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Thiophenes as Traps for Benzyne. 1. The Role of the Precursor[1,2]

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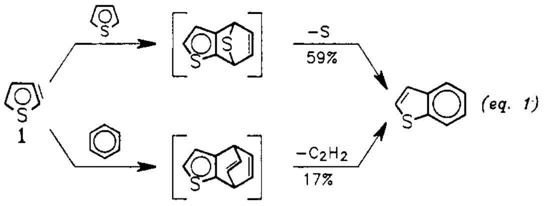
The reaction of thiophene with six different benzyne precursors under benzyne-forming conditions was examined to determine if this heterocycle could enter into cycloaddition or other reactions with this intermediate. The most satisfactory system proved to be diphenyliodonium-2-carboxylate (**4**) at 220 °C, where the yield of benzyne + thiophene derived products approached 50%, the major single product being naphthalene. Other electrophilic precursors such as benzenediazonium-2-carboxylate (**2**) and benzothiadiazole dioxide (**3**) also gave some naphthalene, but in much lower yield and accompanied by tars and compounds suggesting the trapping of nonbenzyne electrophilic intermediates by the thiophene. With 1-aminobenzotriazole (**9**), (*o*-fluorophenyl)magnesium bromide (**5**), and (*o*-fluorophenyl)lithium (**8**), the benzyne generated reacted preferentially with itself (**9**) or with nucleophilic species present rather than with the thiophene, although some naphthalene was obtained with **9** and **5** but not **8**. A comparison of the reaction of thiophene and benzene toward benzyne generated from **4** under identical conditions revealed that the former gave about 3 times as much benzyne-derived product as the latter. Using the isomeric methyl derivatives **17** and **18** of precursor **4** in a reaction with 3-methylthiophene gave an identical mixture of 2,6- and 2,7-dimethylnaphthalene (**20** and **21**), thereby verifying the intermediacy of 4-methylbenzyne (**19**) in these reactions.

Introduction

Thiophene is usually considered to be the most aromatic of the five-membered heterocycles, and as such its relative reluctance, compared with that of pyrrole and especially furan, to exhibit diene reactivity is not surprising.[3,4] Even benzene can display this reactivity, however, given a sufficiently energetic reaction partner such as benzyne.[5,6] Therefore, the apparent failure of thiophene to react with benzyne,[7-9] except under relatively severe gas-phase conditions[10-12] or with the especially reactive polyhalobenzynes,[7,8,13-15] must be regarded as unusual.[16] By the same token, the observation[12] that thiophene is superior to benzene as a cycloaddition partner with the five-membered hetaryne, 2,3-didehydrothiophene (**1**) (eq 1), may be viewed as normal and suggests that the failure to observe this same preference with benzyne may be due to an enhanced ability of thiophene (compared to benzene) to consume certain benzyne precursors in nonbenzyne-producing reactions. If this is true, then regardless of the demonstrated equivalence of benzyne generated from several precursors,[19,20] the expression of the diene reactivity



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[1] Taken in part from the Dissertation of D.D.M. presented in partial fulfillment of the Ph.D. degree at Texas Christian University, 1980.

[2] A portion of this work has appeared in a preliminary communication: Del Mazza, D.; Reinecke, M. G. *Heterocycles* **1980**, *14*, 647.

[3] Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 211.

[4] Lert, P. W.; Trindle, C. *J. Am. Chem. Soc.* **1971**, *93*, 6392.

[5] Miller, R. G.; Stiles, M. *J. Am. Chem. Soc.* **1963**, *85*, 1798.

[6] Friedman, L. *J. Am. Chem. Soc.* **1967**, *89*, 3071.

[7] Callander, D. D.; Coe, P. L.; Tatlow, J. C. *Chem. Commun.* **1966**, 143.

[8] Callander, D. D.; Coe, P. L.; Tatlow, J. C.; Uff, A. J. *Tetrahedron* **1969**, *25*, 25.

[9] Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic: New York, 1967; p 234.

[10] Fields, E. K.; Meyerson, S. *Chem. Commun.* **1966**, 708.

[11] Fields, E. K.; Meyerson, S. *J. Org. Chem.* **1969**, *34*, 2475.

[12] Reinecke, M. G.; Newsom, J. G.; Chen, L. J. *J. Am. Chem. Soc.* **1981**, *103*, 2760.

[13] Hayashi, S.; Ishikawa, N. *Yuki Gosei Kagaku Kyokai Shi* **1970**, *28*, 533 through *Chem. Abstr.* **1970**, *73*, 45241c.

[14] Hayashi, S.; Ishikawa, N. *Nippon Kagaku Zasshi* **1970**, *91*, 1000.

[15] Coe, P. L.; Pearl, G. M.; Tatlow, J. C. *J. Chem. Soc. C* **1971**, 604.

[16] Thiophenes substituted with appropriate electron-donating groups can be effective 4-π components with electron-deficient alkynes, singlet oxygen, and in one unpublished case,[17] benzyne from benzenediazonium-2-carboxylate.[18]

[17] Helder, R. Thesis, University of Groningen, 1974, cited in ref 18.

[18] Benders, P. H.; Reinhoudt, D. N.; Trompenaars, W. P. In *Thiophene and its Derivatives, Part One*; Gronowitz, S., Ed.; Wiley: New York, 1985; Chapter X.

[19] Huisgen, R.; Knorr, K. *Tetrahedron Lett.* **1963**, 1017.

[20] Klanderman, H.; Criswell, J. R. *J. Am. Chem. Soc.* **1969**, *91*, 510.

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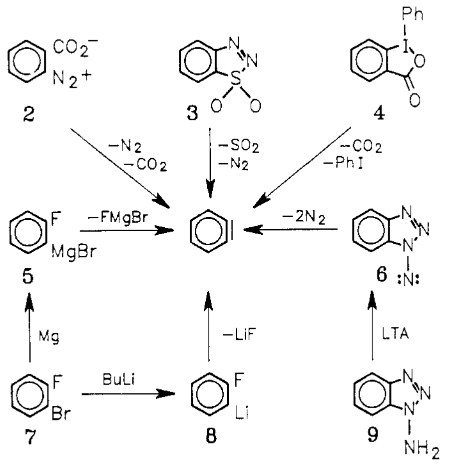
Scheme I



of thiophene with this intermediate may depend markedly on the choice of precursor.

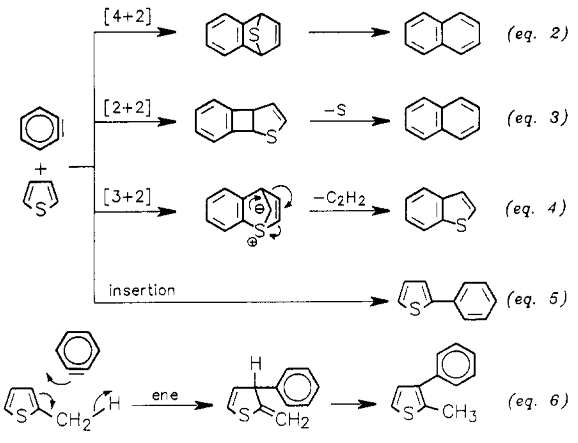
The present research was undertaken to examine this hypothesis with several common benzyne precursors and, if possible, to develop a procedure with at least one of them that would permit a detailed study of the reaction of benzyne and thiophene. This paper reports the findings of this examination and development, while subsequent papers[21] will describe the resulting study and its significance.

