

Inverted Reactivity of Aryllithium Derivatives V. On the Syntheses of Thiocyano-, Phenylsulfinyl-, and Phenoxy Derivatives of Thiophenes and Furans

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The reaction of some diheterocyclic iodonium salts with a variety of nucleophiles has been studied. The reaction was of preparative use for the syntheses of thiocyano, phenylsulfinyl and phenoxy derivatives of thiophenes and furans.

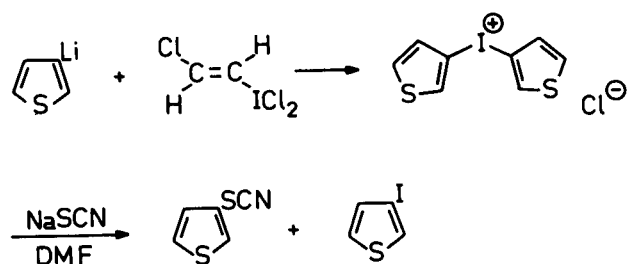
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Introduction

In preliminary reports, we have demonstrated that it is possible to increase the synthetic utility of the nucleophilic thienyllithium, seleniennyllithium and furyllithium derivatives by applying the synthetic strategy of group equivalents with inverted reactivity (3). Through reaction of the lithium derivatives with *trans*-chlorovinyl iodosodichloride, the corresponding diaryliodonium salts were obtained, which are strongly electrophilic reagents. They reacted for instance with sodium nitrite in *N,N*-dimethylformamide to give nitro substituted heterocycles (4,5). In the reaction with other nucleophiles such as cyanide ion or methoxide ion, reduction predominantly occurred. Thus di-(3-thienyl)iodonium chloride gave thiophene, 3-iodothiophene and decomposition products. This could be almost completely overcome by the addition of copper salts or 1,1-diphenylethylene, and the desired 3-methoxy- and 3-cyanothiophenes were obtained in reasonable yields (6). Attempts to use unsymmetrical diaryliodonium salts and direct the attack of the nucleophile to the heterocyclic ring have hitherto failed (7), so we have investigated the synthetic utility of the symmetrical iodonium salts.

Results

Beringer and Nathan (8) found that symmetrical diaryliodonium salts could be prepared from *trans*-chlorovinyl iodosodichloride and two equivalents of the aryllithium derivative, and also prepared di-(2-thienyl)- and di-(2-furyl)iodonium chloride (9) using this method. We have investigated the scope of this reaction (Scheme 1) with heterocyclic lithium derivatives, and the yields obtained, melting points and elemental analyses are given in Table 1. Usually, somewhat higher yields of iodonium



chlorides were obtained by adding the thienyllithium solution to the *trans*-chlorovinyl iodosodichloride in toluene. We were not able, in spite of several attempts and modifications, to obtain the yield (86%) reported (9) for di-(2-furyl)iodonium chloride.

We found that the reaction of di-(3-thienyl)iodonium chloride and of some of its substituted derivatives with sodium thiocyanate in *N,N*-dimethylformamide proceeded smoothly and gave the corresponding thiocyano derivatives in acceptable yields. Thus, the yield of 3-thiocyanothiophene (Scheme 1) was better than that obtained by reacting cyanogen bromide with the sodium salt of 3-thiophenethiol (23), which gave di-(3-thienyl)disulfide as the main product. We obviously illustrate the usefulness of the iodonium salts for the preparation of thiocyano derivatives, by synthesizing compounds which are not available by direct electrophilic thiocyanation. Also, 3-thiocyanoselenophene could be prepared in this way in 48% yield.

The isolation of 3-thiocyanofuran from the reaction of di-(3-furyl)iodonium chloride and sodium thiocyanate caused difficulties. It was formed in low yield and partly decomposed upon distillation. However, by careful distillation followed by preparative glc, a pure sample was


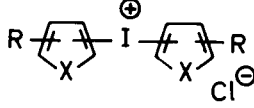
obtained. Using dioxane, glycerol, sulfolane, formamide, *p*-nitrotoluene, nitromesitylene, quinoline, nitromethane, hexamethapole, acetonitrile or water instead of *N,N*-dimethylformamide as solvent, did not improve the yield of 3-thiocyanofuran. Previously, it has been found that the reaction of 3-chloromercurifuran with thiocyanogen gives a mixture of 2-thiocyanofuran (80%) and 3-thiocyanofuran (20%) in low yield (19). 2-Thiocyanofuran is conveniently prepared from furan and thiocyanogen in the presence of aluminium trichloride (19). The yields of thiocyan derivatives prepared, their analytical data and their pmr data are given in Table 2.

