Homolytic Substitution Reactions in Heterocyclic Series. XII.[1] Heteroarylation of Thiophene

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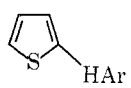
Heteroaryl radicals formed by aprotic diazotization of the corresponding heterocyclic amines in the presence of amyl (or isoamyl) nitrite substitute homolytically on thiophene with the formation of 2-heteroarylthiophenes as main reaction products in overall yields from 20 to 50%. The results of competitive experiments indicate that the reactivity of thiophene in this reaction at 70–80° is slightly higher than that of benzene regardless of the nature of the respective heteroaryl radical. The behavior of thiophene in these reactions is somewhat unusual because its reactivity toward heteroaromatic radicals (which are slightly electrophilic) is lower than the reactivity observed with nucleophilic radicals such as cyclohexyl and benzyl and, to a lesser extent, phenyl radicals. Analytical data (GLC, TLC, and mass spectra) for about 20 heteroarylthiophenes are described. Most of the obtained heteroarylthiophenes are new compounds.

Homolytic substitution reactions of thiophene (arylation,[2] thienylation,[3,4] pyridylation,[5] benzylation,[3a,6] thiylation,[7] amination[8]) have demonstrated, in accordance with previous results,[9] the selective reactivity of the 2 position as compared to the 3 position of this heterocycle.

As a continuation of our systematic studies of heteroarylation in the heterocyclic series, we have decided to investigate the behavior of thiophene toward heteroaryl radicals and to use the selective reactivity of the 2 position in thiophene to synthesize new compounds of general formula A in which HAr represents a heterocyclic group.



A

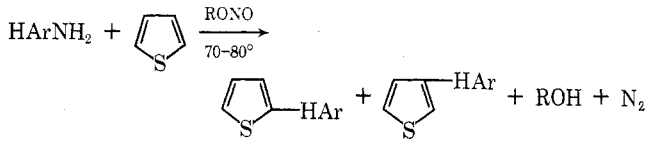
The aprotic diazotization of heteroaromatic amines (pseudo-Gomberg reaction[10,11]) seems to be a better source of heteroaryl radicals than other traditional sources. Our previous work on homolytic thiazolylation reactions in the aromatic[12] and pyridine[1a] series has shown that this radical source possesses many advantages: (i) the amines are generally easily available (commercially or by synthesis), (ii) the reactions are carried out in a homogeneous medium, and (iii) the yields are acceptable. Furthermore, competitive reactions with the system benzene–thiophene should make it possible to study the relative reactivity of these radicals and to compare such results with those obtained in other homolytic substitution reactions.

Results and Discussion

Heteroarylation Products. Decomposition of Heterocyclic Amines in Thiophene in the Presence of Amyl (or Isoamyl) Nitrite. The experimental conditions of this reaction were identical with those previously used in analogous studies in the aromatic and pyridine series. The heteroarylamines were decomposed at 70–80° in excess thiophene in the presence of a slight excess of the nitrite (Table I).

In addition to small amounts of by-products, separation of the crude reaction mixture by preparative thin layer chromatography (TLC) yielded a mixture of two isomers whose structures were assigned on the basis of GLC data and mass spectra (see Assignment of Structures and Mass Spectra).

Table I
Overall Yields of Heteroarylthiophenes Obtained from Aprotic Diazotization of Heteroarylamines in Excess Thiophene at 70–80° [a]



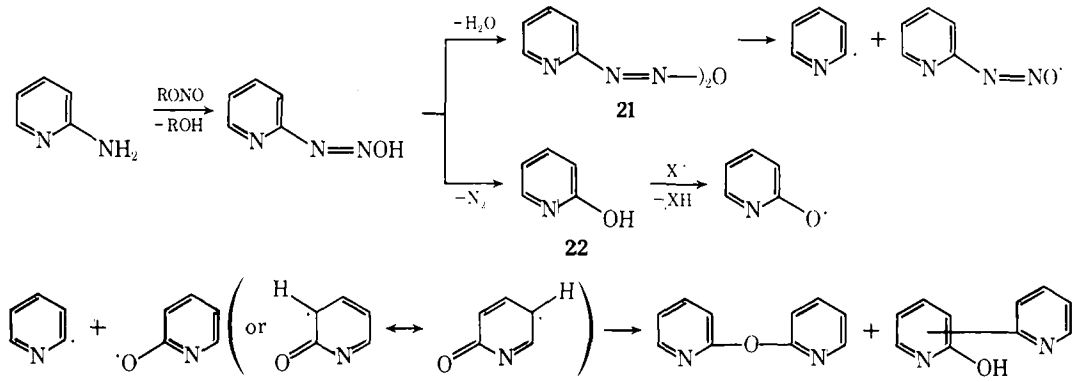
1-10 11-20

Compd	Heterocyclic radical, HAr	Yield, %
1a, 11a	2-Thiazolyl	25
1b, 11b	4-Methyl-5-acetyl-2-thiazolyl	35
1c, 11c	4-Methyl-5-carbethoxy-2-thiazolyl	35
1d, 11d	5-Bromo-2-thiazolyl	20
2, 12	2-Benzothiazolyl	40
3, 13	3-Methyl-5-isothiazolyl	30
4, 14	3,4-Dimethyl-5-isoxazolyl	40
5a, 15a	2-Pyridyl	20
5b, 15b	3-Methyl-2-pyridyl	15
5c, 15c	4-Methyl-2-pyridyl	
5d, 15d	5-Methyl-2-pyridyl	
5e, 15e	6-Methyl-2-pyridyl	
5f, 15f	5-Chloro-2-pyridyl	25
6, 16	3-Pyridyl	42
7, 17	3-Quinolyl	45
8, 18	8-Quinolyl	50
9, 19	2-Pyrazinyl	25
10, 20	2-Pyrimidyl	30

[a] Determined by GLC using an internal standard (usually biphenyl) on PMPE (six ring) or Apiezon L columns. These yields were not altered when reactions were carried out in the presence of oxidizing agents.