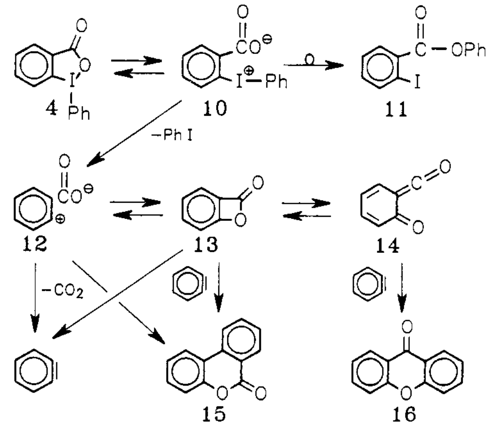
Six of the more common benzyne precursors were examined.[22] Three are simple thermal sources [benzenediazonium-2-carboxylate (**2**), benzothiadiazole dioxide (**3**), and diphenyliodonium-2-carboxylate (**4**)], while the other three [(*o*-fluorophenyl)magnesium bromide (**5**), (*o*-fluorophenyl)lithium (**8**), and the nitrene **6**] are generated in situ by halogen–metal exchange of *o*-bromofluorobenzene (**7**) or by oxidation of 1-aminobenzotriazole (**9**) as shown in Scheme I. In each case thiophene itself was used as a trap, and in several instances 2-substituted and 2,5-disubstituted thiophenes were also examined, both as potentially more reactive analogues and to determine if blocking these positions reduced nonbenzyne side reactions.

The suitability of a particular precursor as a source of benzyne for reaction with thiophene was evaluated from the yield of naphthalene, whether formed by a [4 + 2]- (eq. 2) or a [2 + 2]-cycloaddition process (eq 3), a distinction to be addressed in a subsequent paper.[21a] Although additional benzyne + thiophene derived products could arise from reactions such as [3 + 2]-cycloaddition (eq 4),[23] insertion (eq 5),[24] and, for compounds with thenyl hydrogens, the ene reaction (eq 6),[25] these proved to be relatively minor compared to naphthalene formation and were therefore ignored for evaluation purposes, but generally will be discussed in the sequel.[21a] However, products that indicated the consumption of benzyne or its precursors in any other manner were examined as a guide to selecting precursors and optimizing reaction conditions.

Results and Discussion

Diphenyliodonium-2-carboxylate (4). According to the above criteria, this precursor was judged to be the most suitable, and therefore its evaluation and development will be discussed first. While not one of the more common benzyne precursors,[22] **4** has the inherent advantage of being a stable, crystalline solid, which can be handled safely and be easily purified from the byproducts of its preparation.[26] Although usually shown in its open-chain structure **10**, NMR evidence[27] suggests that the cyclic form **4** is more appropriate. The decomposition of **4** in solution has been shown[28] to be temperature dependent, with intramolecular rearrangement to phenyl *o*-iodobenzoate (**11**) predominating below 150 °C, and loss of iodobenzene and CO_2 to give benzyne becoming the major reaction above 160 °C. The latter process is proposed to proceed via the zwitterion **12**, which can collapse to the α-lactone/ketoketene system **13**/**14** prior to losing CO_2 to give benzyne. In the absence of effective benzyne traps, the benzocoumarin **15** and the xanthone **16** are formed, presumably by reaction of benzyne with **12** (or **13**) and **14**, respectively. Since thiophene is expected to be at best an indifferent benzyne trap,[3,4] the necessity of using high temperatures to generate benzyne from **4** (so as to avoid the rearrangement to **11**) also has the advantage of permitting any thiophene–benzyne reaction to compete more effectively with lactone (**15**) and xanthone (**16**) production.





A preliminary study[2] of the thermolysis of **4**, using naphthalene production (eq 2 and 3) to monitor reaction progress, revealed that maximal yields were obtained in 15 min at 220 °C with thiophene as the solvent. While lactone (**15**) and xanthone (**16**) formation could be totally eliminated by using precursor concentrations below about 0.02 M—the highest naphthalene yield (33%) being obtained at 0.012 M—a slightly higher concentration (0.05

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[21] (a) Reinecke, M. G.; Del Mazza, D. *J. Org. Chem.*, submitted. (b) Reinecke, M. G.; Del Mazza, D.; Obeng, M., in preparation.

[22] Reference 9, Chapter 1.

[23] Del Mazza, D.; Reinecke, M. G. *J. Chem. Soc., Chem. Commun.* **1981**, 124.

[24] Reference 9, p 196.

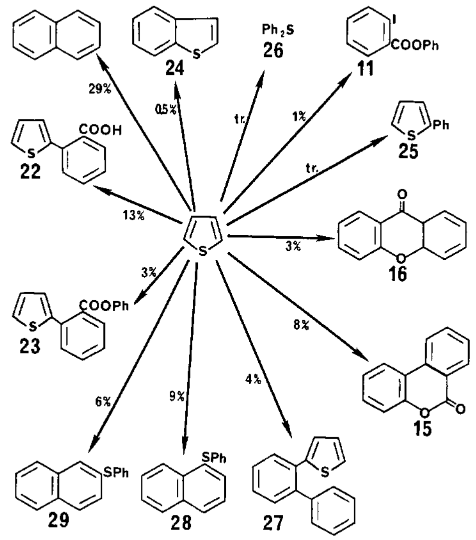
[25] Brinkley, J. M.; Friedman, L. *Tetrahedron Lett.* **1972**, 4141. Tabushi, I.; Yamada, H.; Yoshida, Z.; Oda, R. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 285.

[26] Fieser, L. F.; Haddadin, M. J. *Org. Syn.* **1966**, *46*, 107.

[27] Del Mazza, D.; Reinecke, M. G.; Smith, W. B. *Org. Magn. Reson.* **1980**, *14*, 540.

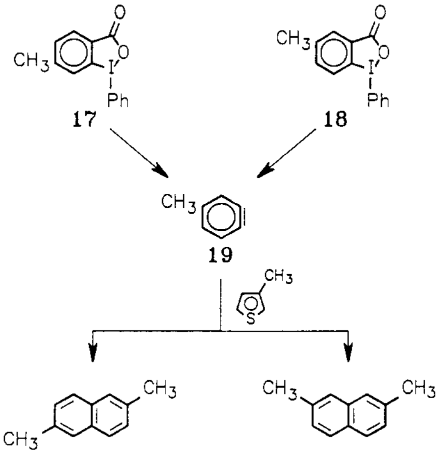
[28] Beringer, F. M.; Huang, S. J. *J. Org. Chem.* **1964**, *29*, 445.

Scheme II



M) of **4** was used to minimize analytical and experimental errors in the more detailed study of this reaction.

