **90**, 2329 (1968).

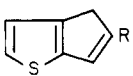
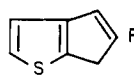
(41) J. L. Ripoll, A. Rouessac, and F. Rouessac, *Tetrahedron*, **34**, 19 (1978).

(42) W. J. Feast, W. K. R. Musgrave, and W. E. Preston, *J. Chem. Soc. Perkin Trans. 1*, 1830 (1972).

(43) Reference 4, p 196.

(29) H. Wynberg and A. Bantjes, *J. Org. Chem.*, **24**, 1421 (1959); C. D. Hurd, R. V. Levett, and A. R. Macon, *J. Am. Chem. Soc.*, **84**, 4515 (1962).

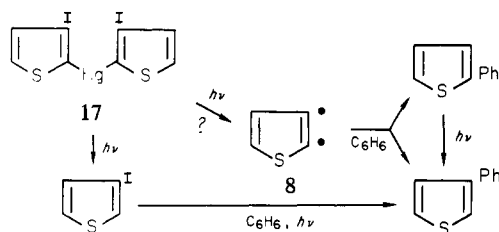
Table IV. Chemical Shifts and Relative Areas of Methylene Hydrogen Resonances of Cyclopenteno[*b*]thiophenes^a

R	δ CH ₂ (relative area)	
		
H ^b	3.34 (60)	3.48 (40)
CH ₃ ^c	2.98 (76)	3.08 (24)
NO ₂ ^d	3.84 (70)	3.97 (30)

^a DCCl₃ solvent. ^b This work. ^c Reference 51. ^d Reference 50.

transformation either with the isomer under plasmolysis conditions⁴⁴ or with the 2-isomer under FVT conditions.

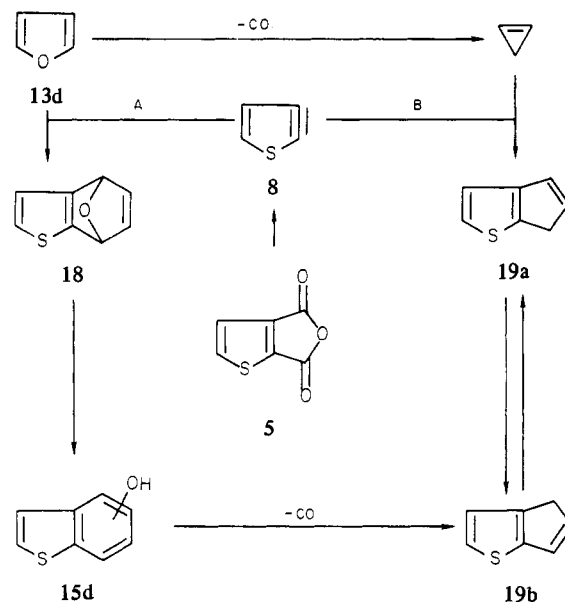
On the basis of the isolation of 3-phenylthiophene from the photolysis of the mercury compound **17** in benzene, Wittig also



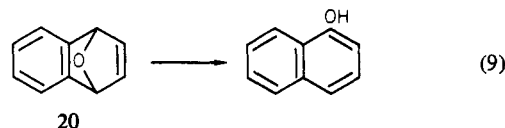
considered the possibility that 2,3-didehydrothiophene (**8**) had been generated and trapped in a formal insertion reaction with the solvent.⁶ The absence of the 2-phenyl isomer was explained by its known photoisomerization to the 3-isomer.⁴⁵ An alternative nonaryne mechanism was also suggested, however, on the basis of the isolation of 3-iodothiophene from the photolysis of **17** and its further transformation to 3-phenylthiophene under these reaction conditions.⁶ In view of the FVT results in the presence of benzene described above, the absence of any thianaphthene (**15a**) in the photolysis of **17** argues against the intermediacy of the aryne **8** in this process. Because of the difference in reaction conditions it is, of course, conceivable, but unlikely,⁴⁶ that the arynes **8** from the FVT and photolytic processes are not identical.

Instead of the expected⁴⁷ adduct **18**, the FVT of the anhydride **5** in the presence of furan (**13d**) gave an unstable oil whose spectral characteristics are consistent with a mixture of the cyclopenteno[*b*]thiophenes (**19**). In particular, the mass spectrum displays a prominent M - H peak typical of indene,⁴⁸ and the NMR shows aromatic, olefinic, and aliphatic hydrogen peaks at chemical shifts similar to those of indene.⁴⁹ The methylene resonance consists of two peaks, however, in a ratio of 2:3, indicating a mixture of the two isomers. By analogy to the 5-nitro-⁵⁰ and 5-methylcyclopenta[*b*]thiophenes,⁵¹ both the relative chemical shifts and, with the assumption of an equilibrium mixture, the peak areas (Table IV) suggest that the 4*H*-isomer **19a** is the major component. The value of the coupling constant for the methylene hydrogens ($J = 2.0$ Hz)⁴⁹⁻⁵¹ and the multiplicity of the peak (a double doublet)⁴⁹ further support the assigned structure **19**. The instability of such compounds has also been observed previously.^{51,52}

The origin of the indene analogues (**19**) can be rationalized in two ways involving the intermediacy of the aryne **8**. In the first mechanism (path A) the aryne **8** is trapped by furan in a typical

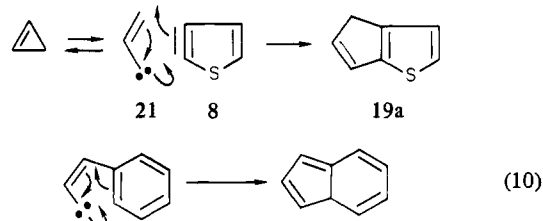


Diels-Alder reaction⁴⁷ to give the adduct **18** which upon thermolysis of the oxygen bridge and decarbonylation of the resulting hydroxythianaphthene (**15d**) leads to **19**. Precedents exist for the thermal decarbonylation of naphthols to indenenes⁵³ and for the acid-catalyzed ring opening of the benzene-furan adduct (**20**) to α -naphthol (eq 9).⁵⁴ Thermal ring opening of the oxygen bridge



of **20** has been postulated, but not demonstrated, to account for the formation of α -naphthol during the gas-phase pyrolysis of several benzyne precursors.⁵⁵

In the second mechanism (path B) the aryne **8** is trapped by cyclopropene, long claimed to be a product of the thermolysis of furan.⁵⁶ Presumably, an electrocyclic reaction with the "vinyl carbene" (**21**),⁵⁷ known to be in equilibrium with cyclopropenes,⁵⁸ leads directly to the product **19**. Intramolecular precedents for this type of thermal cyclization are known (eq 10).⁵⁹



Although neither mechanism can be excluded at this time, path A is supported by the conversion of the adduct **20** to α -naphthol (eq 9) in 45% yield under FVT conditions, thereby demonstrating the feasibility of the step **18** \rightarrow **15d**. Furthermore, the polar fraction of the product mixture from the FVT of the anhydride **5** in furan (**13d**) contained phenolic material (solubility and in-

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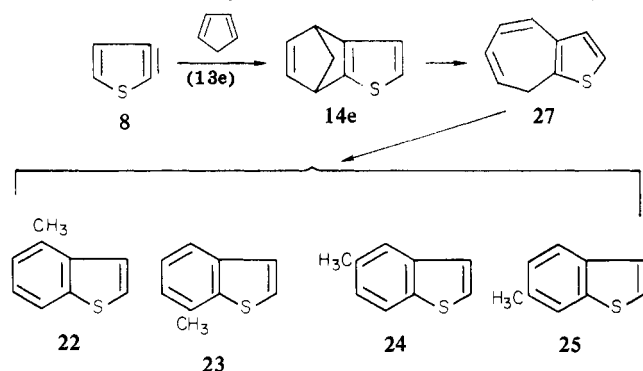
(57) J. H. Davis, W. A. Goddard, III, and R. G. Bergman, *J. Am. Chem. Soc.*, **99**, 2427 (1977); J. A. Pincock and R. J. Boyd, *Can. J. Chem.*, **55**, 2482 (1977).

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(59) M. A. Battiste, B. Halton, and R. H. Grubbs, *Chem. Commun.*, 907 (1967); M. I. Komendantov, R. R. Bekmukhametov, and I. N. Domnin, *Tetrahedron*, **34**, 2743 (1978).