Some of the products so obtained were previously described compounds. Thus, 2- and 3-(2′-pyridyl)thiophenes were obtained in low yields by reaction between appropriately substituted thiophenes and pyridine,[5a,13] while 2- and 3-(3′-pyridyl)thiophenes were prepared (47% yield)[5a] using a modified Gomberg reaction generating the 3-pyridyl radical in thiophene according to the procedure described by Rapoport and coworkers[14] for 3-phenylpyridine. These two latter compounds have also been obtained by

Scheme I
By-products Formed in Aprotic Diazotization of 2-Aminopyridine in the Presence of Isoamyl Nitrite



photochemical decomposition of 3-iodopyridine in thiophene.[5b] A synthesis of 2-(2′-thiazolyl)thiophene has been reported.[15] All the other heteroarylthiophenes described in this study seem to be new compounds. Some overall yields reported in Table I are of the same order as those obtained in arylation reactions (20–50%).[11] The similarity between the two reactions is even more striking when isomer ratios are compared as shown in Table II.

Table II
Isomer Ratios in the Arylation and Heteroarylation of Thiophene at 70–80°

Radical	Isomer amounts, %[a] 2	3	Column (temp, °C)[b]
Phenyl	90 (93.1)	10 (6.9)	B, B′ (180)
p-Tolyl	91.6 (93)	8.4 (7)	A, B (190)
m-Methoxyphenyl	88	15	C (200)
p-Methoxyphenyl	87.5 (91)	12.5 (9)	C (200)
m-Nitrophenyl	88.4 (96)	11.6 (4)	A (190)
p-Nitrophenyl	83 (96)	17 (4)	A (190)
2-Thiazolyl	90	10	B′ (200)
3-Pyridyl	85	15	B, B′, C (190)
3,4-Dimethyl-5-isoxazolyl	85	15	C (200)
3-Quinolyl	85	15	A (200)

[a] Values given in parentheses correspond to those reported by Tiecco and coworkers for the same source of aryl radicals but at 30°.[2] [b] See Experimental Section.

In each case, a mixture of two isomers is obtained, always in the same ratio (87% of the 2 isomer and 13% of the 3 isomer), regardless of the radical structure (within the experimental error ±2%).

In these reactions, as in all other homolytic reactions of this type, a certain number of secondary products are also formed. Thus, in the case of azaaromatic amines such as 2-aminopyridine (or its methyl and chloro derivatives), 2-aminopyrimidine, and 2-aminopyrazine, which are resistant toward diazotization or form oxygen-containing products (mainly the corresponding hydroxy derivatives[16]), symmetrical heterocyclic ethers and, to a lesser extent, hydroxy compounds have been found and identified among reaction products.[17]

For example, in the case of 2-aminopyridine (see Scheme I) these products represent an overall yield of 30–35%. The presence of 2-hydroxypyridine and 2-alkoxypyridine was also detected. The existence of these by-products explains why the yields are lower than those observed with other heteroarylamines.

Furthermore, various tars and colored products (easily visible on TLC), as well as bis heterocyclic compounds (traces only) arising from the dimerization of heteroaryl radicals, and the corresponding unsubstituted heterocycles are also formed. The formation of 2,5-disubstituted products observed by certain authors[4,18,19] in homolytic substitution reactions of thiophene cannot be excluded. Finally, no dithienyls could ever be detected contrary to what is observed in thermal decomposition of aryl or heteroaryl peroxides.[2,20,21]

Scheme II
Aprotic Diazotization of Heterocyclic Primary Amines in the Presence of Thiophene (ThioH)

$$HArNH_2 + R{-}O{-}NO \xrightarrow{-H_2O}$$

$$HAr{-}N{=}N{-}OR \rightleftharpoons HArN_2^+RO^- \quad (23)$$

$$HAr{-}N{=}N{-}OR \xrightarrow{-N_2} HAr\cdot + RO\cdot$$

$$HArN_2^+RO^- + HArNH_2 \xrightarrow{-ROH} HAr{-}N{=}N{-}NHHAr \ (24) \xrightarrow{-N_2} HAr\cdot + HArNH\cdot$$

(a) Coupling in solvent cage

$$HAr\cdot + HArNH\cdot \longrightarrow (HAr)_2NH\ (25) + HAr{-}HArNH_2\ (26)$$

$$HAr\cdot + RO\cdot \longrightarrow HArOR$$

$$2(HAr\cdot) \longrightarrow HAr{-}HAr$$

(b) Radical reaction out of cage

$$HAr\cdot + ThioH \longrightarrow [HArThioH]\cdot\ (27) \xrightarrow{X\cdot} HAr{-}Thio + XH$$

with X· = RO· or HArNH·

Mechanism. It is now well established[22] that most five-membered and some six-membered heterocyclic amines such as 3-aminopyridine and 3-aminoquinoline which are readily diazotized behave like normal aromatic amines[10,23,24] and react via diazoate (**23**) and triazene (**24**) intermediates according to Scheme II.