The possibility that naphthalene formation could involve an addition–elimination rather than an elimination–addition process, as has been observed with some potential precursors of five-membered hetarynes,[29,30] was eliminated by the demonstration that the isomeric precursors **17** and **18** gave an identical 1:1 mixture of 2,6- and 2,7-dimethylnaphthalene (**20** and **21**) when reacted with 3-methylthiophene according to the standard procedure (0.05 M **17** or **18**, 220 °C, 15 min). While this result is required if the naphthalenes are formed via the common intermediate 4-methylbenzyne (**19**), it would be highly unlikely if the reaction involved an addition–elimination process with species analogous to **12** or **13** that retain a memory of their origin. A similar demonstration of the intermediacy of free benzyne in the thermolysis of **4** by means of the three-phase test[31] was reported after this project was complete.[32]



	20	21
17:	50.2	49.8 ± 1.1%
18:	50.4	49.6 ± 0.7%

A detailed analysis of the reaction of **4** with thiophene under the standard conditions revealed the presence of 12 products (Scheme II) that accounted for 76.5% of the precursor charged. Except for the three products **11**, **15**, and **16** derived from the precursor alone, and the major product, naphthalene, all of the others contained sulfur. Two of these, *o*-(2-thienyl)benzoic acid (**22**) and its phenyl ester **23**, demonstrate the thesis that thiophene can intercept benzyne precursors, in this case probably the zwitterion **12** or its equivalent. The acid **22** was identified as its methyl ester by comparison with an authentic sample,[33] and the phenyl ester **23** was tentatively identified from the similarity of its mass spectrum to that of the same methyl ester. The probable origin of **23** is the reaction of **22** with benzyne,[34] although neither the nucleophilic substitution of iodobenzene by **22** nor the radical phenylation of thiophene[35] by **11** can be ruled out.

The remaining six compounds (**24**–**29**) probably all arise from thiophene and benzyne rather than one of its precursors. Benzo[*b*]thiophene (**24**) and 2-phenylthiophene (**25**) formation involves a 1:1 stoichiometry, presumably via eq 4 and 5, respectively. Analogous products have been found with some substituted thiophenes.[21a] Diphenyl sulfide (**26**) probably arises from 2 mol of benzyne plus H_2S, mercaptans, or sulfide-decomposition products of thiophene and has been observed previously in the reactions of benzyne with sulfur compounds.[36] Since **26** is also found with several of the other benzyne precursors in this study, i.e., **2**, **3**, and **5**, iodobenzene is unlikely to be involved in its formation.

A 2:1 benzyne:thiophene ratio characterizes the remaining three compounds found. Identification by comparison with authentic samples of the α- and β-naphthyl phenyl sulfides, **28** and **29**, respectively, suggests the interception by benzyne of some species which leads to naphthalene via eq 2 or 3. Possible mechanisms related to the formation of phenyl vinyl sulfides from 3-pyrrolidinylthiophenes and dimethyl acetylenedicarboxylate[37] can be postulated by using data from substituted thiophenes.[21b] The final product **27** is isomeric with the naphthyl sulfides **28** and **29**, but has quite a different mass spectrum, which displays M – SH and M – H_2S peaks, but neither PhC_3H_2 nor PhCS peaks, which eliminates a diphenylthiophene structure for **27** and is supported by the marked difference of its mass spectrum and that of 2,5-diphenylthiophene. On the basis of these facts and mechanistic considerations to be discussed elsewhere,[21b] **27** was predicted to be *o*-(2-thienyl)biphenyl, which was verified by a GC/MS comparison with an authentic sample.[38]

No other significant products could be detected, so the missing 25% of material must reside in the dark-colored decomposition products that accompany the reaction. Interestingly, when **4** is thermolyzed in benzene instead of thiophene, no dark products are observed, even after 30 min, and a material balance of 98% is achieved (eq 7). Except for a trace of biphenyl, the only benzyne + benzene product detected was the expected[5] benzobarrelene (**30**) in 10% yield. This comparison of thiophene and benzene reactivity toward the benzyne precursor **4** clearly supports

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(29) Reinecke, M. G. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1982; Vol. 2, Chapter 5.

(30) Reinecke, M. G. *Tetrahedron* **1982**, *38*, 427.

(31) Rebek, J.; Gavina, F. *J. Am. Chem. Soc.* **1974**, *96*, 7112.

(32) Gavina, F.; Luis, S. V.; Costero, A. M. Gil, P. *Tetrahedron* **1986**, *42*, 155.

(33) Mataka, S.; Ohshima, T.; Tashiro, M. *J. Org. Chem.* **1981**, *46*, 3960.

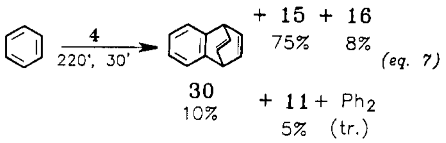
(34) Reference 9, p 124.

(35) A. E. A. Porter in Chapter IX of ref 18.

(36) (a) Reference 9, pp 125, 164. (b) Tabushi, I.; Okazaki, K.; Oda, R. *Tetrahedron Lett.* **1967**, 3827.

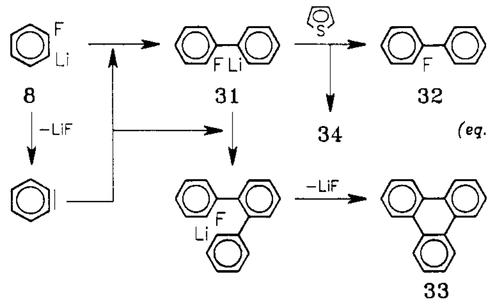
(37) (a) Reinhoudt, D. N.; Okay, G.; Trompenaars, W. P.; Harkema, S.; van den Ham, D. M. W.; van Hummel, G. J. *Tetrahedron Lett.* **1979**, 1529. (b) Reinhoudt, D. N.; Geevers, J.; Trompenaars, W. P.; Harkema, S.; van Hummel, G. J. *J. Org. Chem.* **1981**, *46*, 424.

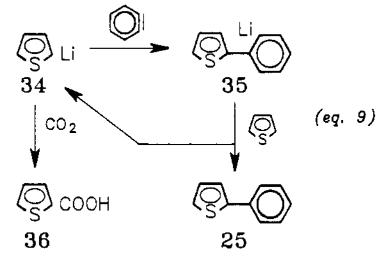
(38) Relyea, D. I.; Hubbard, W. L.; Grahame, R. E. U.S. Patent 4174405, 1979; *Chem. Abstr.* **1980**, *92*, 94229f.

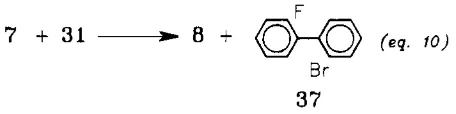


the thesis that the former is the superior diene (higher yield of apparent [4 + 2]-adduct), is more reactive toward benzyne (higher total yield of benzyne-derived products), and is more subject to side reactions (higher yield and greater diversity of nonbenzyne-derived products). These conclusions are further supported by the fact that even in a 2:1 benzene–thiophene solvent mixture the thermolysis of 4 gives a product whose composition, appearance, and material balance are similar to those in Scheme II, and no benzobarrelene (**30**) can be detected.