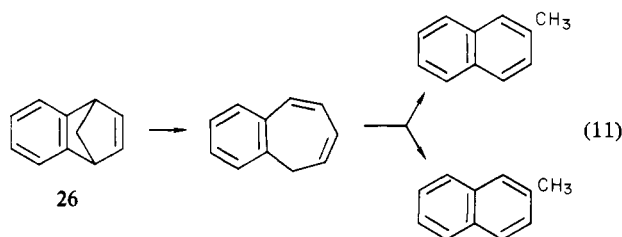
frared) whose mass spectrum was consistent with the hydroxythianaphthenes (**15d**) (probably a mixture of the 4- and 7-isomers).

In the presence of freshly-distilled cyclopentadiene (**13e**), the FVT of the anhydride **5** gives no observable polymer formation and eight VPC-detectable products. Three of these, naphthalene, the cyclopentadiene dimer, and a methylindene, are also found in the FVT of the cyclopentadiene alone. Indene itself probably arises by the reaction of the trap with thiophene as previously discussed (eq 8). The thiophene for this reaction is most likely formed by hydrogen transfer to the aryne **8**, either directly or indirectly, from intermediates leading to the more unsaturated products present, the indenenes and naphthalene. The remaining four products were identified from their spectral properties and from comparisons with independently synthesized samples⁶⁰ as the monomethylthianaphthenes (**22–25**). The 4-isomer (**22**) and



the 7-isomer (**23**) were the major ones formed (Table III). The stabilities of the 5-isomer (**24**) and the 7-isomer (**23**) under the FVT-conditions were demonstrated, thereby indicating that no isomerization of the products occurred.

Once again the simplest explanation for the nature and distribution of the products (**22–25**) involves secondary transformations of the initially formed Diels-Alder adduct **14e** of the aryne **8** and cyclopentadiene (**13e**). As with the analogous benzyne adduct **26** (eq 11),⁶¹ this probably proceeds via a cycloheptatriene

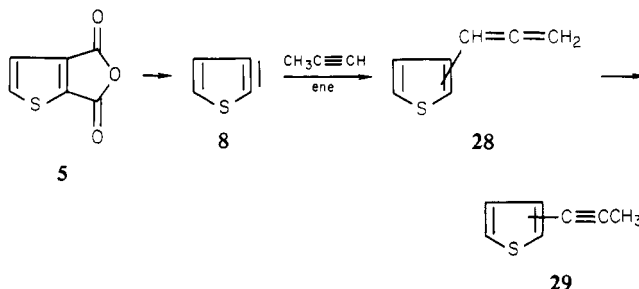


such as **27** which rearranges to give the methylthianaphthenes **22–25**. This mechanism is supported by the qualitative duplication of the chemistry depicted in eq 11 under our FVT conditions and by the observed ratios of the α (**22**, **23**, and 1-methylthianaphthalene) to the β methyl products (**24**, **25** and 2-methylthianaphthalene). In both the naphthalene⁶¹ and the thianaphthalene series, the α -isomers substantially predominate consistent with similar mechanisms.

The major product from the FVT reaction with 2,3-dimethylbutadiene (**13f**) as a trap was identified as 5,6-dimethylthianaphthalene (**15f**) from its spectral and analytical properties and by comparison with an authentic sample prepared from 3,4-dimethylthiophenol by the method of Tilak.⁶⁰ Consistent with the reaction sequence in eq 7, this product is formed by dehydrogenation of the initially formed Diels-Alder adduct **14f** of the aryne **8** and the butadiene (**13f**). Aromatization of analogous dihydronaphthalene derivatives proceeds rapidly in the presence of noble or transition metals,⁶² sulfur,⁶³ quinones,⁶⁴ or possibly

even thermal disproportionation.⁶⁵ Since each of these catalysts and/or hydrogen acceptors are, or may, be present during the FVT of the anhydride **5** (a bare Nichrome wire is used as the internal heat source, elemental sulfur is not an unlikely product from the thermolysis of thiophenes,^{29,30} and traces of the quinone **11** are often produced), the proposed dehydrogenation of **14f** to **15f** is quite reasonable.

In addition to Diels-Alder reactions (eq 7), arynes and dienes can undergo the ene reaction.⁶⁶ Although no ene products were observed in any of the other examples in Table III, the FVT of the anhydride **5** in the presence of propyne did give evidence for the formation of the expected ene product with the aryne **8**, i.e., the allene **28**. The product of this reaction was an unstable,



nonpolar liquid which easily decomposed to an intractable tar and, according to GC analysis, consisted of at least two unresolvable components. The mass spectrum of this mixture displayed a molecular ion at 122 and the appropriate $M + 2$ intensity for one sulfur atom. The infrared spectrum had characteristic absorptions for both an allene (1955 and 855 cm^{-1})⁶⁷ and an alkyne (2240 cm^{-1} , weak).⁶⁸ The NMR spectrum confirmed the presence of both compound types as well as positional isomers of each. In addition to the aromatic absorption at δ 6.6–7.3, typical⁶⁹ allene proton peaks were observed at δ 6.1 and 5.1. These peaks (relative area 1:2) were mutually coupled with the expected⁷⁰ $J = 6\text{ Hz}$ and appeared as a pair of partially overlapping triplets and a doublet, respectively. On the basis of the relative area of the allene and the aromatic protons, only about half of the mixture consists of the allenylthiophenes **28**. The other half appears to be a mixture of the propynylthiophenes **29**, presumably formed by an allene-acetylene rearrangement.⁷¹ This is substantiated by the presence of two closely spaced singlets in the NMR at δ 1.95, similar to other methyl groups attached to an acetylenic carbon.⁷²

Because of its Diels-Alder reactivity with arynes,⁷³ anthracene was considered as a potential trap for the aryne **8**. Although the expected adduct **30** is not known, related heterotriptycenes such as **31**⁷⁴ and **32**⁷⁵ have been made and are relatively stable com-



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(66) G. Wittig and H. Durr, *Justus Liebigs Ann. Chem.*, **672**, 55 (1964); P. Crews and J. Beard, *J. Org. Chem.*, **38**, 522 (1973); J. A. Berson, P. B. Dervan, R. Malherbe, and J. A. Jackson, *J. Am. Chem. Soc.*, **98**, 5937 (1976).

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(72) J. Dale in ref 71, Chapter I, p 45.

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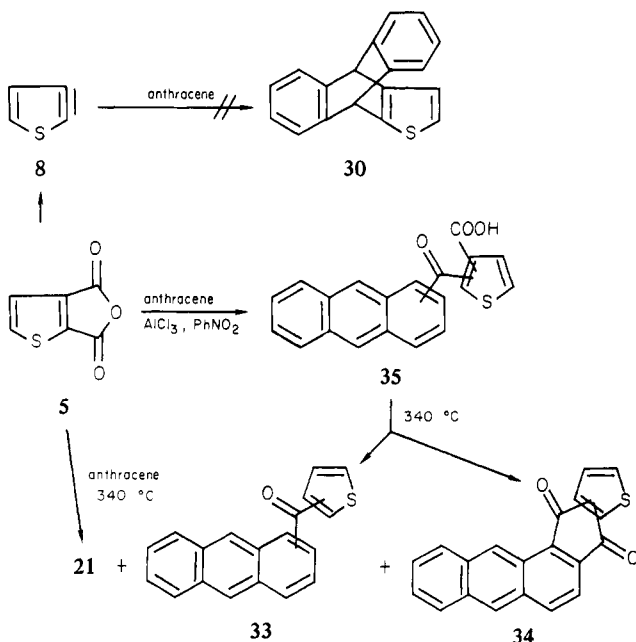
(60) A. V. Sunthakar and B. D. Tilak, *Proc. Indian Acad. Sci., Sect. A*, **32A**, 396 (1950); J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, 981 (1964).

(61) S. J. Cristol and R. Caple, *J. Org. Chem.*, **33**, 585 (1966).

(62) E. A. Braude, R. P. Linstead, and P. W. D. Mitchell, *J. Chem. Soc.*, 3578 (1954).