However, no systematic studies of the mechanism of this reaction have been carried out. When these reactions are carried out at low temperatures (0–20°) with isoamyl nitrite in aqueous acetic acid or with sodium nitrite in a dilute acid solution, heteroaryltriazenes are quickly formed. They have been isolated for the following amines: 3-aminopyridine,[23,25] 5-amino-3,4-dimethylisoxazole,[25] 3-amino-1*H*-pyrazole,[26] various substituted 3-aminotriazoles,[27,28] 2-methyl-5-aminotetrazole,[29] 5-aminoisothiazoles,[25,30] and 5-amino-1,2,4-thiadiazoles.[31] The triazenes then undergo thermal decomposition with the formation of nitrogen, heteroaryl, and heteroarylamino radicals.[25]

Table III
Relative Reactivity of Thiophene (with Respect to Benzene) toward Heterocyclic Radicals[a]

Radical, HAr	Relative reactivity[b]
2-Thiazolyl	0.85
5-Bromo-2-thiazolyl	1.3
5-Carbethoxy-4-methyl-2-thiazolyl	1.1
5-Acetyl-4-methyl-2-thiazolyl	1.1
2-Benzothiazolyl	1.0
3,4-Dimethyl-5-isoxazolyl	1.4
3-Methyl-5-isothiazolyl	1.35
1-Methyl-2(1(*H*),3,4-triazol)yl	0.8
2-Pyridyl	0.95
3-Methyl-2-pyridyl	0.75
4-Methyl-2-pyridyl	1.1
5-Methyl-2-pyridyl	1.0
5-Chloro-2-pyridyl	1.15
6-Methyl-2-pyridyl	1.05
3-Pyridyl	1.35
2-Pyrimidyl	1.25
2-Pyrazinyl	1.15
3-Quinolyl	1.35
8-Quinolyl	1.70

[a] Obtained by aprotic decomposition of the corresponding heteroaromatic amines ($\sim 10^{-2}$ *M*) in an equimolar mixture of benzene and thiophene (2 hr at 70–80°). [b] Overall relative reactivity of thiophene toward HAr as compared with that of benzene (=1.0).

Table IV
Relative Reactivity of Thiophene (with Respect to Benzene) toward Aryl and Alkyl Radicals[a]

Radical	Relative reactivity	Radical	Relative reactivity
Phenyl	1.4[b]	1-Naphthyl	1.9
4-Methylphenyl	1.45[b]	2-Naphthyl	1.5
2-Methoxyphenyl	1.2	2-Biphenylyl	2.2
3-Methoxyphenyl	1.16	4-Biphenylyl	1.7
4-Methoxyphenyl	1.06[b]	Cyclohexyl	3.0[c]
2-Acetylphenyl	5.0	3-Cyclohexenyl	2.0[c]
3-Nitrophenyl	1.96	Benzyl	9.0[c]
4-Nitrophenyl	1.3[b]		

[a] Cf. footnotes *a* and *b*, Table III. [b] The corresponding values found by Tiecco and coworkers[2] using the same aryl radical source but at 30° are 2.6 (C_6H_5), 2.4 (4-MeC_6H_4), 1.7 (4-$MeOC_6H_4$), 3.6 (4-$NO_2C_6H_4$). At 40° we found the relative reactivity of thiophene toward phenyl radical equal to 1.75. [c] These radicals were generated by photochemical decomposition of cyclohexane, cyclohexene, or toluene, respectively, in the presence of di-*tert*-butyl peroxide.[3a,37a]

Recombination of these radicals at the position with high unpaired electron density, in the solvent cage, gives the secondary amine (**25**), while the mesomeric forms of heteroarylamino radicals lead to the amino derivatives (**26**). A similar behavior of this type of radicals has been observed in thermal or photochemical rearrangement of diazoamino compounds,[10a] *N*-α-phenethylaniline,[32] *N*-chloroacetanilide,[33] 3-acetamidopyridine,[34] and aryl ethers.[32,35] However, contrary to what is observed with aniline or its N-substituted derivatives, we were not able to show the formation of such by-products, probably because of a longer lifetime of heteroaryl radicals under study. These radicals migrate out of the solvent cage and substitute homolytically on the thiophene ring to give the intermediate σ complex (**27**) which is then oxidized by sufficiently active radicals (alkoxy or heteroarylamino radicals) before dimerization or disproportionation (cf. Scheme I). The presence of commonly used agents (copper, lead tetraacetate, nitrobenzene, etc.) does not alter the reaction yield. This insensitivity to oxidizing agents has also been observed[11f] in the decomposition of pentafluoroaniline at 80° in benzene in the presence of amyl nitrite.

Table V
Relative Retention Times (α_r) of Some 2-Heteroarylthiophenes and Heteroarylbenzenes on Different Columns

Substituent	2-Heteroarylthiophene (α_r relative to 2-phenylthiophene) A (160°)[a]	2-Heteroarylthiophene (α_r relative to 2-phenylthiophene) B′ (200°)[b]	Heteroarylbenzene (α_r relative to biphenyl) A (160°)[a]	Heteroarylbenzene (α_r relative to biphenyl) B (200°)[b]
Phenyl	1.0	1.0	1.0	1.0
2-Pyridyl	1.4	1.7	1.35	1.65
3-Methyl-2-pyridyl	1.34	1.82	1.31	1.75
4-Methyl-2-pyridyl	2.18	2.7	1.95	2.5
5-Methyl-2-pyridyl	2.27	2.0	2.1	2.1
6-Methyl-2-pyridyl	1.56		1.45	
3-Pyridyl	1.5	1.95	1.48	2.0
2-Pyrimidyl	1.45	1.85	1.38	1.75
2-Pyrazinyl	1.54		1.5	
2-Thiazolyl	1.2	1.52	1.2	1.46
3-Methyl-5-isothiazolyl	1.6		1.54	
3,4-Dimethyl-5-isoxazolyl	2.0		2.1	
5-Chloro-2-pyridyl	*3.0*		*2.8*	
3-Quinolyl	*5.9*[c]		*5.7*	
8-Quinolyl	*5.5*[c]		*5.0*	
5-Bromo-2-thiazolyl		(3.0)		(2.97)
2-Benzothiazolyl		10.4		9.6
4-Methyl-5-carbethoxy-2-thiazolyl		8.2 (7)		8.0 (7)
4-Methyl-5-acetyl-2-thiazolyl		8.0 (7)		8.0 (7)