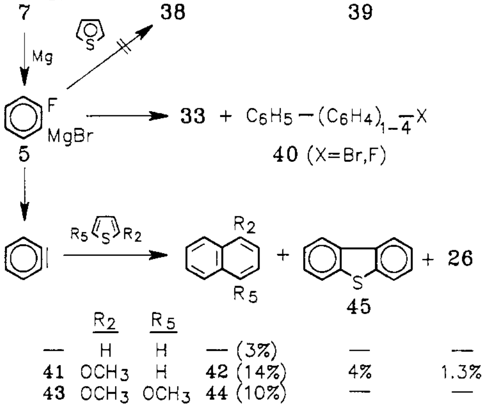
(*o*-Fluorophenyl)lithium (8). The most commonly used and most successful precursors for generating polyhalobenzynes for reaction with thiophenes have been the polyhalo derivatives of this aryne precursor.[7,8,13,15] With 8 itself, however, thiophene apparently fails to react,[7] the benzyne reacting preferentially with this highly nucleophilic precursor to give 2-fluorobiphenyl (**32**) and triphenylene (**33**) according to eq 8.[39] This report was substantiated under a variety of conditions, although when excess thiophene and a low concentration of precursor 8 were used, two thiophene-derived products (but not naphthalene via eq 2 or 3) were obtained: 2-thenoic acid (**36**) (after carboxylation) and 2-phenylthiophene (**25**). While **25** is formally the insertion product of benzyne and thiophene (eq 5), a more likely origin is the addition to benzyne of 2-thienyllithium (**34**), a species whose presence in the reaction mixture is demonstrated by the formation of the 2-thenoic acid (**36**) (eq 9). Some of this 2-thienyllithium (**34**) undoubtedly comes from the excess butyllithium used to generate **8** from **7**, but at least half must arise from other metalating agents present, probably one of the more basic phenyllithium species **31** or **35**, as shown in eq 8 and 9, respectively. The formation of **36** as the only acid in this reaction is consistent with the α-hydrogens of thiophene being the most acidic ones present[40] and also indicates the incompatability of α-unsubstituted thiophenes with benzyne precursors that are strong bases or that generate strong bases during the reaction. An attempt to overcome this problem by using 2,5-dimethylthiophene as the potential benzyne trap still failed to yield any naphthalenes, the only new product detected being a bromofluorobiphenyl, probably **37**, on the basis of its mass spectrum and likely origin[41] by the halogen–metal exchange reaction shown in eq 10.







(*o*-Fluorophenyl)magnesium Bromide (5). The lower nucleophilicity and basicity of this magnesium precursor compared to the corresponding lithium compound 8[42] promised to minimize benzyne-consuming side reactions such as eq 8 and 9, thereby allowing the reaction with thiophene (eq 2) to compete. This strategy was at least partially successful in that, as expected,[43] no evidence for transmetalation to 2-thienylmagnesium bromide (**38**) was obtained in the form of either 2-phenylthiophene (**25**) or 2-deuteriothiophene (**39**) (after D_2O quench) formation according to eq 9 (**38** for **34**) and 11, respectively. Naphthalene was not detected, however, while triphenylene (**33**) and polyphenylene halides **40**[44] were still present, thereby indicating that even organomagnesium intermediates can compete successfully with thiophene for benzyne according to eq 8 (MgBr for Li). Only by using the maximum possible excess of thiophene over 7 (30:1) with which enough THF was still present to permit the Grignard precursor **5** to be generated, was a low yield (3%) of naphthalene obtained. With only a 2-fold excess of the more reactive 2-methoxythiophene (**41**), however, 1-methoxynaphthalene (**42**) was produced in 14% yield, along with small amounts of diphenyl sulfide (**26**) and dibenzothiophene (**45**). An equimolar amount of the still more reactive[45] 2,5-dimethoxythiophene (**43**) gave 1,4-dimethoxynaphthalene (**44**) in 10% yield, but for unknown reasons generation of precursor **5** was not reproducible with this trap. It is perhaps noteworthy that, in contrast to the



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[39] Nefedov, O. M.; D'yachenko, A. I.; Prokof'ev, A. K. *Russ. Chem. Rev. (Engl. Transl.)* **1977**, *46*, 941. Reference 9, pp 109–111, 203.

[40] Streitwieser, A.; Scannon, P. J. *J. Am. Chem. Soc.* **1973**, *95*, 6273.

[41] Callander, D. D.; Coe, P. L.; Tatlow, J. C. *Tetrahedron* **1966**, *22*, 419. Gilman, H.; Gaj, B. J. *J. Org. Chem.* **1957**, *22*, 447.

[42] Reference 9, p 236.

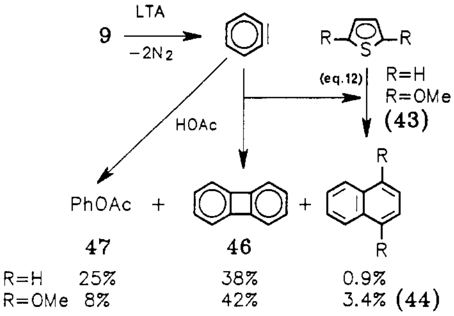
[43] Reinecke, M. G. In *Thiophene and its Derivatives, Part Two*; Gronowitz, S., Ed.; Wiley: New York, 1986; Chapter III, p 401.

[44] The detection of some polyphenylene halides containing only bromine indicates that *o*-bromophenyl anions must have been generated, presumably by the known addition of bromide ion to benzyne, ref 9, p 125.

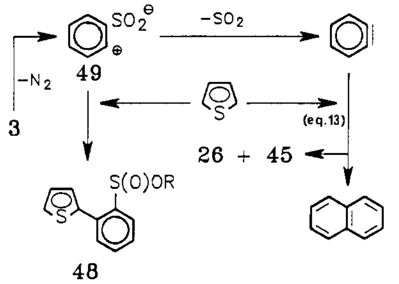
[45] Barker, J. H.; Huddleston, P. R.; Shutler, S. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2483.

other benzyne precursors in this study, **5** and **8** gave relatively light colored reaction mixtures, suggesting that the tar-like decomposition products arise from side reactions between thiophene and electrophilic intermediates other than benzyne.

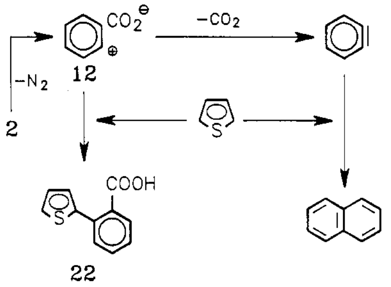
1-Aminobenzotriazole (9) upon oxidation generates benzyne, probably via the nitrene **6**.[46] With lead tetraacetate as the oxidant, this precursor is unique in its tendency to give the benzyne dimer biphenylene (**46**) in high yield, presumably due to some type of metal–benzyne complex. This property persisted in the presence of thiophene and even 2,5-dimethoxythiophene (**43**) with both dimerization to **46** and addition of acetic acid to give phenyl acetate (**47**) exceeding naphthalene formation (eq 12). Clearly the presence of the oxidant and its byproducts makes this method of generating benzyne for reaction with thiophenes unacceptable.