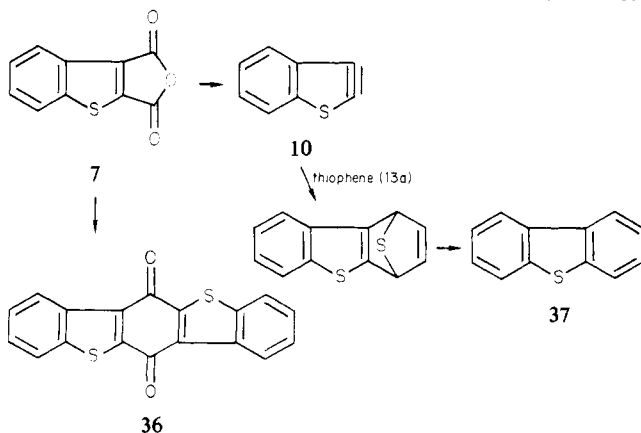
(63) R. Weiss, "Collective Volume of Organic Synthesis", Vol. 3, Wiley, New York, 1955, p 729.

pounds. Unfortunately the relatively low volatility of anthracene precluded its use in our FVT apparatus (several attempts were made) so the anhydride **5** was decomposed in a melt of anthracene. Three products were isolated by preparative TLC, none of which corresponded to the aryne adduct **30**. In addition to the ubiquitous quinone **11**, a ketone **33** and another quinone **34** were obtained



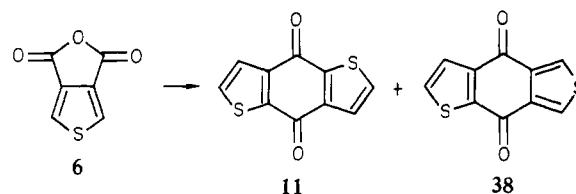
in low yield. The ketone could not be obtained pure, but its infrared (1670 cm^{-1}) and mass spectra [$M^+ = 288$, $M - \text{CO}$, $M - \text{C}_{14}\text{H}_9$ (base peak)] were consistent with one of the thenoylanthracenes **33**. The partial structure (**34**) for the quinone is supported by elemental analysis, infrared (1640 cm^{-1}), and mass spectra ($M^+ = 314$, $M - \text{H}$, $M - \text{CO}$, $M - 2\text{CO}$). The angular arrangement of the rings, rather than a linear one, was chosen because of the high intensity of the $M - \text{H}$ peak as is typical of such quinones.⁷⁶ Further confirmation of the structures of these compounds, as well as an indication of their probable source, came from the pyrolysis of the ketoacid **35**, obtained by a standard aluminum chloride-catalyzed Friedel-Crafts reaction between anthracene and the anhydride **5** in nitrobenzene. At 340°C for 90 s, the two products **33** and **34** were formed, indicating their original mode of formation involves uncatalyzed Friedel-Crafts reactions and decarboxylation.

Thermolysis Studies on Thianaphthene-2,3-dicarboxylic Acid Anhydride (7). Only two experiments were carried out with this anhydride. A sealed-tube pyrolysis of **7** gave a dimeric quinone **36** in 80% yield. The transoid structure was chosen by analogy



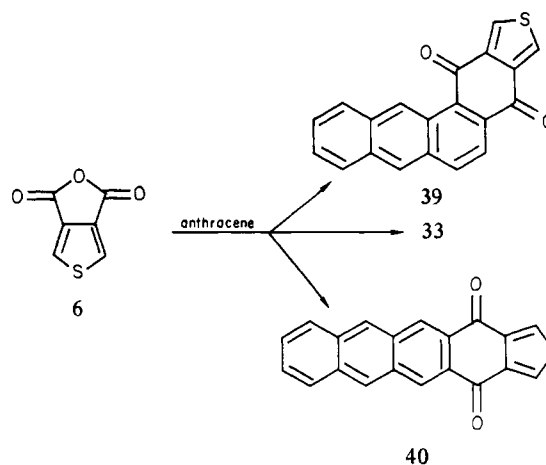
to the thiophenequinone **11**. In an FVT experiment with thiophene as the trap, dibenzothiophene **37** was obtained in 35% yield, presumably by loss of sulfur from the Diels-Alder adduct of thiophene and 2,3-didehydrothianaphthene (**10**). This same aryne recently has been suggested from another precursor,⁷⁵ but alternative explanations are still under consideration.

Thermolysis Studies of Thiophene-3,4-dicarboxylic Acid Anhydride (6). Although the mass spectral results discussed earlier (Tables I and II) predict that **6** ought to be as good an aryne source as its isomer **5**, this compound was stable to FVT even up to 700°C , the limit of our apparatus. This surprising result has been noted by others⁷⁷ and is also observed in the sealed-tube pyrolysis of the anhydride **6** in that more severe conditions (470°C , 30 s) are needed than for the isomer **5**. Only two products were isolated in very low yield (<1%), once again the quinone **11** and its known^{21,28} isomer **38** probably formed by an uncatalyzed, Frie-



del-Crafts self-condensation of the anhydride **6** with concurrent or subsequent decarboxylation. Although rare, analogous self-condensations of aromatic acids and their derivatives are known⁷⁶ and may also play a role in the formation of the quinone **11** and **36** from the anhydrides **5** and **7**.

Heating the anhydride **6** in an anthracene melt gave products analogous to those found from the isomeric **5**. In addition to a trace of an impure compound whose spectral properties indicated a thenoylanthracene identical or isomeric with **33**, two crystalline quinones isomeric with **34** were isolated in about 2% yield each. One displayed a very prominent $M - \text{H}$ peak in its mass spectrum⁷⁶ as noted for **34** and was therefore assigned the angular structure **39** while the other isomer must therefore be **40**. Clearly only typical Friedel-Crafts chemistry and no arynes appear to be involved.



Possible Nonaryne Explanations. Although no actual Diels-Alder adducts of dienes and the five-membered hetarynes **8** and **10** were isolated in the above experiments, a consistent and rational explanation of the origin of the major products from the FVT reactions as discussed demands their presence. Therefore, if no arynes were involved in these reactions, the Diels-Alder adducts (**14**) would have to arise by some other mechanism. As discussed in the Rationale section, an addition-elimination process (eq 1) has the greatest historical precedence.⁶ The variety of dienes used

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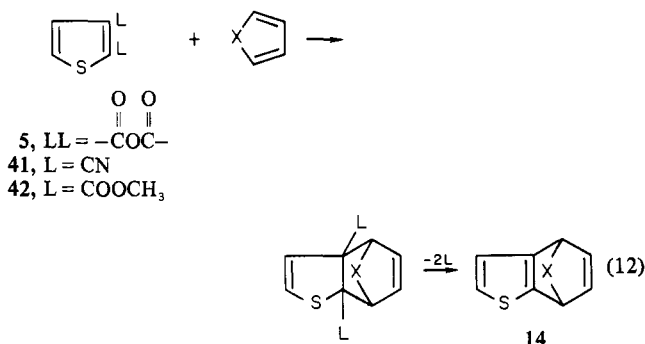
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(76) D. R. Buckle and E. S. Waight, *Org. Mass Spectrom.*, **1**, 273 (1968).

(77) B. E. Ayers, S. W. Longworth, and J. F. W. McOmie, *Tetrahedron*, **31**, 1755 (1975).

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for the present study and their moderate reactivity compared to the "ambiguous" dienes cited earlier^{6,16-19} strongly disfavor this possibility unless the maleic anhydride moiety of **5** itself displays unprecedented dieneophilic reactivity (eq 12). If this were the



case, 2,3-dicyano- (**41**) and 2,3-dicarbomethoxythiophene (**42**) should reasonably display similar properties, and they do not. Both are recovered unchanged from FVT experiments with thiophene as a trap. Also arguing against *any* reaction between the anhydride **5** itself and electron-rich aromatic traps such as furan and thiophene under FVT conditions is the absence of Friedel-Crafts products such as are formed from the reactions in molten anthracene. Finally, in contrast to those dienes which react by an addition-elimination mechanism (eq 1),⁶ there is no evidence that the presence of the traps in any way induces the decomposition of the anhydride **5** since even in their absence extensive reaction occurs. Therefore, although based partially on negative evidence, only a fortuitous combination of coincidences would allow the origin of the Diels-Alder adducts **14** to involve a direct reaction between the traps and the anhydride **5** itself as in eq 12.