[a] $\alpha_r = (t'_R)_{HAr\text{-}Thio}/(t'_R)_{2\text{-}Ph\text{-}Thio} \simeq (t'_R)_{HAr\text{-}Ph}/(t'_R)_{Ph\text{-}Ph}$ where t'_R represents the reduced retention time. For biphenyl and 2-phenylthiophene, t'_R = 200 and 220 sec, respectively, on Apiezon L (A) at 160°. [b] Retention times for biphenyl, 2-phenylthiophene, and 3-phenylthiophene on PMPE column (B′) at 200° were 400, 460, and 500 sec, respectively. Values in parentheses are at 220°. Values printed in italics are for 200°. [c] For the isomeric 3-(3′- and 8′-quinolyl)thiophenes α_r = 6.3 and 6.6, respectively.

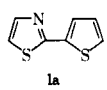
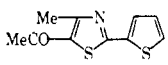
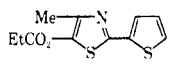
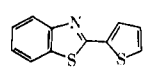
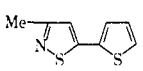
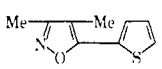
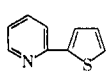
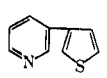
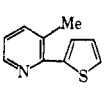
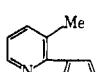
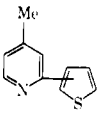
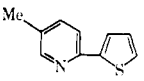
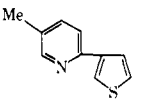
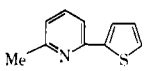
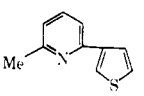
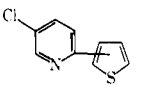
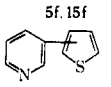
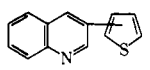
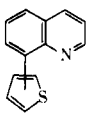
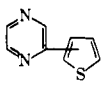
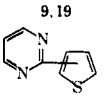
In the case of 2-aminopyridine and other six-membered azaaromatic amines already mentioned, main by-products observed arise from the recombination of 2-pyridyl with 2-pyridyloxy radicals (or their mesomeric forms) generated from diazo anhydride (**21**) and 2-hydroxy derivatives (**22**) (cf. Scheme I) via diazo hydroxide intermediate according to a mechanism similar to that postulated by Rüchardt and coworkers.[36]

Competitive Studies. In order to compare the relative reactivities of the radicals under study, we used the method of competitive reactions with the system benzene–thiophene (equimolar amounts). The experimental conditions were the same as those mentioned above.

The results in Table III show an almost total absence of selectivity of the heteroaromatic radicals toward thiophene, for which the overall reactivity is slightly higher than that of benzene. At the same time the reactivity of the 2 position of thiophene at 80° is roughly three times higher than the reactivity of benzene while that of the 3 position is about three times lower regardless of the nature of the heteroaromatic radical. We have also compared these results with those obtained with hydrocarbon radicals, such as aryl (including biphenyl), benzyl, and cyclohexyl radicals. The latter two were obtained by the photochemical decomposition of di-*tert*-butyl peroxide in toluene[3a] and cyclohexane.[37] These results are presented in Table IV.

It can be seen, first of all, that the relative rates of sub-

Table VI
Mass Spectra of Some 2-Heteroarylthiophene Derivatives, Principal Fragments, and Relative Intensities[a]