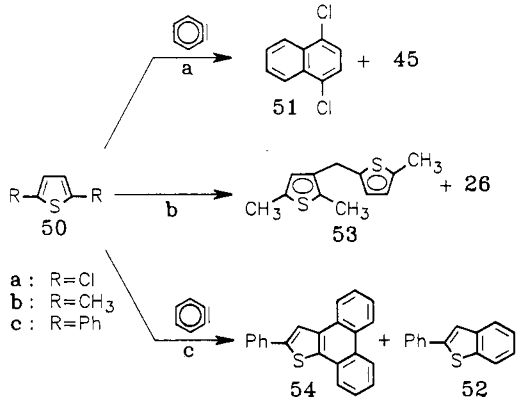


Benzothiadiazole dioxide (3) was briefly examined as a nonnucleophilic, low-temperature benzyne source that does not require the presence of any coreagents.[47] When a large excess of thiophene was used, naphthalene, diphenyl sulfide (**26**), and dibenzothiophene (**45**) were identified in low yield in the neutral portion of the dark reaction mixture (eq 13). Esterification (CH_2N_2) of the acidic fraction gave a complex mixture, from which preparative TLC separated a small amount of compound whose spectral properties were consistent with the structure **48** (R = CH_3), thereby suggesting the trapping by thiophene of an electrophilic species **49**. Such an intermediate has been previously postulated on the basis of trapping by nucleophiles[48] and is analogous to the carboxylate species **12**, apparently formed in the thermolyses of the benzyne precursors **2** and **4**. Because of this similarity and the relative difficulty in preparing **3** compared to **2** and **4**, no further studies of this precursor were undertaken.



Benzenediazonium-2-carboxylate (2) initially appeared to be a promising benzyne source because of its ready availability and well-studied chemistry.[22,49] Thermolysis at temperatures between those required by **3** and **4** apparently proceeds via the same zwitterion **12**[50] as the latter precursor, but with little or no indication that the subsequent benzyne cycloaddition products **15** or **16** are being formed.[51] Under a variety of conditions of temperature and concentration, either in neat thiophene or with 1,2-dichloroethane present as an accelerator,[52] the thermolysis of **2** gave naphthalene in only 2–5% yield. The major byproduct, *o*-(2-thienyl)benzoic acid (**22**), was found in up to 17% yield, thereby indicating that thiophene intercepted substantial portions of a benzyne precursor (**2** or **12**). As with the other electrophilic benzyne precursors studied (**3**, **4**, and **9**), dark decomposition products were formed. Attempts to block these side reactions by using 2,5-disubstituted thiophenes (**50**) failed. With 2,5-dichlorothiophene (**50a**), a small amount of the expected (eq 2) naphthalene **51** was found, but not with the dimethyl (**50b**) or diphenyl (**50c**) analogues. In addition to dibenzothiophene (**45**) from **50a**, diphenyl sulfide (**26**) from **50b**, and 2-phenylbenzo[*b*]thiophene (**52**) from **50c** (eq 4), the only other neutral products identified were the known[53] solvent dimer **53** from **50b** and, on the basis of analytical, spectral, and mechanistic considerations, the phenanthrothiophene **54**. The latter product could arise by an unusual[18] but known[54] [4 + 2]-cycloaddition between benzyne and the 4-π system comprising one double bond of the thiophene ring and one "Kekulé bond" of the phenyl substituent of **50c** followed by aromatization to the isolated product.





Conclusion

It is clear from these studies that thiophenes can react with a powerful dieneophile such as benzyne to give naphthalenes in at least moderate yield if the benzyne

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precursor and reaction conditions are carefully selected. Strongly nucleophilic or basic species (**5** and **8**), which might preferentially add to benzyne or abstract the acidic α-proton of the thiophene, must be avoided. Similarly, precursors such as **2**, **3**, and **9** that decompose to benzyne via powerful electrophilic intermediates such as **12**, **49**, or **6** lead to tar formation, probably initiated by attack of these species on the thiophene ring. Since thiophene is, as expected, at best a reluctant participant in cycloaddition reactions—but, as demonstrated in this study, better than benzene—a combination of precursor and conditions must be used that does not permit appreciable quantities of electrophilic species other than benzyne to build up during the reaction. The best system found for this purpose is rather dilute solutions of the precursor **4** at 220 °C. Under these conditions about 50% yields of products derived from benzyne plus thiophene are obtained, which permits the detailed study of these reactions with substituted thiophenes that will be reported in subsequent papers.[21]

Experimental Section

General. Melting points were measured on a Thomas-Hoover apparatus and are uncorrected. Analyses were performed by M-H-W Labs of Garden City, MI and Phoenix, AZ. Mass spectra were obtained on either Finnigan 1015SL or 1020 OWA instruments at 70 eV unless otherwise noted, with pertinent peaks reported as *m/e* (relative intensity). Proton NMR spectra were obtained on a JEOL JNM-MH-100 and ^{13}C NMR spectra on a JEOL JNM-FX-60 instrument and are reported in parts per million downfield from TMS in δ. Non-first-order multiplicities and coupling constants (J in hertz) are reported as observed, and $CDCl_3$ is the solvent unless otherwise noted. Infrared spectra were recorded on Beckman 33 or Perkin-Elmer 237 instruments as liquid films or in KBr matrix and are reported in cm^{-1}. Ultraviolet spectra were measured on a Cary 15 instrument using matched quartz cells and 95% ethanol or hexane as solvent. The ligroin used had bp 68–70 °C and the petroleum ether 35–60 °C.

Analytical Procedures. VPC analyses of the reactions of precursors **2**, **3**, **5**, **8**, and **9** were carried out on an Aerograph Autoprep A-7000 instrument with thermal conductivity detection and 0.25-in. copper columns of the indicated lengths packed with Gas Chrom Z 80-100M and the following phases: 1, 20% Carbowax 20M, 1.5 m; 2, same, 5 m; 3, 25% of the same, 1.5 m; 4, 30% SE-30, 1.2 m; 5, 20% OV-17, 1.7 m. All other analyses used a Perkin-Elmer Sigma 3 instrument with FID[55] and the following 1.6-mm-i.d. nickel columns packed as above: A, 10% Carbowax 20M, 3 m; B, 7% same, 2 m; C, 3% same, 1.8 m; D, 7% Bentone-34 plus 5% SE-52, 3 m. GC–MS analyses were performed on the Finnigan 1020 OWA quadrupole mass spectrometer by using a 1.8-m glass column at 200 °C with a 3% OV-1 liquid phase.

The area of the peaks (always very symmetrical) was determined by the height-times-width-at-half-height method. The relative response factors (RRF) for all the naphthalenes were determined by using standard solutions of authentic samples and assuming identical RRF for isomeric compounds. All reported naphthalene yields are the averages of three injections and are reproducible within 10%. All other compounds have been assumed to have RRF of 1.00. The estimated errors in the yields of these products are 10–20%, except for the smaller compnents (3% yield or less), fcr which the error could be 30–40%. The error reported for the dimethylnaphthalenes **20** and **21** is the estimated standard deviation.[56]

Materials. The following known starting materials and authentic samples of products were synthesized by the indicated literature procedures, or where modified preparations were used, the physical properties (mp, NMR, MS) were identical with cited literature values or were consistent with the expected structures: benzenediazonium-2-carboxylate (**2**),[57] benzothiadiazole dioxide (**3**),[47] diphenyliodonium-2-carboxylate (**4**),[26] 1-aminobenzotriazole (**9**),[46] phenyl *o*-iodobenzoate (**11**),[58] 3,4-benzocoumarin (**15**),[59] 4-methyldiphenyliodonium-2-carboxylate (**18**),[60] *o*-(2-thienyl)benzoic acid (**22**),[61] 2-phenylthiophene (**25**),[62] *o*-(2-thienyl)biphenyl (**27**),[38] 1-naphthyl phenyl sulfide (**28**),[63] 2-naphthyl phenyl sulfide (**29**),[64] 2-methoxythiophene (**41**),[65] 2,5-dimethoxythiophene (**43**),[45] 1,4-dimethoxynaphthalene (**44**),[66] biphenylene (**46**),[46] 2,5-diphenylthiophene (**50c**),[67] 2-phenylbenzo[*b*]thiophene (**52**),[68] methyl *o*-(2-thienyl)benzoate,[33] 2-iodo-4-methylbenzoic acid.[69] All other materials were commercially available.