Although the aryne interpretation therefore remains the most reasonable, the possibility that the adducts (**14**) as well as the ene product **28** arise from a reaction between the traps and some decomposition intermediate or product of the anhydride **5** other than the aryne **8** must also be considered. This topic will be the subject of a forthcoming paper.⁷⁹

Experimental Section

Infrared spectra were recorded on Perkin-Elmer 237, Beckman IR-10, or Beckman 33 instruments, were calibrated with the use of polystyrene film, and are expressed in cm^{-1} . Liquids were measured as thin films between sodium chloride plates and solids as 1% dispersions in a KBr disk. Mass spectra (MS) were obtained on a Finnigan 1015 S/L instrument at 70 eV and are reported as m/e (relative intensity). All peaks greater than and some less than ca. 10% of the base peak are reported. NMR spectra were obtained on a Varian A-60A instrument in deuteriochloroform unless otherwise noted. A JEOL JNM-MH-100 instrument was used for 100 MHz spectra. Chemical shifts relative to internal tetramethylsilane are expressed in the δ scale, and apparent first-order coupling constants (" J ") are in Hz.

Gas chromatographic analyses were performed on an Aerograph Autoprep A-700 instrument.

Ultraviolet spectra were obtained in 95% ethanol on a Cary 15 spectrophotometer with the use of matched quartz cells and are reported as λ_{max} in nm (log ϵ).

Melting points were obtained on a Thomas-Hoover apparatus and are uncorrected.

Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

2,3-Thiophenedicarboxylic Anhydride (5). A solution of 7.9 g (45 mmol) of 2,3-thiophenedicarboxylic acid²⁰ in 40 mL of freshly distilled acetic anhydride was heated under reflux for 2 h; the excess acetic anhydride was removed with a rotary evaporator, and the residue was recrystallized from benzene-heptane (3:2), yielding 7.08 g (99.7%) of 2,3-thiophenedicarboxylic anhydride (**5**) as light brown plates. Sublimation yielded snow white crystals: mp 138–40 °C (lit.⁸⁰ 140 °C); NMR 7.40 (d, 2 H), 7.82 (d, 2 H, $J = 5.5$); IR 3100, 1830, 1750, 1520, 1445, 1370, 1270, 1237, 1090, 1078, 840, 700; MS 156 (7), 155 (9), 154 (27),

110 (100), 84 (53), 82 (56), 45 (30), 38 (19), 37 (19).

3,4-Thiophenedicarboxylic Anhydride (6). Following the same procedure as above, 26.9 g (0.156 mol) of 3,4-thiophenedicarboxylic acid²¹ and 75 mL of acetic anhydride gave 20.4 g (85%) of snow white 3,4-thiophenedicarboxylic anhydride (**6**): mp 144–146 °C (lit.⁸⁰ 145–146 °C); IR 3110, 1850, 1775, 1510, 1215; MS 154 (23), 110 (100), 82 (54), 81 (29), 50 (40), 45 (35), 36 (36), 37 (26).

2,3-Thianaphthenedicarboxylic Anhydride (7). In the same way as above, 3.01 g (35 mmol) of 2,3-thianaphthenedicarboxylic acid²⁰ and 16 mL of acetic anhydride after being heated under reflux for 15 h gave, without sublimation, 2.54 g (89%) of 2,3-thianaphthenedicarboxylic anhydride (**7**): mp 169.5–170 °C (lit.⁸⁰ 171 °C); MS 204 (55), 160 (100), 132 (53), 92 (21).

Pyrolysis of 2,3-Thiophenedicarboxylic Anhydride (5). An evacuated, thick-walled, Pyrex ampule containing 205 mg (1.33 mmol) of the anhydride **5** was heated in a eutectic salt bath at 270 °C for 2.5 h. The ampule was cooled and cracked open in a closed system (balloon), and the gases were collected with a gas-tight syringe and dissolved in standardized sodium hydroxide. Titration with standard acid to a phenolphthalein end point indicated⁸¹ the presence of 15.1 mg (35% yield on the basis of reacted anhydride) of carbon dioxide. The methylene chloride insoluble portion of the ampule contents consisted of 29.9 mg of a shiny, black, brittle polymer. The methylene chloride solution was vigorously stirred for 1 h with 5 mL of 3 N sodium hydroxide, separated and washed with 2 \times 10 mL portions of water. The combined aqueous layers were acidified with 6 N hydrochloric acid to give 61.8 mg of 2,3-thiophenedicarboxylic acid equivalent to 55.3 mg (27% of unreacted anhydride) of **5**. The methylene chloride layer was dried (MgSO_4) and evaporated and the residue sublimed to give 25.8 mg (24%) of a yellow solid which after recrystallization from acetic acid gave 20 mg of the quinone **11**: mp 258–259 °C (lit.²¹ 258–260 °C); NMR (CDCl_3 -Eu(fod)₃) 7.75 (d, 2 H), 7.95 (d, 2 H, $J = 5$); MS 222 (7), 221 (13), 220 (100), 192 (56), 164 (43), 142 (8), 120 (22), 119 (8), 111 (10), 110 (13), 93 (10), 83 (12), 81 (33), 80 (20), 68 (14), 45 (27), 39 (12). The IR was identical with that of an authentic sample provided by MacDowell.^{21,28}

FVT Apparatus. FVT reactions were carried out in the reactor shown in Figure 1 and are described as follows.

A is a 250-mL two-neck round-bottom flask which serves as the reservoir for either the trapping agent or the carrier gas. If the trapping agent was a liquid, it was heated to reflux in this reservoir and fed into the system through capillary B. If the trapping agent was a gas, the reflux condenser was replaced with a rubber septum pierced by two 26-gauge syringe needles. One needle was connected via rubber tubing ($1/4$ in.) to the gas cylinder and the other served as an outlet. A slight positive pressure of the gas was maintained throughout the course of the reaction. Attached to A by means of a rubber adapter is B, a thick-walled Pyrex capillary (o.d. 1 mm, i.d. 0.2 mm) which has been drawn to give an exceedingly small opening through which the trapping agent enters the system as a gas. A separate capillary was made for each trapping agent such that the internal pressure of the system did not exceed 5 mmHg during the course of a reaction. C is a 2-ft section of vacuum tubing (o.d. 1 in., i.d. $1/4$ in.) which previously was leached of soluble organic material by passing the vapors of hot thiophene through its interior for 2 h. The exterior of this tube was coated with collodion. For high-boiling trapping agents, C was wrapped with heating tape to prevent condensation.

Sublimation chamber D consists of a 10-cm Pyrex tube (i.d. 3.5 cm) wrapped with heating tape and having a standard taper 24/40 female joint on one end and an 8-cm piece of $1/4$ -in. Pyrex tubing on the other.

The actual hot zone E consists of a 9-cm Pyrex tube (i.d. 3.5 cm) with both male and female 24/40 standard taper joints, and a heating element consisting of a 15-cm piece of 22-gauge Nichrome wire coiled to an approximate length of 3.5 cm. This wire is attached by brass sleeves to two tungsten leads which pierce the walls of the Pyrex chamber through glass-to-metal seals. E is connected to a vacuum pump through two dry ice-acetone cooled traps.

The hot-zone temperature was calibrated by placing a high-temperature thermometer with its bulb inside, but not touching, the Nichrome coil and evacuating the system. Transformer settings for various temperatures were noted and assumed to correspond to the hot-zone temperature during an FVT experiment. The temperature of the sublimation chamber was estimated from that of a thermometer wrapped in the heating tape at different transformer settings.

General Procedure for FVT Reactions. The compound to be thermolyzed, if it was a solid, was finely powdered and dispersed as evenly as possible throughout the length of the sublimation chamber to a depth of

(79) M. G. Reinecke, L. J. Chen, and J. G. Newsom, to be submitted for publication.

(80) R. P. Linstead, E. G. Noble, and J. M. Wright, *J. Chem. Soc.*, 911 (1937).

(81) H. H. Willard, N. H. Furman, and E. K. Bacon, "A Short Course in Quantitative Analysis", Van Nostrand Co., New York, 1957, p 82.