Compd	Principal fragments (rel intensity, %)
 1a	169 (10), 168 (10), *167* (96), 110 (4), 109 (3), 69 (5), 60 (6), 59 (5), 58 (100), 57 (5), 45 (8), 39 (5)
 1b	225 (10), 224 (13), *223* (100), 210 (8), 211 (10), 208 (90), 180 (17), 169, 168, 139 (10), 114 (7), 110 (11), 90, 72 (12), 71 (30)
 1c	255 (10), 254 (15), *253* (100), 227, 226, 225 (30), 224 (15), 210, 209, 208 (45), 207 (5), 183, 182, 181 (30), 180 (15), 144, 139, 116 (26), 111 (18), 110 (35), 109 (8), 104, 100, 98 (20), 72 (20), 71 (40), 70 (20), 69 (15), 45 (35)
 2	219 (10), 218 (15), *217* (100), 216 (12.5), 191, 190, 185 (4), 184 (4), 173 (7.5), 172 (5), 140, 109, 108 (32.5), 82 (7.5), 71, 69 (22.5), 58 (10), 43 (5), 44 (10)
 3	183 (11), 182 (12), *181* (100), 180 (5), 153, 149, 148 (6), 142, 141, 140 (30), 110, 109, 108 (8), 96 (35), 82 (5), 74 (9), 69 (9)
 4	181 (4), 180 (10), *179* (100), 138 (6), 122 (8), 121 (6), 111 (50), 110 (44), 109 (12), 96 (9), 85 (6), 83 (7), 77 (8), 68 (17), 66 (11), 51 (7), 45 (8), 43 (8), 42 (11), 41 (13), 40 (8)
 5a	163 (7), 162 (15), *161* (100), 160 (41.6), 135 (8), 134 (6), 133, 128 (10), 117 (26), 116 (10.5), 90 (6.5), 89 (8), 80, 78 (12), 69 (4), 67, 63, 51 (9), 50, 45 (5), 39 (6)
 15a	163 (6.0), 162 (13), *161* (100), 160 (62), 135 (9), 134, 117 (22), 116 (7), 104 (5), 94 (6), 91, 90, 80, 78
 5b	177 (4), 176 (9), *175* (90), 174 (100), 142 (6), 141 (6), 130 (15), 110 (4), 109 (9), 108 (4), 80 (8), 65 (15), 39 (23)
 15b	177 (4.5), 176 (10), *175* (100), 174 (90), 142 (65), 130 (54), 109 (60)
 5c, 15c	177 (6), 176 (16), *175* (100), 174 (30), 173 (6), 160 (4), 149 (4), 147 (4), 143 (5), 131 (6), 130 (9), 109 (7), 92 (4), 81 (4), 65 (6), 51 (3), 45 (3), 39 (9)
 5d	177 (6), 176 (14), *175* (100), 174 (35), 149 (4), 148 (7), 147 (13), 143, 142, 141, 131 (8), 130 (9), 121 (4), 115 (16), 109, 108 (17), 107 (8), 103, 92, 81, 80, 65, 51
 15d	This mass spectrum is very similar to that of its isomer 5d, except for the relative intensities of fragments at 108 (5) and 131 (3).
 5e	177 (7), 176 (4), *175* (100), 174 (30), 160 (4), 149 (3), 147 (3), 143, 142, 141, 131 (7), 130 (9), 108 (6.5), 92 (7), 91 (20), 80, 77, 69, 66, 65, 45, 39
 15e	177 (6), 176 (14), *175* (100), 174 (40), 160 (3), 149, 147, 143, 142, 141, 131 (8), 118, 108 (7), 92, 91 (9), 80, 77, 69, 66, 65, 45, 39
 5f, 15f	198 (12), 197 (35), 196 (16), *195* (100), 171, 162 (6), 160 (9), 151 (10), 133 (4), 116, 115, 114, 113, 89, 76, 69, 63, 62, 58, 51, 50, 45, 39
 6, 16	163 (5), 162 (16), 161 (100), 160 (18.5), 117 (25), 108 (9), 89 (15), 69, 63, 62, 51, 50, 45, 39
 7, 17	213 (7), 212 (17), *211* (100), 210 (17), 183, 167 (9), 166 (9), 140 (4), 105 (6.5), 92 (11), 79 (6), 63, 62, 58, 39
 8, 18	213 (4), 212 (10.5), *211* (70), 210 (100), 178 (28), 141 (10), 140 (14), 139 (14), 101 (14)
 9, 19	164 (6), 163 (10), *162* (100), 135 (10), 109 (55)
 10, 20	164 (5), 163 (8), *162* (100), 161 (4), 135 (3), 110 (7.5), 109 (50), 108 (7), 81 (8), 63, 59, 58, 53, 52, 45, 39

[a] Molecular ions are printed in italics.

stitution of thiophene in the case of aryl radicals are much lower than those observed by Tiecco and coworkers[2] and that the differences in reaction temperature (30° in Tiecco's experiments and 80° in our case) are not sufficient to explain this.

In general, the reactivity of a radical depends on its stability: the lower its stability and the lower its selectivity, the higher is its reactivity.[38] In this respect, the data obtained with cyclohexyl and especially benzyl radicals are in agreement with this principle.

The results obtained by Rüchardt and coworkers[36] on the relative selectivities of aryl and alkyl radicals are similar to our results obtained in the present study. These authors studied the action of structurally very different radicals on the system CCl_4–$CBrCl_3$. They have shown an absence of influence of para substituents on the phenyl radical (except with *o*-tolyl and 2,4,6-trimethylphenyl radicals, where this is due to steric hindrance), and they have also demonstrated that cyclohexyl and benzyl radicals are respectively 4 and 12 times more selective than phenyl radicals in this reaction.[36a]

Assignment of Structures and Mass Spectra. Our assignment of the structures of heteroarylthiophenes was based on three types of evidence:[39] (a) the preferred formation of 2 isomers in free-radical substitutions of thiophene; (b) the GLC data; and (c) the mass spectra.

Distinction between the isomeric 2- and 3-heteroarylthiophenes was primarily based on the well-known fact that in homolytic substitution reactions occurring on the thiophene ring it is the 2 isomer which is the chief reaction product, regardless of the structure of the radical used in the reaction (cf. Table II).

On nonpolar chromatographic columns, the 2 isomers have a shorter retention time than the 3 isomers. According to Martin's additivity principle,[40] retention increments (α_r or ΔI) of a heteroaryl group must be the same regardless of the nature of the molecule to which this heteroaryl group is bonded. Because of this, relative retention times of 2-heteroarylthiophenes (expressed with respect to 2-phenylthiophene as reference) and those of hereroarylbenzenes (expressed with respect to biphenyl as reference) are in good agreement (Table V). For the same reason, a close similarity must exist between the retention times of 3-heteroarylthiophenes (expressed with respect to 3-phenylthiophene as reference) and the above-mentioned data for arylbenzenes and 2-heteroarylthiophenes (on the same column and at the same temperature).

Finally, coupled GLC–mass spectral data were found to be satisfactory for further confirmation of the structures of heteroarylthiophenes. However, GLC columns used in this case were somewhat less efficient than those used for GLC analysis only (cf. Experimental Section). Because of this, the 3 isomers after separation were slightly contaminated with the 2 isomers. Mass spectra recorded for the compounds **5** and **15** were very similar to those observed for other isomeric substituted thiophenes[41] and, therefore, the assignments of structures in this case were based chiefly on mass spectral data.