Pmr shift assignments in disubstituted derivatives are based on additivity considerations using the substituent-

caused shifts of the monosubstituted derivatives (24). All compounds showed strong absorption in their ir spectra at 2165 cm^{-1} , characteristic for aromatic thiocyan derivatives. We also checked if isothiocyanates were formed in these reactions. By combined glc-mass spectrometry it could be shown that isothiocyanothiophenes were probably produced but that their concentrations in the reaction mixtures in general were less than 3% of those of the thiocyanothiophenes. The indication for the formation of e.g. 3-isothiocyanothiophene from the reaction of di-(3-thienyl)iodonium chloride and sodium thiocyanate was that the mass spectra of 3-thiocyanothiophene and the other component were quite similar. Both products gave the same molecular ions ($M^+ = 141, 142, 143$), but $m/e =$

Table 1

Yields and Analytical Data for Some Heterocyclic Iodonium Chlorides

Lithium derivatives 	Iodonium chloride 	Yield %	M.p.	Elemental analyses			
				C	H	I	
2-Thienyl (10)	di-(2-thienyl)	69	188-190 (a,b)				
3-Thienyl (11)	di-(3-thienyl)	84	239-240 (b)	Found	29.3	1.76	38.9
				Calcd.	29.2	1.84	38.6
4-Bromo-3-thienyl (12)	di-(4-bromo-3-thienyl)	66	206-208 (c)	Found	20.2	1.09	26.2
				Calcd.	19.7	0.83	26.1
4-Bromo-2-thienyl (13)	di-(4-bromo-2-thienyl)	42	137-138 (c)	Found	20.0	0.87	26.2
				Calcd.	19.7	0.83	26.1
4-Methyl-3-thienyl (12)	di-(4-methyl-3-thienyl)	58	223-227 (b)	Found	33.2	2.64	35.7
				Calcd.	32.7	2.83	35.6
4-[2-(1,3-dioxolanyl)-3-thienyl] (14)	di-[4-(2-(1,3-dioxolanyl))-3-thienyl]	52	176-178 (b)	Found	35.3	2.97	27.0
				Calcd.	35.6	2.99	26.8
4-Methylthio-3-thienyl (15)	di-(4-methylthio-3-thienyl)	61	183-185 (b)	Found	28.0	2.47	30.2
				Calcd.	28.5	2.40	30.2
2-Chloro-3-thienyl (16)	di-(2-chloro-3-thienyl)	71	195-197 (b)	Found	24.4	1.07	32.2
				Calcd.	24.2	1.01	31.9
2-Chloro-4-thienyl (17)	di-(2-chloro-4-thienyl)	65	125-127 (b)	Found	24.3	1.00	32.3
				Calcd.	24.2	1.01	31.9
4-Chloro-3-thienyl	di-(4-chloro-3-thienyl)	64	156-157 (b)	Found	24.4	1.04	31.8
				Calcd.	24.2	1.01	31.9
2-Furyl (18)	di-(2-furyl)	35	dec. > 175 (c)	Found	32.4	2.14	43.0
				Calcd.	32.4	2.04	42.8
3-Furyl (19)	di-(3-furyl)	54	249-250 (c)	Found	32.3	2.05	42.4
				Calcd.	32.4	2.04	42.8
2-Selenienyl (20)	di-(2-selenienyl)	71	121-122 (b)	Found	22.7	1.41	30.0
				Calcd.	22.7	1.43	30.0
3-Selenienyl (21)	di-(3-selenienyl)	57	170-171 (b)	Found	22.7	1.41	30.2
				Calcd.	22.7	1.43	30.0

(a) Lit. value (22): 229-230°. (b) Recrystallized from water. (c) Recrystallized from methanol.