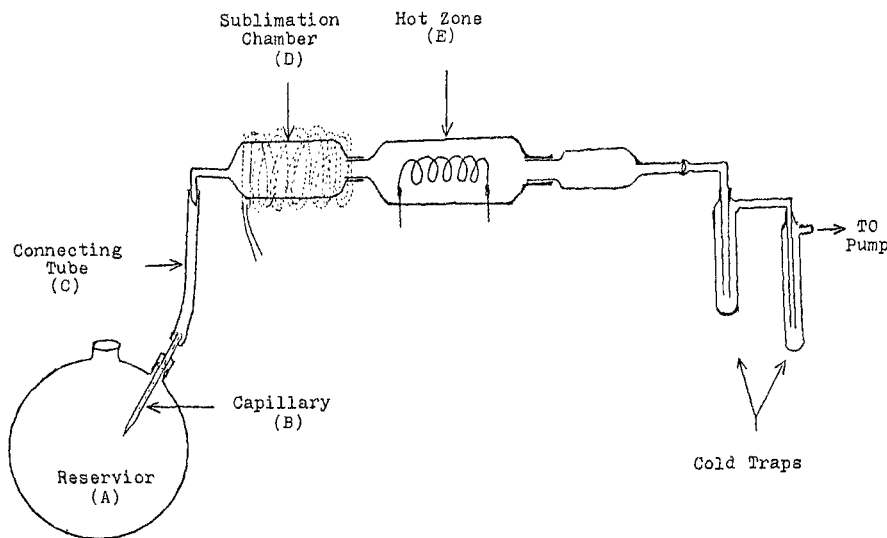


Figure 1. Flow vacuum thermolysis apparatus.

several millimeters. The apparatus was then assembled as shown in the figure and the sublimation chamber wrapped with heating tape. In those experiments when nitrogen or a gaseous trapping agent was employed, the reservoir was purged with the appropriate gas and the system evacuated to a pressure allowed by the diameter of the capillary B (1–5 mmHg). After 5 min, so as to allow the system to be swept free of air, the heating tape around the sublimation chamber was heated to approximately 80 °C and the hot zone heated to 500 °C.

Before a liquid trapping agent reached its reflux temperature, the connecting tube C was heated to 50–80 °C and the sublimation chamber D and the hot zone E were gently warmed so as to prevent condensation of the trap therein. The system was then evacuated, and D and E were brought up to reaction temperature.

General Workup Procedure. After sublimation of the starting material was complete (~1 h), the apparatus was disassembled, and the contents of the cold traps and any material which condensed in the transfer lines beyond hot zone E were washed out with methylene chloride. This solution was stirred for 2 h with 10–15 mL of 3% sodium hydroxide to remove unreacted anhydride as its diacid. The organic phase then was usually dried (MgSO_4), chromatographed through 10–15 g of silica in a 30 cm \times 1.8 cm column, and then analyzed or separated by GC or TLC.

FVT of 2,3-Thiophenedicarboxylic Anhydride (5) with a Nitrogen Sweep. Sublimation of 258 mg (1.7 mmol) of anhydride 5 through the hot zone with nitrogen as a carrier gas led to considerable charring. Workup yielded 43.6 mg of diacid, equivalent to 39 mg (15.1%) of unreacted anhydride 5 and 33 mg of chromatographed residue. Preparative TLC (SiO_2 , CH_2Cl_2 : petroleum ether 1:1) gave four colored bands, two of which were present in sufficient quantity to allow identification. A yellow solid, $R_f = 0.38$ (10.5 mg, 2.8%), was identified as the previously isolated quinone 11 by IR and MS comparison. The second compound, a noncrystalline reddish solid, $R_f = 0.45$, was tentatively identified as the dithiafluorenone 12 (4 mg, 1.2%): IR 3100, 1695 (lit.⁸² 1696), 1600, 1450, 1380, 1230, 1080; MS 194 (7), 193 (13), 192 (100), 164 (46), 159 (18), 149 (22), 120 (20), 111 (52), 82 (30), 76 (18), 45 (20), 39 (12), 38 (12); UV 320 sh (3.25), 290 sh (3.47), 267 sh (3.88), 258 (3.90) [lit.⁸² (cyclohexane) 474 br (3.10), 290 sh (3.75), 267 (4.49), 258 (4.48)].

FVT of Thiophene (13a). Approximately 20 mL of thiophene was passed through the FVT apparatus under the standard conditions. The material in the traps was collected and dried over magnesium sulfate, and the excess thiophene removed by rotary evaporation to leave approximately 5 mg of a dark brown residue whose GC analysis as below gave no indication of thianaphthene. The MS of this residue indicated the possible presence of bithienyls because of a peak at m/e 166.

FVT of 2,3-Thiophenedicarboxylic Anhydride (5) in the Presence of Thiophene. The FVT reaction of the anhydride 5 (390 mg, 2.5 mmol) in a stream of thiophene was worked up as usual except that a sublimate of sulfur (MS) coated the apparatus and the column chromatography used petroleum ether– CH_2Cl_2 (3:1) as the eluant. The first 60 mL were dried (MgSO_4) and concentrated by rotary evaporation and the residue subjected to GC (6 ft \times 0.25 in. 5% SE-30 on Chromosorb W at 120 °C).

Only one compound, thianaphthene (15a) (197 mg, 59%), was observed as identified by comparison of its IR and NMR spectra with those of an authentic sample.

FVT of Indanetrione in the Presence of Thiophene. Indantrione (440 mg, 2.47 mmol) was sublimed (160 °C) through the hot zone in a stream of thiophene. The usual workup (without chromatography or base wash) gave upon removal of the solvent by rotary evaporation 221.5 mg of residue which was subjected to preparative TLC to give four bands A, B, C, and D with R_f 's of 0.94, 0.54, 0.44, and 0.27, respectively. Band A, 112 mg, was identified as a mixture of the four compounds: naphthalene, 2-phenylthiophene, biphenylene, and triphenylene, in the relative ratios 25:15:56:4, respectively, by GC retention time (4 ft \times 0.25 in. 30%Se-30 on Chromosorb W at 155 °C) and NMR comparisons with authentic samples. Band B, 11.6 mg (5%), an orange solid, is believed to be fluorenone by comparison of its IR, R_f mp, and retention time with those of an authentic sample. Band C, 22.5 mg (6.9%), yellow prisms, is probably benzocyclobutenedione by comparison of its mp, IR, and UV data with those in the literature.³⁸ Band D, 10.3 mg (4%) is an orange compound which was identified as phenanthraquinone by mp, R_f value, and IR comparisons with those of an authentic sample. All of these compounds except naphthalene and 2-phenylthiophene are found in the FVT of indanetrione alone.³⁸

FVT of Thiophene (13a) in a Stream of Cyclopentadiene (13e). Thiophene (200 mg) was passed from the sublimation chamber at 25 °C and through the hot zone at 500 °C in a stream of excess cyclopentadiene from the reservoir. After the reaction was complete, the material from the cold traps was dried over magnesium sulfate, and excess cyclopentadiene and thiophene were removed by rotary evaporation. Preparative GC (5 ft \times 0.25 in. 5%PPE on Chromosorb W at 130 °C) gave only one peak not present in the FVT of cyclopentadiene alone under identical conditions. This peak was identified as indene by NMR comparison with that of an authentic sample. The yield was approximately 10% as determined by GC isolation from an aliquot.

FVT of 2,3-Thiophenedicarboxylic Anhydride (5) in the Presence of 1,3-Cyclohexadiene (13b). The FVT reaction of the anhydride 5 (750 mg, 4.8 mmol) in a stream of 1,3-cyclohexadiene was worked up as usual except that the column chromatography used petroleum– CH_2Cl_2 (3:1) as the eluant. The concentrated material was committed to preparative GC (5 ft \times 0.25 in. 5%PPE on Chromosorb W at 130 °C) to give 88 mg (14%) of thianaphthene (15a) identified by MP, IR, and NMR comparisons with those of an authentic sample.

FVT of 2,3-Thiophenedicarboxylic Anhydride (5) in the Presence of Benzene (13c). Normal workup of the FVT of the anhydride 5 (300 mg, 1.95 mmol) in a stream of benzene gave a residue of 272 mg which was committed to preparative TLC with the use of methylene chloride as an eluant. The major band ($R_f = 0.81$) was subjected to GC analysis (18 ft \times 0.25 in. 25%PPE on Chromosorb W at 200 °C) to reveal peaks in the ratio of 80:11:2:7. Upon isolation, the first was identified by IR, MS, and GC retention time comparisons with those of an authentic sample of thianaphthene (15a) (44 mg, 17%). The second peak was tentatively assigned the structure of dithienylbenzene from its spectral properties: MS 242 (3), 216 (6), 210 (9), 197 (7), 190 (22), 184 (29), 171 (6), 162 (7), 161 (14), 160 (100), 159 (7), 149 (21), 134 (14), 128 (21), 121 (12), 116 (23), 115 (46), 105 (16), 102 (13), 93 (12), 90 (25), 85 (14), 83 (12), 82 (12), 81 (12), 77 (21), 71 (18), 69 (30), 57 (36), 55 (23), 51 (32),

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50 (25), 45 (43), 43 (27), 41 (30), 39 (40); IR 3100, 1450, 1370, 1255, 1200, 1080, 1000, 850, 780, 730, 670; UV 255 (3.86), 226 (3.81). The third peak was identified as 2-phenylthiophene (0.6 mg, 0.2%) by comparisons of its UV, MS, and GC retention time with those of an authentic sample.⁸³ The final peak was identified as 3-phenylthiophene (2.7 mg, 0.9%): mp 86–88 °C (lit.⁶ 89–90 °C); UV 227 (4.17), 259 (4.12) [lit.⁸³ 227 (4.11), 259 (4.13)]; MS 162 (6), 161 (13), 160 (100), 159 (8), 134 (7), 128 (17), 116 (17), 115 (53), 102 (7), 89 (15), 80 (6), 79 (6), 77 (6), 69 (7), 63 (15), 51 (13), 50 (8), 45 (17), 39 (17).