The mass spectral data obtained for 2-heteroarylthiophenes are summarized in Table VI. All of the heteroarylthiophenes exhibit the parent molecular ions (base peaks) as the most abundant species in their mass spectra. This observation reflects the great stability of the thiophene ring increased by conjugation with another heteroaromatic ring. The low-intensity fragments (except for 2-thiazolyl derivatives) are characteristic of the cleavage of both the thiophene ring ($M^+ - C_2H_2$, $M^+ - HS$, $M^+ - CS$) and of the heteroaryl substituents.[41]

Experimental Section

Reagents. Most reagents and heterocyclic amines were commercial products: *n*-amyl and isoamyl nitrite (Merck), thiophene (Fluka), di-*tert*-butyl peroxide (Fluka AG Buchs), *p*-toluidine (Prolabo), *m*-anisidine (Koch-Light Laboratories Ltd.), *p*-anisidine (Fluka), *p*-nitroaniline (Prolabo), *o*-ethylaniline (Fluka), 2- and 4-aminobiphenyl (Fluka), 2-aminopyridine (Fluka), 3-aminopyridine (Eastman), 4-methyl-2-aminopyridine (Eastman), 3-methyl-2-aminopyridine (Eastman), 5-methyl-2-aminopyridine (Eastman), 2-amino-5-chloropyridine (Aldrich), 3- and 8-aminoquinoline (Eastman), 2-aminopyrimidine (Eastman), 2-aminothiazole and 2-aminobenzothiazole (Fluka), 3-amino-5-methylisoxazole (Fluka), and 5-amino-3,4-dimethylisoxazole (Fluka). 5-Substituted 2-aminothiazoles were prepared according to the methods reported in previous work.[12c]

Heteroarylation Procedure. Synthetic scale reactions were generally carried out in the following manner. Isoamyl nitrite (20 g, 0.17 mol) was added to a stirred mixture of the heteroarylamine (0.1 mol) and 500 ml of thiophene in a 1-l. flask equipped with a reflux condenser. The reaction mixture was kept at room temperature for 24 hr and then refluxed for 1 hr. The cooled mixture was filtered to remove tars and thiophene, and isoamyl alcohol and other volatile products were distilled off on a rotary evaporator. The oily residue was first steam distilled in the presence of an acid to eliminate nonbasic impurities and the steam distillation was repeated in the presence of a base. The organic material was then extracted with ether and treated in the usual manner (see Analysis).

In other experiments, the reaction was allowed to proceed at 75–80° and it was sufficiently exothermic to bring the solution to this temperature without external heating.

The less volatile 2-heteroarylthiophenes were separated from colored by-products by preparative TLC.

Competitive Experiments. The following general procedure was followed. Isoamyl nitrite (0.015 mol) was added to a solution of the heterocyclic amine (0.01 mol) and an equimolar (1:1) mixture of benzene and thiophene (0.2 mol) in a 100-ml round-bottomed flask equipped with a reflux condenser. The reaction was allowed to proceed at 75–80° on a bath until the evolution of gas had ceased. Excess of solvents was distilled off in vacuo. The residue was analyzed by gas chromatography.

To determine isomer ratios and relative reactivities more accurately, 2-heteroarylthiophenes were then separated by preparative TLC. The desired fraction was extracted and examined again by GLC. Generally no difference was found between the two chromatograms. All the reactions were carried out in duplicate.

Experiments with arylamines were performed in a similar manner.

Analysis. Details of the analytical conditions are as follows.

TLC. All reaction mixtures were analyzed by TLC according to Stahl's standard procedure.

Preparative TLC was carried out on silica gel $PF_{254+366}$ plates with benzene as eluent for less polar compounds, and with benzene–methanol (20:1) for more polar compounds. The desired fraction, localized mainly in the middle of the plate, was extracted with acetone and examined again by TLC, GLC, and GLC–MS. The R_f values of some aryl- and heteroarylthiophenes are reported in Table VII.

Table VII
R_f Values of Some Aryl- and Heteroarylthiophenes[a]

Compd	R_f
Biphenyl	0.90
2-Phenylthiazole	0.21
2-(2′-Thiazolyl)thiophene	0.23
3-(2′-Thiazolyl)thiophene	0.16
2,2′-Bithiophene	0.28
3,4-Dimethyl-5-phenylisoxazole	0.25
2- and 3-(3,4-Dimethyl-5-isoxazolyl) thiophenes	0.20, 0.25
2- and 3-(2′-Benzothiazolyl)thiophenes	0.32, 0.35
2- and 3-(4′-Methyl-5′-carbethoxy-2′-thiazolyl)thiophenes	0.14
2- and 3-(2′-Pyridyl)thiophenes	0.14, 0.20
2- and 3-(6′-Methyl-2′-pyridyl)thiophenes	0.26, 0.33

[a] On silica gel $HF_{254-366}$ with benzene as eluent in an unsaturated atmosphere. Values for the Stahl dye-test mixture Desaga were 0.06, 0.14, and 0.46, respectively. With more polar compounds such as pyridyl-, pyrazinyl-, and pyrimidylthiophenes, a mixture of benzene and methanol (20:1) was used as eluent. R_f ranged from 0.50 to 0.60.