125 which was of high abundance in the spectrum of the assumed 3-isothiocyanothiophene was absent in the fragmentation pattern of 3-thiocyanothiophene. When efforts were made to improve the yield of 3-thiocyanothiophene by the addition of copper sulfate, it was found that this favored the formation of 3-isothiocyanothiophene and 3-chlorothiophene both in *N,N*-dimethylformamide and in dimethylsulfoxide as solvents. Large relative amounts of copper sulfate strongly suppressed the yield of 3-thiocyanothiophene. However, even high concentrations of copper ions did not completely eliminate its formation. If di-(3-thienyl)iodonium chloride, sodium thiocyanate and copper sulfate were in a ratio of 1.0:3.1:3.1, the product contained 3-thiocyano- and 3-isothiocyanothiophene in the relative proportions of 1:3. The total yields of the isomers were, however, much lower than in the absence of copper ions, due to extensive formation of 3-chlorothiophene. Even if di-(3-thienyl)iodonium tetrafluoroborate was used instead of the chloride in the copper sulfate-catalyzed reaction, the total yield of both 3-thiocyano- and 3-isothiocyanothiophene was lower than in the uncatalyzed reaction.

Attempts to prepare selenocyanates in the same way failed. When di-(3-thienyl)iodonium chloride was reacted with potassium selenocyanate in *N,N*-dimethylformamide, only 3-iodothiophene and traces of (3-thienyl)diselenide were obtained. Similar results were obtained with diphenyliodonium chloride. Furthermore, neither cyanates nor isocyanates could be prepared by the reaction of iodonium salts and potassium cyanate.

The reaction of sodium phenylsulfinate with iodonium salts might be of some preparative use for the preparation of heterocyclic phenylsulfones. Thus di-(3-thienyl)-, di-(4-methyl-3-thienyl)-, and di-(4-methylthio-3-thienyl)iodonium chloride gave phenyl-3-thienylsulfone, phenyl (4-methyl-3-thienyl)sulfone, and phenyl (4-methylthio-3-thienyl)sulfone in 28, 22, and 46% yield, respectively. Due to the low yield, it would in most cases probably be better to prepare the sulfones by oxidation of the corresponding sulfides, except when several sulfide groups are present. For instance, the last-mentioned sulfone could hardly be prepared by selective oxidation of 4-methylthio-3-phenylthiophene. The reaction of iodonium salts with thiophenolates is hardly of any preparative importance. Although 3-thienylphenyl sulfide is obtained in 26% yield in the reaction of di-(3-thienyl)iodonium chloride and sodium thiophenolate in water, the same compound has been obtained in 75% yield from 3-bromothiophene and sodium thiophenolate (25). Thus, the route *via* iodonium salts to thienylphenyl sulfides seems to be inferior to other known methods, but can of course be an alternative in some special cases. On the other hand, di-(3-thienyl)iodonium chloride and sodium phenolate in

water gave 3-thienylphenyl ether in 23% yield. It is essential to use water solution, when methanol was used as solvent, the yield was low and considerable amounts of thiophene were formed. In this case, the reaction of 3-bromothiophene or 3-iodothiophene with sodium phenoxide in methanol in the presence of copper(II) oxide gave only 2% of the thienylphenyl ether even after 96 hours of reflux. The same reaction with sodium methoxide is a convenient method for the preparation of 3-methoxythiophene (26).

Diphenyl ethers have previously been prepared from diphenyliodonium salts and sodium phenolate (27,28). The use of dithienyliodonium salts has now extended this synthetic method to thienylphenyl ethers, the synthesis of which does not seem to have been reported previously. Unfortunately, this method could not be extended to the synthesis of 3-furylphenyl ether. In the presence of cuprous chloride, 2% of 3-furylphenyl ether could be isolated in the reaction of di-(3-furyl)iodonium chloride. The main products were 3-chloro- and 3-iodofuran.