Thermolysis of Diphenyliodonium-2-carboxylate (4) in Thiophene (Standard Procedure). The anhydrous precursor **4**[26] (50 mg) that had been stored over P_2O_5 in a vacuum was mixed in a ca. 13-mL thick-walled glass vial (12 mm i.d., 16 mm o.d.) with 3 mL of distilled thiophene that had been kept over 4A molecular sieves for at least 24 h. The vial was evacuated to ~1 mm, cooled in liquid N_2, flame-sealed, warmed to room temperature, wrapped in wire gauze, and immersed in a stirred oil bath at 220 ± 20 °C to the level of the liquid contents (**CAUTION**: pressure buildup; use shield and eye protection in case of tube failure). The precursor **4** was only partially soluble at room temperature, but dissolved when the internal temperature reached 100–120 °C. After 15 min, the vial was removed from the oil bath, allowed to cool, and then placed in liquid N_2 for opening. Portions of the yellow to brown contents were mixed with the indicated internal standard and analyzed by VPC on columns A (200 °C) or C (210 °C) or by GC–MS as follows: for naphthalene, 2-methylnaphthalene and VPC; for **22** (as methyl ester after treatment of acid fraction with diazomethane), anthraquinone and VPC; and for all other products, dibenzothiophene (**45**) and GC–MS. The results are given in Scheme II. All products except **23** and **27** were identified by GC–MS comparisons with authentic samples. Naphthalene was also isolated by preparative VPC and identified by its spectral properties. The mass spectrum of **23** had $M^+ = 280$ (4) and $M - OPh$ 187 (100) and was similar to that of the methyl ester of **22**, which also had a base peak at $M - OCH_3$. A comparison of the mass spectrum of **27** with those of the phenyl naphthyl sulfides **28**[63] and **29** and of 2,5-diphenylthiophene (**50c**)[70] shows significant differences: **27**, 236 (100), 235 (56), 234 (27), 203 (69), 202 (63); **28** or **29**, 236 (100), 235 (50), 234 (30), 203 (12), 202 (15), 115 (21); **50c**, 236 (100), 235 (3), 234 (4), 203 (3), 202 (6), 121 (30), 115 (10).

Thermolysis of a mixture of iodobenzene (34 mg), naphthalene (29 mg), **26** (11 mg), **16** (15 mg), and **15** (15 mg) in 9 mL of thiophene for either 15 min at 200 °C or 40 min at 190 °C produced neither color nor a change in composition as measured by VPC on column C at 210 °C.

Thermolysis of 4 in Benzene. The standard procedure was followed except that the thiophene was replaced with benzene and the reaction time was extended to 30 min. Benzobarrelene (**30**) was identified from its mass spectrum[71] and its yield determined by VPC using naphthalene as an internal standard.

5-Methyldiphenyliodonium-2-carboxylate (17) was prepared from 2-iodo-4-methylbenzoic acid[69] according to the procedure used for **4**[26] in 23% yield: mp 222–223 °C dec after two recrys-

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tallizations from chloroform; IR 3060, 1620, 1480, 1445, 1350, 775, 735; ^{1}H NMR ($CDCl_3$-DMSO-d_6, 1:1) 7.86 (m, 3), 7.46 (m, 3), 7.18 (d, 1, J = 7), 6.25 (s, 1), 2.09 (s, 3); ^{13}C NMR[27] 166.7, 144.8, 137.1, 132.6 (2), 131.8 (2), 131.2, 126.1, 115.7, 115.1, 21.5.

Anal. Calcd for $C_{13}H_{10}IO_2$: C, 49.7; H, 3.3. Found: C, 50.1; H, 3.4.

Thermolysis of 17 and 18 in 3-Methylthiophene. Each of these precursors was separately reacted according to the standard procedure, with the thiophene replaced by 3-methylthiophene. The isomeric dimethylnaphthalenes **20** and **21** were identified by GC–MS comparisons with authentic samples and their *combined* yields determined by VPC (column A, 160 °C, 2-methylnaphthalene internal standard) to be 19% from **17** and 16% from **18**. Separation of **20** and **21** was achieved at 175 °C with a tandem arrangement of column B followed by column D[72] and revealed the **20**:**21** ratio to be 50.2:49.8 ± 1.1% from **17** and 50.4:49.6 ± 0.7% from **18**. GC–MS analysis of the remaining products in either reaction mixture indicated, by rationalization of the fragmentation patterns,[1] the presence of another dimethylnaphthalene (1.3% from **17** and 0.9% from **18**), a methylbenzo[*b*]thiophene (<0.5%), two ene products (2.5, 2.8%), three or four double ene products[21a,25] (3.5, 7.5, and 3.5% from **17** and 3, 5, and 8% from **18**), two solvent dimers analogous to **53** (0.7, 0.5%) and two different methyl analogues of **11** (1.4%), one from **17** and one from **18**. The yields were VPC determined as above except for the last two products, which were quantified on the GC–MS by using **20** as an internal standard.

(*o*-Fluorophenyl)lithium (8) and Thiophene. Dropwise addition of 2.9 mL of a 1.6 M hexane solution (4.6 mmol) of BuLi diluted with 2 mL of THF over a 10-min period to a cooled (−30 °C) mixture of thiophene (7 mL), THF (1 mL), and *o*-bromofluorobenzene (**7**) (0.66 g, 3.86 mmol) in a 25-mL, three-necked flask, fitted with a low-temperaure thermometer, a dropping funnel, and a magnetic stirrer, gave after an additional 15 min a red solution, which was quenched with CO_2. The resulting yellow solution was washed with water, dried, and evaporated to dryness to leave 0.33 g of an oil. Preparative VPC (column 1, 180 °C) of 0.19 g of this oil led to the separation of 25 mg (13%) of a compound identified as *o*-fluorobiphenyl (**32**) on the basis of its MS: m/e 172 (100), 171 (45), 170 (21), 152 (5), 151 (5), 85 (14). 2-Phenylthiophene (**25**) (10 mg, 2.7% yield), mp 66–69 °C (lit.[73] mp 70 °C), was also isolated and was identified by MS comparison with an authentic sample. Acidification of the water extracts separated 0.2 g (40%) of a white solid, which was crystallized from water, mp 124–126.5 °C (lit.[74] mp 129–130 °C), and identified as 2-thenoic acid (**36**) by ^{1}H NMR and MS comparison with an authentic sample.

In another run, the precursor **8**, preformed at −78 °C in THF (2 mL) from the same amount of **7**, was transferred through a cooled transfer line (−78 °C) into 11 mL of refluxing thiophene. Evaporation of the solvents and column chromatography (10 g of SiO_2, ligroin) led to the separation of 135 mg (50%) of a mixture of triphenylene (**33**) and *o*-fluorobiphenyl (**32**), as concluded from ^{1}H NMR and VPC analysis.