GLC. The crude products of these reactions and fractions isolated by preparative TLC were analyzed by gas chromatography using an Intersmat IGC 15 gas chromatograph equipped with a flame ionization detector and coupled with a Vidar Autolab integrator. The following three stainless steel 8-in. columns were used: A was a 7-ft column packed with Apiezon L (5%) on Chromosorb W HMDS (80–100 mesh) precoated with 3% KOH. The retention times of biphenyl on this column at 160 and 200° were 200 and 120 sec, respectively. B and B′ were 5- and 10-ft columns packed with polymetaphenyl ether (PMPE six ring, 5%) on Chromosorb W, AW HMDS (60–80 mesh) (retention time of biphenyl was 400 sec on B′ column at 200°). C was a 5-ft column packed with Carbowax 20M (10%) on Chromosorb Q (80–100 mesh) (retention time of biphenyl on this column was 215 sec at 190°). Other columns were also used (OV 225, SE-30). In all cases, the injector and detector temperature was 250°, carrier gas was hemixal (N_2 + He), flow rate 20–25 ml min^{-1}, inlet pressure 28 psi. Difficulty was experienced in finding a suitable column to separate the 2- and 3-aryl and -heteroarylthiophene isomers. The best separation was obtained on the column B′ for more volatile compounds, while for the less volatile compounds (benzothiazolyl, quinolyl, biphenylyl, and naphthylthiophene derivatives) Apiezon L, Silicone SE-30, or OV 225 columns were more suitable. Table V summarizes the relative retention times of some aryl- and heteroarylthiophenes. Kováts indices[43] are reported in Table VIII. These values are usually known as more reproducible than the relative retention times which depend on temperature.

No correction for the average response factors of aryl- and heteroarylthiophenes (in competitive experiments) was applied, these compounds being very similar. However, in the determination of yields with biphenyl as internal standard, an average response fac-

Table VIII
Kováts Indices *I* of Some Heteroarylthiophenes[a]

2-Heteroarylthiophene	*I*
	A (160°)[b]
3-Pyridyl	1705
2-Pyridyl	1692
3-Methyl-2-pyridyl	1690
4-Methyl-2-pyridyl	1795
5-Methyl-2-pyridyl	1800
6-Methyl-2-pyridyl	1720
2-Pyrimidyl	1700
2-Pyrazinyl	1715
2-Thiazolyl	1630
3-Methyl-5-isothiazolyl	1720
3,4-Dimethyl-5-isoxazolyl	1780
	A (230°)[b]
4-Methyl-5-carbethoxy-2-thiazolyl	2190[c]
4-Methyl-5-acetyl-2-thiazolyl	2150
2-Benzothiazolyl	2320[d]
2-Naphthyl	2015
2-Biphenyl	1950
4-Biphenyl	2210
	B′ (200°)[b]
2-(3-Pyridyl)	1965
3-(3-Pyridyl)	2015
2-(2-Pyridyl)	1990
2-(3,4-Dimethyl-5-isoxazolyl	2020
3-(3,4-Dimethyl-5-isoxazolyl)	2060
2-(2-Thiazolyl)	1930

[a] Kováts indices were calculated according to the general formula[43] $I = 200\ [\log(d'_R)_X - \log(d'_R)_Z]/[\log(d'_R)_{Z+2} - \log(d'_R)_Z] + 100Z$, where d'_R represents the reduced retention distance. These values were almost the same on an SE-30 column at 230°. [b] Column and temperature (cf. text). [c] For 2-phenyl-4-methyl-5-carbethoxythiazole, I = 2130. [d] For 2-phenylbenzothiazole, I = 2250.

tor of 2 was used on the column C, whereas 1.4 was used on SE-30 or Apiezon L columns.

GLC–MS. These analyses were performed using Aerograph Model 1400 and Varian MAT 111 instruments at 80 eV, source temperature 200°, accelerating voltage 820 V, and trap current 270 A. Columns used were 5 ft × 0.125 in. Apiezon L (3%), or PMPE six ring (3%) W/W on Varaport (100–120 mesh), operated in programmed temperature 150–250°, 6° min^{-1}. Major peaks and their relative intensities are summarized in Table VI.

The mass spectral data on the heterocyclic ethers of the type HAr–O–HAr have been reported.[20]

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Registry No.—**1a,** 42140-95-4; **1b,** 56421-61-5; **1c,** 56421-62-6; **1d,** 56421-63-7; **2,** 34243-38-4; **3,** 56421-64-8; **4,** 56421-65-9; **5a,** 3319-99-1; **5b,** 56421-66-0; **5c,** 56421-67-1; **5d,** 56421-68-2; **5e,** 56421-69-3; **5f,** 56421-70-6; **6,** 3319-99-1; **7,** 34243-33-9; **8,** 56421-71-7; **9,** 56421-72-8; **10,** 56421-73-9; **11a,** 42140-96-5; **11b,** 56421-74-0; **11c,** 56421-75-1; **11d,** 56421-76-2; **12,** 56421-77-3; **13,** 56421-78-4; **14,** 56421-79-5; **15a,** 21308-81-6; **15b,** 56421-80-8; **15c,** 56421-81-9; **15d,** 56421-82-0; **15e,** 56421-83-1; **15f,** 56421-84-2; **16,** 21298-55-5; **17,** 56421-85-3; **18,** 56421-86-4; **19,** 56421-87-5; **20,** 56421-88-6; isoamyl nitrite, 111-46-3; thiophene, 110-02-1; 2-thiazolamine, 96-50-4; 4-methyl-5-acetyl-2-thiazolamine, 30748-47-1; 4-methyl-5-carbethoxy-2-thiazolamine, 7210-76-6; 5-bromo-2-thiazolamine, 3034-22-8; 2-benzothiazolamine, 136-95-8; 3-methyl-5-isothiazolamine, 24340-76-9; 3,4-dimethyl-5-isoxazolamine, 19947-75-2; 2-pyridinamine, 504-29-0; 3-methyl-2-pyridinamine, 1603-40-3; 4-methyl-2-pyridinamine, 695-34-1; 5-methyl-2-pyridinamine, 1603-41-4; 6-methyl-2-pyridinamine, 1824-81-3; 5-chloro-2-pyridinamine, 1072-98-6; 3-pyridinamine, 462-08-8; 3-quinolinamine, 580-17-6; 8-quinolinamine, 578-66-5; 2-pyrazinamine, 5049-61-6; 2-pyrimidinamine, 109-12-6.