Since both 1,1-diphenylethylene and copper salts had favored the formation of 3-methoxythiophene in the reaction of di-(3-thienyl)iodonium chloride and methoxide ion (6), it was of interest to find out if di-(2-furyl)iodonium chloride and methoxide would give 2-methoxyfuran. This compound has previously been obtained from the reaction of methyl 2-bromofuran-5-carboxylate with methoxide ion in methanol, followed by hydrolysis and decarboxylation (29) or by elimination of methanol from 2,5-dihydro-2,5-dimethoxyfuran at 200-250° (30). As expected, in the absence of 1,1-diphenylethylene or copper salts, di-(2-furyl)iodonium chloride and methoxide ion in methanol gave only furan and 2-iodofuran. However, when 1,1-diphenylethylene was added, 2-methoxyfuran could be isolated in 20% yield. Copper ions were also found to be effective in catalyzing the formation of 2-methoxyfuran: with cuprous chloride, a 10% yield was obtained. The latter catalyst is recommended in spite of the lower yield, because of the large amounts of 1,1-diphenylethylene which are needed. The utility of iodonium salts for the synthesis of alkoxy derivatives was also shown by the preparation of 3-thienyl-1-hexyl ether in 23% yield from the copper sulfate-catalyzed reaction of di-(3-thienyl)iodonium chloride and sodium hexoxide in 1-hexanol.

From di-(3-thienyl)iodonium chloride and sodium chloride in *N,N*-dimethylformamide 3-chlorothiophene could be prepared in a copper sulfate-catalyzed reaction in 53% yield. However, all of our attempts to use the iodonium salts for the preparation of fluorothiophenes failed. The reaction between fluoride ion and di-(3-thienyl)iodonium tetrafluoroborate, prepared by treatment of the chloride with a silver tetrafluoroborate, was attempted

Table 2
 Yields, Analytical Data and Nmr Data of Thiocyno-substituted Heterocycles Obtained in the
 Reaction of Iodonium Salts with Sodium Thiocyanate in *N,N*-Dimethylformamide

Thiocyano derivative	Yield %	B.p. °C/mm Hg	Elemental analyses			Nmr Data (CDCl ₃)
			C	H	N	S
3-Thiocyanothiophene	43	107-110/11 (a)				
2-Chloro-3-thiocyanothiophene	44	120-126/12	Found 34.1	1.13	7.76	
			Calcd. 34.2	1.15	7.98	$\delta_4 = 7.08$ ppm.; $\delta_5 = 7.25$ ppm. $J_{45} = 5.7$ Hz
3-Methylthio-4-thiocyanothiophene	23	164-168/11 m.p.: 47.8-48.4	Found 38.3	2.71		51.3
			Calcd. 38.5	2.69		51.4
3-Bromo-4-thiocyanothiophene	37	150-153/12 m.p.: 54.6-56.0	Found 27.2	1.00		29.2
			Calcd. 27.3	0.91		29.1
2-Chloro-4-thiocyanothiophene (b)	17	121-124/11	Found 33.2	1.13	7.54	
			Calcd. 34.2	1.15	8.02	
3-Thiocyanoselenophene	48	131-137/15	Found 31.5	1.61	7.16	
			Calcd. 31.8	1.60	7.41	
3-Thiocyanofuran (c)						
						$\delta_2 = 7.43$ ppm.; $\delta_5 = 7.70$ ppm. $J_{25} = 3.4$ Hz
						$\delta_3 = 7.03$ ppm.; $\delta_5 = 7.37$ ppm. $J_{35} = 1.7$ Hz
						$\delta_2 = 8.24$ ppm.; $\delta_4 = 7.40$ ppm.; $\delta_5 = 8.11$ ppm.; $J_{25} = 2.6$ Hz; $J_{24} = 1.4$ Hz; $J_{45} = 5.6$ Hz
						$\delta_2 = 7.74$ ppm.; $\delta_4 = 6.62$ ppm.; $\delta_5 = 7.57$ ppm. $J_{24} = 0.7$ Hz; $J_{25} = 1.5$ Hz; $J_{45} = 1.9$ Hz

(a) Lit. value (23): 114-115°/15 mm Hg. (b) Not quite pure after preparative glc. (c) Obtained through preparative glc.

using sodium and potassium fluoride, both in the presence and absence of copper sulfate in solvents such as *N,N*-dimethylformamide, dimethylsulfoxide, nitrobenzene, acetonitrile and water. Attempts to pyrolyze di-(3-thienyl)iodonium fluoride, prepared by metathesis in the same way as described for diphenyliodonium fluoride (31), gave only 3-iodothiophene and polymeric products as in the reaction mentioned above. The reaction of di-(3-thienyl)iodonium tetrafluoroborate and potassium fluoride in the presence of disilver fluoride (32) failed both in dimethylsulfoxide and in nitrobenzene. Likewise, all our attempts to prepare acetoxy or hydrazine derivatives of thiophenes through the reaction of iodonium salts with acetate or hydrazines were unsuccessful. From the reaction of di-(3-thienyl)iodonium chloride with triethylphosphite, a 3% yield of diethyl-3-thienylphosphonate was obtained.