FVT of 2-Phenylthiophene. FVT of 2-phenylthiophene⁸³ under the above conditions with a nitrogen sweep gave only recovered starting material. GC analysis as above did not detect thianaphthene (15a).

FVT of 2,3-Thiophenedicarboxylic Anhydride (5) in the Presence of Furan (13d). The FVT of 400 mg of the anhydride **5** in a stream of furan was worked up as previously described except that petroleum ether was used as the eluant. The first 60 mL were dried (MgSO₄) and concentrated by rotary evaporation at room temperature to give 25 mg of colorless liquid which was subjected to GC analysis (5 ft × 0.25 in. 5%PPE on Chromosorb W at 135 °C). Two peaks of relative area 1:7 (*t_R* 4.5 and 5.2 min, respectively) were observed. The latter of these contained a small shoulder and was collected and identified as the mixture of indenenes (**19**) with an unknown impurity: IR 3300 (impurity?) 3110, 3095, 1600, 1440, 1380, 1350, 1250, 1110, 930, 840; MS 124 (6), 123 (9), 122 (28), 121 (24), 86 (15), 84 (26), 78 (13), 77 (10), 69 (13), 63 (15), 51 (43), 49 (100), 48 (10), 47 (28), 45 (24), 39 (24), 38 (10), 37 (13), 35 (26). The NMR (100 MHz) contained several peaks at variable positions from 0.5–3.0 in different samples. The consistently observed resonances were as follows: 3.34 (1.2 H, dd, *J* = 2.0), 3.48 (0.8 H, dd, *J* = 2.0), 6.85 (1 H, m), 7.15 (1 H, m), 7.3–7.7 (3 H, m). The extra H in the last resonance must belong to the impurity or to decomposition products. Samples of **19** were unstable and decomposed in 6 h at 0 °C as was evident from the appearance of new peaks in the IR at 1850, 1775, and 1742 cm⁻¹. The basic fraction from the reaction workup was neutralized with 6 N HCl and extracted with 3 × 10 mL portions of methylene chloride. The combined extracts were dried over magnesium sulfate, and the solvent was removed with a rotary evaporator to give 5 mg (1.2%) of a brown solid, believed to be the hydroxythianaphthenes **15d**: IR 3700–3400, 1595, 1564, 1452, 1419, 1332, 1262, 1154, 915, 680; NMR 8.0–6.9 (m); MS 152 (6), 151 (10), 150 (100), 122 (42), 121 (56), 96 (14), 51 (22), 50 (14), 45 (36), 39 (22). Repeated attempts to purify this compound by TLC on silica with CH₂Cl₂, benzene, ethyl acetate, and methanol in various proportions of petroleum ether were unsuccessful.

FVT of 1,4-Epoxy-1,4-dihydronaphthalene (20). FVT of the adduct **20**⁸⁴ (244 mg, 1 mmol) with nitrogen as the carrier gas gave, after the usual workup, a basic wash which was acidified with 6 N HCl, extracted with methylene chloride, and dried (MgSO₄). The solvent was removed by rotary evaporation to yield 110 mg (45%) of a brown solid which was sublimed to give white crystals, mp 90–91 °C, identified as 1-naphthol by comparison of its IR, MS, NMR, and GC retention time with those of an authentic sample. No 2-naphthol was detected at the appropriate GC retention time.

FVT of 2,3-Thiophenedicarboxylic Anhydride (5) in the Presence of Cyclopentadiene (13e). FVT of the anhydride **5** (1 g, 6.4 mmol) in a stream of freshly distilled cyclopentadiene gave, after the usual workup (except that chromatography was done with CH₂Cl₂–petroleum ether, 1:3), 180 mg of residue which upon GC analysis (18 ft × 0.25 in. 25%PPE on Chromosorb W at 165 °C) revealed the presence of at least eight compounds. Peaks 1 and 5 were identified as the cyclopentadiene dimer and naphthalene by their retention times and comparison of the IR and NMR spectra of GC-collected samples with those of authentic material. Peaks 3 and 4 were incompletely resolved and appeared to consist primarily of a methylindene: MS 129 (13), 128 (100), 127 (68), 110 (42); NMR 2.3–2.4 (CH₃), 3.1–3.4 (CH₂), 5.8–6.15 (=C–H), and 7.0–7.15 (aromatic hydrogens). These, and only these, peaks are observed in the GC of the product of the FVT of cyclopentadiene alone. Peaks 2, 6, 7, and 8 were identified by comparison of the retention times, IR,⁸⁵ and MS of GC-collected samples with those of authentic materials to be indene, 7-methylthianaphthene (**23**),⁶⁰ an equimolar mixture of 5- and 6-methylthianaphthene (**24** and **25**),⁶⁰ and 4-methylthianaphthene (**22**),⁶⁰ respectively. The isolated yields of the thianaphthenes were 57 (5.8%), 10 (1.0%), and 64 mg (6.8%) for **23**, **24** + **25**, and **22**, respectively. The composition of the GC-unresolved mixture of **24** and **25** was determined by IR comparisons with those of known mixtures of authentic⁶⁰ **24** and **25**.

FVT of 7-Methylthianaphthene (23) and 6-Methylthianaphthene (25). In separate reactions, both 7- (**23**) and 6-methylthianaphthene (**25**) were subjected to typical FVT as pure compounds.⁶⁰ GC analysis of the pyrolysates (18 ft × 0.25 in. 25%PPE on Chromosorb W at 165 °C) showed them to consist of starting material only.

FVT of Benzonorbornadiene (26). The products from the FVT of benzonorbornadiene (**26**)⁸⁴ (242 mg, 1.8 mmol) in a stream of nitrogen were washed from the apparatus with benzene. The solvent was removed by rotary evaporation to give a residue which was subjected to preparative GC (15 ft × 0.25 in. 20% DCQF-1 on Chromosorb W at 140 °C) to give in addition to unreacted benzonorbornadiene three products. One was identified as 1,2-benzocycloheptatriene: NMR (100 MHz, CCl₄), 7.0–7.4 (m, 4 H), 6.6–5.7 (m, 4 H), 3.0 (d, 2 H, *J* = 6) [lit.⁶¹ 6.8–7.2 (m, 4 H), 5.3–6.5 (m, 4 H), 2.9 (d, 2 H, *J* = 6.2)]; UV (CCl₄) 278 (3.53) [lit.⁶¹ 278 (3.80)]; MS 143 (12), 142 (88), 141 (100), 128 (7), 116 (7), 115 (60), 89 (12), 63 (17), 51 (12), 50 (9), 39 (16). The others were identified as 1-methylnaphthalene and 2-methylnaphthalene by GC retention time and NMR spectral comparisons with those of authentic samples.