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Reactions of 2,3-Diphenylthiirene 1,1-Dioxide with Nucleophiles

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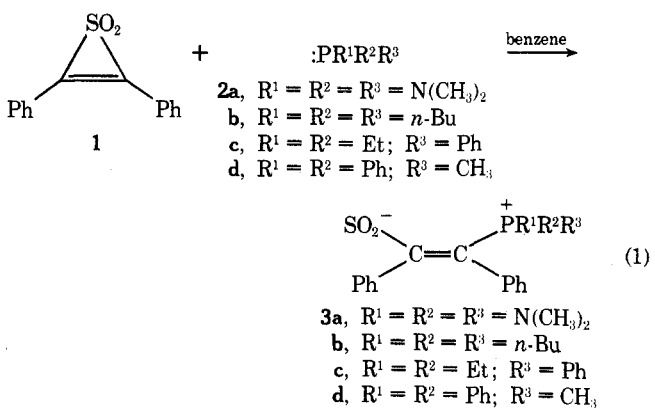
2,3-Diphenylthiirene 1,1-dioxide (1) reacts with tertiary phosphines, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), dimethylamine, sodium cyanide, and sodium benzenesulfinate in aprotic solvents by initial attack at the carbon centers of the three-membered ring. The reaction of 1 with dimethylamine in benzene gives a high yield of (*E*)-1,2-diphenyl-1-*N*,*N*-dimethylaminoethene. Tertiary phosphines and DBN react with 1 to give a new class of betaines. The complete X-ray structure of the betaine **3d** derived from 1 and diphenylmethylphosphine is reported. Cyanide and benzenesulfinate ions in DMF add across the carbon–carbon double bond in 1 to give an intermediate anion which undergoes electrocyclic ring opening to vinylsulfinates (**16** and **17**, respectively). These sulfinates were converted into their respective methyl sulfones (**18** and **19**) with methyl iodide.

Although the physical and chemical properties of cyclopropenones[1] indicate that these compounds enjoy a relatively high degree of stability owing to their aromatic character, the corresponding sulfones, thiirene 1,1-dioxides, are not sufficiently well characterized to draw a similar conclusion.[2] A good deal of information is now available on the reactions of cyclopropenones,[1] but far less is known about similar reactions with the unsaturated episulfones. In view of this, we have investigated the reactions of 2,3-diphenylthiirene 1,1-dioxide (1) with nucleophiles.

Results and Discussion

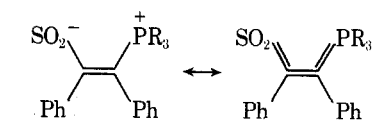
α,β-Unsaturated sulfones,[3] like other alkenes substituted with electron-withdrawing groups,[4] are susceptible to nucleophilic additions. Typical nucleophiles used are alkoxides, amines, thiolates, sulfinates, cyanide, and carbanions.[4] Tertiary phosphines also are reactive, but their reactions with the activated alkenes tend to be highly reversible.[5] Because of the nature of the strained ring system in 2,3-diphenylthiirene 1,1-dioxide (1), it seemed likely that 1 would react irreversibly with nucleophiles such as tertiary phosphines either by attack at the sulfur or α-carbon positions. Indeed, 1 reacted rapidly in benzene solvent with a number of reactive tertiary phosphines (2) to give 1:1 adducts in quantitative yield.[6] The structure of the adduct of 1 with diphenylmethylphosphine (**2d**) was established as **3d** by an X-ray crystallographic analysis.



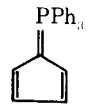
(1)

An ORTEP drawing of **3d** from the X-ray determination is given in Figure 2; bond lengths and angles are shown in Figure 1. The A and B phenyl rings, which are attached to the central C=C, are twisted by steric interactions out of the double bond plane by angles of 67 and 47°, respectively. The shortest ring A···ring B distance of 3.37 Å (Figure 2) is virtually identical with the 3.4-Å van der Waals thickness of an aromatic ring. The O(1)–S–O(2) and Ph–P–Ph angles are approximately bisected by the double bond plane, and the orientations of both the SO_2 and PCH_3Ph_2 groups appear to be governed by steric factors. Newman projections illustrating the conformations about C(2)–P and C(3)–S are given in Figure 3. The SO_2 group is pyramidal (the sum of the three angles around S is 315.9°; sum of three perfectly tetrahedral angles, 109.5°, is 328.5°), and with the assumption that the unshared electron pair on S (form I) is positioned, relative to the C and two O atoms, to give a S tetrahedron, it is clear that the SO_2's orientation maximizes the electron pair–P^+ interaction (S···P 3.20 Å).

The resonance structure extremes for **3d** are represented by canonical form I, a sulfinophosphonium betaine, and form II, a phosphonium ylide–sulfene.[7] Bond lengths (Figure 1) for the central P–C–C–S part of the molecule have the usual values for P–C, C=C, and C–S, all of which would pertain to structure I. The P–C(2) distance is typical of P–C (sp^2, phenyl) lengths; phosphonium ylides with some P=C character normally show a distance of about 1.72 Å. Several representative distances are given below.



I II

	$HOCH_2$-$SO_2^-Na^+$		CH_2=CH_2
Bond	C-S[9]	ring-C-P[10]	C-C[11]
Bond length, Å	1.838	1.718	1.34