(*o*-Fluorophenyl)lithium (8) and 2,5-Dimethylthiophene (50b). Except for the use of **50b** for thiophene, the reaction was run similarly to that above and the neutral fraction chromatographed on silica gel with ligroin–methylene chloride–methanol gradient elution. The early fractions contained 91 mg of a mixture of **32** (13%) and **37** (8%) [MS (20 eV): 252 (46), 250 (46), 171 (74), 170 (100)] as determined by VPC (column 1, 220 °C). Later fractions contained mixtures of **33** and halopolyphenyls according to their ^{1}H NMR and MS spectra.

(*o*-Fluorophenyl)magnesium Bromide (5) and Thiophene. A solution of 1.32 g (7.7 mmol) of *o*-bromofluorobenzene (**7**) in 17 mL of a 20:7 thiophene–THF mixture was added dropwise to 0.2 g (8.2 mg-atom) of freshly cut Mg in some of the same solvent mixture at reflux in a 50-mL flask with the usual precautions against air and moisture. After 12 h, the reaction mixture was washed with water, dried, and analyzed by VPC (column 4, 160 °C, 2-methylnaphthalene, internal standard) to reveal naphthalene in 3.3% yield.

In another run, in which equimolar amounts of **7** and thiophene were used, the reaction was complete in about 20 min. The washed and dried organic solution was evaporated to dryness, to leave a yellow oil, from which crystallization with hot EtOH separated 30 mg (5%) of triphenylene, identified by MS and ^{1}H NMR comparison with an authentic sample. Removal of the solvent gave a residue, which was sublimed and analyzed by MS to show peaks corresponding to the molecular ions of the polyphenyl halides **40** (X = F, n = 1–4) (172, 248, 324, 400) and **40** (X = Br, n = 1–3) (232/234, 308/310, 384/386).

(*o*-Fluorophenyl)magnesium Bromide (5) and 2-Methoxythiophene (41). Magnesium (0.2 g, 8.2 mg-atom) was suspended in a refluxing solution of 2-methoxythiophene (**41**) (1.76 g, 15.4 mmol) in 8 mL of dry THF, and the mixture was kept under a N_2 blanket. A solution of 1.32 g (7.7 mmol) of *o*-bromofluorobenzene (**7**) in 5 mL of THF was added dropwise over a period of 3 h, and the mixture was heated at reflux overnight. After being quenched with saturated NH_4Cl solution, the mixture was dried and concentrated before being analyzed by VPC (column 3, 195 °C, 2-methylnaphthalene internal standard). 1-Methoxynaphthalene (**42**) (14%), diphenyl sulfide (**26**) (1.3%), and dibenzothiophene (**45**) (4%) were identified by comparison of their retention times with those of authentic materials. The last compound was also separated by preparative VPC, and the structure was confirmed by MS, IR, and UV comparison with a true sample.

(*o*-Fluorophenyl)magnesium Bromide (5) and 2,5-Dimethoxythiophene (43). Mg (0.20 g, 8.22 mg-atom) was suspended in a refluxing solution of 1.38 g (7.69 mmol) of 2,5-dimethoxythiophene (**43**) in 8 mL of dry THF. The *o*-bromofluorobenzene (**7**) (1.32 g, 7.96 mmol) dissolved in 5 mL of THF was then added slowly, and the reaction mixture was stirred overnight at room temperature. Quenching with 10% aqueous HCl and ether extraction afforded a brown liquid, which was analyzed by VPC (column 4, 185 °C) with 2-methoxynaphthalene as internal standard. The product, 1,4-dimethoxynaphthalene (**44**) (10%), was identified on the basis of the identity of its retention time with that of authentic material. This reaction could not be consistently reproduced due to failure of the Grignard reagent **5** to form.

1-Aminobenzotriazole (9) and Thiophene. 1-Aminobenzotriazole (**9**) (0.20 g, 1.49 mmol) was dissolved in 3 mL of dry thiophene. Solid lead tetraacetate (0.66 g, 1.49 mmol) was added in small portions with vigorous stirring over 5 min, and the resulting mixture was diluted with CH_2Cl_2 and filtered. The filtrate was extracted with saturated $NaHCO_3$ and brine, dried over Na_2SO_4, and analyzed by VPC (column 4, 160 °C), with 2-methylnaphthalene as internal standard. Phenyl acetate (**47**) (25%), naphthalene (0.9%), and biphenylene (**46**) (38%) were identified by comparison of their retention times with those of authentic samples. In a similar reaction in the presence of 0.60 g (4.34 mmol) of K_2CO_3, the yield of phenyl acetate was 11.6%, of naphthalene 0.6%, and of biphenylene 61%.

1-Aminobenzotriazole (9) and 2,5-Dimethoxythiophene (43). 1-Aminobenzotriazole (**9**) (0.20 g, 1.49 mmol) was dissolved in 2 mL of dry CH_2Cl_2, together with 0.43 g (2.98 mmol) of 2,5-dimethoxythiophene (**43**). Solid K_2CO_3 (0.60 g, 4.34 mmol) was suspended in the mixture. A solution of 0.66 g (1.49 mmol) of lead tetraacetate in 3 mL of dry CH_2Cl_2 was added dropwise over 75 min. The dark reaction mixture was filtered and concentrated for VPC analysis (column 4, 190 °C, 2-methylnaphthalene internal standard), which revealed phenyl acetate (**47**) (8%), biphenylene (**46**) (42%), and 1,4-dimethoxynaphthalene (**44**) (3.4%).

Benzothiadiazole Dioxide (3) and Thiophene. The stable benzothiadiazoline dioxide (0.545 g, 3.20 mmol) was oxidized with $Pb(OAc)_4$ (1.40 g, 3.16 mmol) in 30 mL of dry CH_3CN as described by Wittig.[47] The resulting benzothiadiazole *S*-dioxide (**3**) was then dissolved in 20 mL of thiophene at 10 °C, and the temperature was allowed to rise to room value overnight. The dark reaction mixture was extracted with 10% aqueous NaOH, concentrated, and VPC analyzed (column 4, 160 °C, 2-methylnaphthalene internal reference). Naphthalene (2%), diphenyl sulfide (**26**) (1%), and dibenzothiophene (**45**) (1.7%) were identified by comparison

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of their retention times with those of authentic samples. An unidentified component was also present in an amount comparable to the above.

The alkaline solution was acidified with concentrated HCl and extracted with CH_2Cl_2 to give 156 mg of a bright red paste, which after esterification with CH_2N_2 was chromatographed through 27 g of neutral Al_2O_3 (CH_2Cl_2), to give 96 mg of an oil. Preparative plate chromatography (SiO_2, CH_2Cl_2) afforded 17 mg (2.2%) of an impure oil, tentatively identified as methyl *o*-(2-thienyl)benzenesulfinate (**48**, R = CH_3): IR (neat) 1470, 1130 (S=O),[75] 970, 760; MS (20 eV) 240 (7), 239 (10), 238 (68), 207 (41), 190 (22), 179 (55), 178 (28), 174 (42), 163 (18), 147 (42), 135 (24), 115 (100); ^{1}H NMR 8.01 (m, 1), 7.01–7.50 (m, 6), 3.44 (s) and 3.40 (s) (total integration 3 H) (diasterotopic OMe possibly due to hindered rotation around the thienyl–phenyl bond?).