FVT of 2,3-Thiophenedicarboxylic Anhydride (5) in the Presence of 2,3-Dimethylbutadiene (13f). The anhydride **5** (600 mg, 3.9 mmol) was subjected to FVT in a stream of 2,3-dimethylbutadiene and the reaction worked up with the use of petroleum ether–CH₂Cl₂ (3:1) for column chromatography. The first 90 mL of eluant was dried (MgSO₄), concentrated on a rotary evaporator, and committed to preparative GC (18 ft × 0.25 in. 25%PPE on Chromosorb W at 185 °C) which showed three peaks. The second and major peak was isolated (80 mg, 13%) and identified as 5,6-dimethylthianaphthene (**15f**): mp 81–83 °C; IR 3100, 2960, 1620, 1450, 1393, 1325, 1270, 1155, 1085, 1030, 895, 870, 840, 800, 755, 695; NMR 2.40 (s, 6 H), 7.67 (s, 1 H), 7.30 (s, 1 H), 7.53–7.67 (apparent unresolved quartet, 2 H); MS 164 (7), 163 (11), 162 (100), 161 (80), 147 (74), 134 (52), 128 (21) 115 (90), 103 (15), 102 (22), 81 (38), 80 (31) 69 (41), 65 (29), 51 (58), 45 (48), 39 (58). Anal. Calcd for C₁₀H₁₀S: C, 74.07; H, 6.17; S, 19.50. Found: C, 74.19; H, 6.30; S, 19.81.

5,6-Dimethylthianaphthene (15f). A 10-mL round-bottom flask was charged with 25 mL of absolute ethanol and 0.32 g (14.4 mmol) of sodium. After the evolution of hydrogen had ceased, 2 g (14.4 mmol) of 3,4-dimethylthiophenol⁸⁶ in 20 mL of absolute ethanol was added followed by 2.37 g (14.4 mmol) of 2-bromodiethyl acetal. After the mixture had been heated under reflux for 2 h, the excess ethanol was removed by distillation. The residue was triturated with 25 mL of water and extracted with 2 × 30 mL portions of ether. The combined ether fractions were dried over magnesium sulfate, and the solvent was removed by rotary evaporation. The crude 3,4-dimethyl-5-(2',2'-diethoxyethyl)-thiophenol (1.8 g, 58%) was placed in a separatory funnel on a 100-mL two-neck flask containing 45 mL of polyphosphoric acid and equipped for vacuum distillation. The funnel tip was attached to a piece of 8-cm glass tubing extending below the surface of the acid, and the flask was heated with a mantle. When the temperature of the acid reached 160 °C, as determined by a thermometer temporarily inserted in the liquid, the thermometer was removed, the system evacuated to 3 mmHg with a vacuum pump, and the contents of the separatory funnel allowed to slowly disperse below the surface of the acid. A violent reaction ensued and the product instantly distilled from the reaction mixture. Preparative GC (18 ft × 0.25 in. 25%PPPe of Chromosorb W at 140 °C) gave, as the first component, 40 mg (3%) of 5,6-dimethylthianaphthene (**15f**): mp 81–83 °C; IR identical with that of sample **15f** obtained from FVT reaction of **5** and 2,3-dimethylbutadiene. A second component isolated as a liquid (15 mg, 1.2%) was 4,5-dimethylthianaphthene: NMR 2.41 (s, 3 H), 2.54 (s, 3 H), 7.38 (s, 2 H), 7.10 and 7.58 (AB quartet, 2 H, *J* = 8); IR 3112, 2940, 2900, 1575, 1460, 1440, 1390, 1340, 1220, 1182, 1160, 1110, 1020, 1000, 930, 880, 833, 800, 770, 690; MS 164 (6), 163 (13), 162 (100) (picrate, mp 110.5–111.5 °C). Anal. Calcd for C₁₀H₁₀S: C, 74.07; H, 6.17. Found: C, 74.33; H, 6.35.

FVT of 2,3-Thiophenedicarboxylic Anhydride (5) in the Presence of Propyne. FVT of the anhydride **5** (460 mg, 3 mmol) in a stream of propyne gave, after the usual workup and chromatography over silica with use of petroleum ether–CH₂Cl₂ (3:1), 60 mL of eluent which on drying (MgSO₄) and concentration on a rotary evaporator left a residue of 33 mg. Preparative GC (6 ft × 0.25 in. 5%PPE on Chromosorb W at 110 °C) gave two poorly resolved peaks which were collected as one. This material (**28** + **29**) began to visibly darken after several minutes at room temperature, and no further purification was attempted. **28** + **29**: IR 3110, 2980, 2930, 2863, 2240 w, 1955, 1525, 1445, 1380, 1360, 1272, 1240, 1198, 1082, 860, 770, 740, 695, 660, 635; MS 124 (8), 123 (10), 122 (100), 121 (73), 96 (59), 95 (26), 93 (14), 91 (96), 89 (11), 78 (52), 77 (64), 71 (11), 70 (13), 69 (39), 63 (40), 62 (14), 61 (11), 51 (39), 50 (26), 45 (39), 39 (37); NMR (100 M/Hz) (s, 0.7 H), 1.97 (s, 0.6 H),

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5.1 (d, 1.1 H, $J = 6$), 6.1 (dt, 0.5 H, $J = 6$), 6.6–7.4 (m, 3 H).

Pyrolysis of 2,3-Thiophenedicarboxylic Anhydride (5) in the Presence of Anthracene. An intimate mixture of 450 mg (2.9 mmol) of the anhydride (5) and 520 mg (2.9 mmol) of anthracene was sealed in an evacuated, thick-walled ampule and heated in a eutectic salt bath for 90 s at 340 °C. The ampule was cooled and opened; the contents were dissolved in methylene chloride and vigorously stirred with 10 mL of 3 N sodium hydroxide for 1 h to remove unreacted anhydride. The methylene chloride layer was dried (MgSO_4) and slowly concentrated until crystallization began. Filtration removed most of the unreacted anthracene. The remaining solvent was removed with a rotary evaporator, yielding approximately 40 mg of residue which upon preparative TLC on silica with methylene chloride–heptane (1:1) revealed three colored bands with R_f 's 0.38; 0.30, and 0.25.

The first component, **33** (2.3 mg, 0.2%) is a red gum which failed to be purified upon attempted recrystallization from acetic acid, water–ethanol, or benzene–heptane: mp 80–140 °C; IR 2980, 2960, 1670, 1590, 1278, 690; UV 382 (3.89), 362 (3.95), 352 (4.55), 343 (3.94), 327 (3.96), 220 (4.06); MS 290 (8), 289 (23), 288 (50), 287 (25), 260 (5), 208 (75), 180 (75), 177 (25), 176 (33), 152 (80), 151 (55), 150 (30), 111 (100), 83 (40), 76 (60), 57 (42), 55 (34), 43 (35), 39 (29).

The second component, **34** (13 mg, 3%), is a rusty orange solid: mp 196–200 °C; IR 3100, 3080, 1640, 1590, 1540, 1515, 1430, 1380, 1350, 1275, 1245, 1025, 875, 790, 755, 730, 720; NMR 7–8.5 (m, 8 H), 8.5–9.0 (m, 2 H); MS 316 (7), 315 (25), 314 (79), 313 (84), 286 (28), 285 (58), 258 (37), 257 (15), 256 (25), 224 (23), 213 (79), 211 (25), 187 (52), 157 (40), 129 (100), 128 (50), 116 (45), 106 (83), 113 (26), 112 (23), 111 (29), 99 (25), 98 (23), 87 (23), 75 (23), 74 (21), 71 (23), 69 (26), 57 (37). Anal. Calcd for $\text{C}_{20}\text{H}_{10}\text{O}_2\text{S}$: C, 76.42; H, 3.21; S, 10.20. Found: C, 76.18; H, 3.36; S, 10.08.

The last component (11.1 mg 3%) proved to be the quinone **11** by comparison of its IR and MS with those of an authentic sample.

Reaction of 2,3-Thiophenedicarboxylic Anhydride (5) with Anthracene and Aluminum Chloride. A 50-mL flask was charged with 231 mg (1.4 mmol) of anthracene, 200 mg of the anhydride **5**, 267 mg (2 mmol) of AlCl_3 , and 20 mL of freshly distilled nitrobenzene. The flask was protected from moisture with a calcium chloride drying tube and heated gently on a steam bath for 3 h. After the reaction was complete, the nitrobenzene was removed by steam distillation. The remaining aqueous layer was rendered basic with 1 N sodium hydroxide and filtered to remove unreacted anthracene. Upon acidification with 6 N hydrochloric acid, a yellow precipitate formed which was collected by suction filtration. The precipitate was recrystallized from 1:1 acetic acid–water, yielding 350 mg (81%) of the ketoacid **35**: mp 208–212 °C; MS 334 (7), 333 (24), 332 (60), 288 (50), 261 (30), 260 (89), 214 (24), 177 (100), 176 (100), 111 (45), 82 (20).