Benzenediazonium-2-carboxylate (2) and Thiophene. Benzenediazonium-2-carboxylate (**2**), prepared[57] from 3 g of anthranilic acid (21.9 mmol) and 4.11 mL of isoamyl nitrite (30.6 mmol) in THF, was washed twice with cold thiophene and was then suspended in about 40 mL of this solvent at 0 °C. The cold slurry was added in portions to a 100-mL, three-necked flask swept with N_2, in which 10 mL of thiophene had been brought to vigorous reflux. Violent foaming took place during the addition, and a tarry material separated. An additional 10 mL of thiophene was used to rinse the final portion of **2** into the reaction flask. The dark reaction mixture was cooled, diluted with ether, filtered, and extracted with 10% aqueous NaOH. The organic phase was analyzed by VPC (column 2, 240 °C, 2-methylnaphthalene as internal standard). Naphthalene (3%) was identified by comparison of its retention time with that of authentic material and by preparative VPC isolation and ^{1}H NMR, UV, and MS comparison with the authentic compound. No other neutral compounds of significant intensity were detected.

The NaOH solution was acidified with concentrated HCl and extracted with CH_2Cl_2, and the organic layer was esterified with CH_2N_2 and analyzed by VPC (column 1, 250 °C). The methyl esters of *o*-(2-thienyl)benzoic acid (**22**, CH_3 for H), benzoic acid, and salicylic acid were detected in 12, 0.5, and 2% yield, respectively, and identified by enhancement with authentic materials.

When the above reaction was carried out in thiophene at 50 °C, instead of at reflux temperature, the yield of naphthalene was only 1.8%, and *o*-thienylbenzoic acid (**22**) was isolated in 17% yield by column chromatography of the acidic fraction (SiO_2, $CHCl_3$) and identified by MS, ^{1}H NMR, and IR comparison with an authentic sample.

The reaction of **2** in 50:50 thiophene–dichloroethane was carried out in the same way at reflux, by using the solvent mixture instead of pure thiophene. The following compounds were identified by VPC comparison with authentic materials, as described above: naphthalene (5%), **22** (3%), salicylic acid (1%), benzoic acid (1.5%), *o*-chlorobenzoic acid (0.6%), and chlorobenzene (0.7%).

Benzenediazonium-2-carboxylate (2) and 2,5-Dichlorothiophene (50a). Precursor **2** was prepared as in the reaction with thiophene, suspended in 20 mL of 1,2-dichloroethane, and added portionwise to 20 mL of 2,5-dichlorothiophene (**50a**) at 85–90 °C. After extraction with 10% aqueous NaOH and H_2O, the mixture was concentrated to 2 mL and chromatographed through 50 g of SiO_2 with ligroin. The first fraction contained 78 mg (3.6%) of 1,4-dichloronaphthalene (**51**): ^{1}H NMR 8.14 (dd, 2), 7.50 (dd, 2), 7.34 (s, 2); ^{13}C NMR 131.7, 131.0, 127.8, 125.9, 125.0 (lit.[76] 131.6, 130.9, 127.7, 125.9, 125.0); MS 200 (12), 198 (66), 196 (100), 163 (12), 161 (34), 126 (66). From a later fraction, a small amount (1%) of dibenzothiophene (**45**) was isolated and identified by ^{1}H NMR and MS comparison with authentic material.

Benzenediazonium-2-carboxylate (2) and 2,5-Dimethylthiophene (50b). Precursor **2** was prepared as in the reaction with thiophene and the slurry added in portions to 6 mL of **50b** maintained at 90 °C. An additional 5 mL of **50b** was used for the final rinsing. After dilution with ether, filtration afforded 440 mg of a brown, powdery material, which sinters at 170–190 °C, and whose IR spectrum shows absorptions in the carbonyl region. After extraction with 10% aqueous NaOH and water, the reaction solution was concentrated on a Kugelrohr apparatus at 100–110 °C and ambient pressure. The residue (about 10 mL) was chromatographed through 100 g of SiO_2 by gradient elution with petrolum ether, CCl_4, and $CHCl_3$. A fraction of 186 mg appearing after unreacted **50b** was subjected to preparative VPC (column 5, 180 °C) to give diphenyl sulfide (**26**) (3.8%), identified by ^{1}H NMR, IR, and MS comparison with an authentic sample, and 24 mg of the solvent dimer **53**: ^{1}H 6.50 (br s, 2), 6.42 (s, 1), 3.86 (s, 2), 2.38 (s, 3), 2.34 (s, 3), and 2.31 (s, 3) [lit.[53] (CCl_4) 6.38 (s, 1), 6.33 (s, 1), 6.30 (s, 1), 3.77 (s, 2), 2.38 (s, 3), 2.33 (s, 3), and 2.28 (s, 3)]; MS 224 (7), 223 (12), 222 (59), 221 (13), 207 (85), 125 (21), 124 (100), 111 (33), 59 (30).

Benzenediazonium-2-carboxylate (2) and 2,5-Diphenylthiophene (50c). To a refluxing solution of 2.6 g (11 mmol) of 2,5-diphenylthiophene (**50c**) in 15 mL of 1,2-dichloroethane was added, in portions, over 30 min, a slurry, in 3 mL of the same solvent, of **2** prepared[57] from 1.5 g (11 mmol) of anthranilic acid. On cooling, the clear red solution deposited 0.73 g of unreacted **50c**. The solution was extracted with 10% aqueous NaOH and evaporated to dryness, and the sticky residue triturated with 50 mL of hot EtOH. An additional 1.28 g of **50c** remained undissolved or precipitated on cooling of the ethanolic solution. Evaporation of the ethanol left 750 mg of residue, which was chromatographed through 32 g of SiO_2, with petroleum ether–CH_2Cl_2, 96:4, as eluant. The first 70 mg contained **50c** and 2-phenylbenzothiophene (1%) (**52**), identified after purification by preparative plate chromatography (SiO_2, petroleum ether) by MS and UV comparison with the authentic material. The next fraction from the column was identified as pure 2,5-diphenylthiophene (**50c**) (100 mg, 81% total recovery). In a third fraction, 60 mg (0.8%) of **54** was obtained as a yellow solid, mp 147–148 °C from cyclohexane: ^{1}H NMR[77] 8.66 (d, 1), 8.64 (d, 1), 8.31 (dd, 1), 8.12 (s, 1), 8.09 (d, 1), 7.80 (d, 2), 7.5–7.7 (d, 4), 7.46 (t, 2), 7.35 (t, 1); ^{13}C NMR[77] 143.3, 136.1, 135.9, 134.3, 129.1, 129.0, 128.64, 128.57, 128.1, 128.0, 127.2, 127.1, 126.3, 126.2, 126.0, 124.2 (2), 123.6, 123.5, 118.7; MS 312 (8), 311 (27), 310 (100), 309 (9), 308 (23), 155 (58), 154 (28), 153 (10); IR 1605, 1505, 1485, 1450, 1265, 1245, 825, 750 (o-subst), 720, 685 (monosubst).

Anal. Calcd for $C_{22}H_{14}S$: C, 85.1; H, 4.5. Found: C, 85.0; H, 4.7.

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(77) These spectra were taken on a Varian XL-300 instrument at 299.936 (proton) and 75.427 (carbon) MHz; the structure assignment is also supported by a 2D NMR analysis to be published elsewhere.