Pyrolysis of the Keto Acid 35. The ketoacid **35** (200 mg, 0.5 mmol) was sealed in an evacuated, thick-walled ampule and heated in a eutectic salt bath for 90 s at 340 °C. The ampule was cooled and opened, and the contents were dissolved in methylene chloride and vigorously stirred with 10 mL of 3 N sodium hydroxide for 30 min. Neutralization of the aqueous phase with 6 N HCl gave no unreacted **35**. The methylene chloride solution was dried (MgSO_4) and concentrated by rotary evaporation to leave 160 mg of residue which was committed to preparative thin-layer chromatography on silica with an eluant of methylene chloride–heptane (1:1). Two bands which had R_f values identical to those of **33** and **34** were observed and collected and their MS peaks were also shown to be identical with those of **33** and **34**.

Pyrolysis of 2,3-Thianaphthenedicarboxylic Anhydride (7). An evacuated, thick-walled Pyrex tube containing 241 mg (1.3 mmol) of the anhydride **7** was heated for 50 min at 270 °C in a salt bath. The ampule was cooled and opened, and its contents were dissolved in methylene chloride. This solution was vigorously stirred with 15 mL of 0.3 N sodium hydroxide to remove unreacted anhydride. The organic phase was dried over magnesium sulfate, and the solvent was removed by rotary evaporation, yielding 144 mg (80%) of a yellow solid (**36**): mp 252–254 °C; IR 2920, 1700, 1490, 1420, 1234, 1150, 790, 760, 707; UV 397 (3.86), 352 (3.94), 286 (3.24), 279 (4.27), 267 (4.33), 266 (4.58); MS 322 (10), 321 (19), 320 (100), 292 (16), 264 (20), 220 (20), 219 (22), 187 (15), 160 (12), 146 (19), 132 (73), 110 (18), 93 (27), 88 (32), 87 (16), 82 (11), 69 (23), 63 (11), 62 (15), 45 (10), 39 (15). Anal. Calcd for $\text{C}_{18}\text{H}_8\text{O}_2\text{S}_2$: C, 67.50; H, 2.50. Found: C, 67.45; H, 2.74.

FVT of 2,3-Thianaphthenedicarboxylic Anhydride (7) in the Presence of Thiophene. FVT of the anhydride **7** (420 mg, 2.1 mmol) in a stream of thiophene (**13a**) gave after the usual workup (no base wash) a residue which was subjected to TLC on silica with use of petroleum ether– CH_2

(1:1) as an eluant. Except for unreacted anhydride, only one other component ($R_f = 0.8$) was observed, collected, and purified by GC (6 ft \times 0.25 in. 5% SE-30 on Chromosorb W at 160 °C) to give 120 mg (35%) of dibenzothiophene (**37**): mp 98–100 °C (lit.⁸⁷ 99.5–100 °C); MS 186 (7), 185 (14), 184 (63), 152 (100) 76 (22).

Pyrolysis of 3,4-Thiophenedicarboxylic Anhydride (6). The anhydride **6** was stable for 2.5 h at 260 °C so 957 mg (6.2 mmol) in four evacuated ampules was pyrolyzed for 30 s at 470 °C in a eutectic salt bath. The cooled ampules were opened and their contents dissolved in methylene chloride. The solution was filtered to remove polymer and then vigorously stirred for 1 h with 0.3 N sodium hydroxide to remove unreacted anhydride. The organic phase was dried (MgSO_4) and concentrated by rotary evaporation to give 20 mg of residue which upon preparative TLC on silica with methylene chloride–heptane (4:1) displayed two distinct yellow bands ($R_f = 0.5$ and $R_f = 0.4$) which were collected.

The first compound after sublimation gave 1.6 mg (1.2%) of a yellow solid, mp 250–257 °C (lit.²¹ 258–259 °C), whose IR proved to be identical with that of the quinone **21**.

The second band also was sublimed to give 5 mg (0.36%) of a yellow solid (**38**): mp 295–297 °C (lit.²¹ 296–297 °C), whose IR was identical with that of an authentic sample.²⁸

Pyrolysis of 3,4-Thiophenedicarboxylic Anhydride (6) in the Presence of Anthracene. An intimate mixture of 513 mg (3.3 mmol) of the anhydride **6** and 528 mg (3.3 mmol) of anthracene was sealed in an evacuated, thick-walled ampule. The mixture was pyrolyzed at 315 °C for 12 min in a eutectic salt bath. The ampule was cooled and opened, and its contents were dissolved in methylene chloride. This solution was vigorously stirred for 1 h with 10 mL of 3 N sodium hydroxide to remove unreacted anhydride. The methylene chloride layer was dried (MgSO_4) and concentrated by rotary evaporation to leave 100 mg of brown residue which was committed to preparative TLC on silica with methylene chloride–heptane (3:1) as eluant. Aside from anthracene, five bands were observed but only the first three (R_f 0.57, 0.43, 0.32) were present in sufficient amounts for further examination. Band A, (3 mg, 0.3%) was not obtained pure but from spectral properties is believed to be a thenoylanthracene (**33**): IR 1640; UV 382 (3.57), 362 (3.60), 353 (4.37), 344 (3.53), 328 (3.45); MS 290 (19), 289 (5), 288 (79), 287 (47), 271 (10), 261 (10), 260 (18), 259 (10), 258 (11), 255 (10), 226 (10), 215 (10), 208 (10), 205 (26), 180 (16), 178 (58), 177 (58), 176 (10), 175 (10), 152 (20), 151 (24), 150 (23), 149 (10), 144 (10), 130 (10), 113 (21), 112 (10), 111 (100), 83 (47), 81 (58), 76 (16), 75 (13), 74 (10), 71 (23), 69 (23), 57 (37), 55 (32), 50 (10), 45 (10), 43 (47), 39 (14).

Band B was purified by repeated chromatography on TLC and sublimation to give 18 mg (1.8%) of a yellow solid which is believed to be quinone (**40**): mp 233–235 °C; IR 3105, 1655, 1450, 1255, 1215, 1010, 720; NMR(acetone- d_6) 8.93–7.1 (m); UV 468 (3.23), 394 (3.23), 365 (3.46), 318 (4.48), 244 (4.68); MS 316 (6), 315 (21), 314 (100), 313 (28), 286 (12), 258 (18), 257 (9), 256 (10), 225 (10), 224 (10), 214 (12), 213 (44), 211 (14), 187 (13), 176 (16), 174 (13), 163 (13), 157 (50), 142 (21), 129 (66), 128 (51), 121 (13), 116 (34), 113 (49), 112 (17), 111 (18), 107 (73), 100 (12), 99 (12), 98 (12), 87 (18), 86 (13), 82 (19), 75 (19), 74 (19), 63 (20), 51 (16), 50 (17), 45 (26), 39 (16). Anal. Calcd for $\text{C}_{20}\text{H}_{10}\text{O}_2\text{S}$: C, 76.42; H, 3.18; S, 10.20. Found: C, 76.19; H, 3.36; S, 9.93.

Band D was purified by sublimation, giving 15 mg (1.6%) of a red solid believed to be quinone (**39**): mp 227–228 °C; IR 3100, 1631, 1550, 1500, 1440, 1410; NMR(acetone- d_6) 8.98–7.48 (m); UV 427 (3.82), 377 (3.53), 262 (4.63), 241 (4.61); MS 316 (6), 315 (21), 314 (99), 313 (100), 286 (8), 285 (15), 258 (12), 225 (15), 214 (41), 213 (13), 212 (18), 188 (13), 177 (10), 175 (10), 164 (9), 157 (59), 151 (12), 130 (71), 129 (51), 121 (17), 116 (20), 113 (20), 112 (20), 106 (66), 99 (13), 98 (13), 93 (20), 87 (17), 86 (12), 85 (16), 83 (23), 75 (19), 74 (17), 63 (19), 51 (12), 50 (12), 45 (21), 44 (16). Anal. Calcd for $\text{C}_{20}\text{H}_{10}\text{O}_2\text{S}$: C, 76.42; H, 3.18; S, 10.20. Found: C, 76.39; H, 3.02; S, 10.36.

FVT of 2,3-Dicyanothiophene (41) and Dimethyl Thiophene-2,3-dicarboxylate (42) in the Presence of Thiophene. Both the nitrile **41**⁸⁸ and the ester **42**⁸⁰ were recovered unchanged from typical FVT at 600 °C in yields of 97% and 96%.

Acknowledgment. This research was supported by the Robert A. Welch Foundation and the TCU Research Foundation.

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