Beringer, *et al.*, found that ethyl sodio-oxalacetate and diphenyliodonium salts gave phenyl malonates (27). They also tried to synthesize phenyl malonates from iodonium salts and sodium diethyl malonate, but in general the yields were low due to side-reactions (33). However, our attempts to extend these reactions to the thiophene series failed.

EXPERIMENTAL

General

Gas chromatographic analyses were performed with a Perkin-Elmer 900 apparatus equipped with a flame ionization detector and connected to a Varian 480 digital integrator. The columns were made of stainless steel with 3 mm o.d. Nitrogen was used as carrier gas. The following analytical columns were used: Column A: 10% Butane-1,4-diolsuccinate (BDS) on Chrom. W (80/100 mesh), 2.0 m. Column B: 3% OV1 on Gas-Chrom. Q (80/100 mesh), 2.5 m. Nmr spectra were recorded on a Varian A-60 instrument. Tetramethylsilane was used as internal standard. A Perkin-Elmer 257 ir spectrometer was used for ir spectra. Mass spectra were recorded on an LKB 9000 mass spectrometer at 70 eV.

Most of the elemental analyses were performed by the Department of Analytical Chemistry at the University of Lund, Sweden and a few by Miss Ilse Beetz, Mikroanalytisches Laboratorium, Kronach, West Germany.

3-Bromo-4-chlorothiophene.

To a 4-bromo-3-thienyllithium (12) solution, prepared from 97 g. (0.40 mole) of 3,4-dibromothiophene (34) in 150 ml. of ether and 370 ml. of 1.13 *M* (0.42 mole) butyllithium in hexane, 100 g. (0.42 mole) of hexachloroethane dissolved in 300 ml. of ether was added at -70°. After stirring at -70° for 2.5 hours the cooling bath was removed; after the temperature had risen to 0°, the reaction mixture was poured into water. The ether phase was separated and the water phase extracted with ether, whereupon the combined ether phases were washed with water and dried over magnesium sulfate. Distillation gave 49 g. (62%) of 3-bromo-4-chlorothiophene at 76-80°/10 mm. Column: A. Nmr (deuteriochloroform): δ (ring hydrogens) = 7.16 ppm and 7.27 ppm

$J_{25} = 3.6$ Hz.

Anal. Calcd. for C_4H_2BrClS (197.5): C, 24.3; H, 1.02. Found: C, 24.2; H, 1.18.

Symmetrical Dithienyliodonium Chlorides. General Procedure.

To 0.10 mole of *trans*-chlorovinylidioso dichloride (6) in 200 ml. of dry toluene cooled to -70°, a thienyllithium solution was transferred through a rubber tube. The thienyllithium solution was prepared from 0.20 mole of thiophene or bromothiophene in 100 ml. of ether and 0.21 mole of commercial butyllithium in hexane. The mixture was stirred at -70° for 2-3 hours, whereupon the cooling bath was removed. When the temperature had risen to 0°, the mixture was poured into water and the precipitated iodonium salt filtered off, washed with water, acetone and ether, dried and directly used for synthesis. Yields, analytical data and references to the preparations of the thienyllithium derivatives are given in Table 1. The salts should, in order to minimize decomposition, be stored at about 0°, if not used within a few days.

Di-(3-thienyl)iodonium Tetrafluoroborate.

Ten g. (0.030 mole) of di-(3-thienyl)iodonium chloride was dissolved in 200 ml. of boiling water, whereupon a silver tetrafluoroborate solution, prepared by dissolving 5.5 g. (0.024 mole) of silver oxide in 20 g. of 35% hydrogen tetrafluoroborate solution, was added. The silver chloride formed was filtered off and the water phase concentrated. After cooling, the solid phase was filtered off and dried. Di-(3-thienyl)iodonium tetrafluoroborate (4.6 g., 41%) was obtained. The yield depends strongly upon how much the water phase is concentrated. For further purification the resulting salt was dissolved in water at about 20°. Most of the water was then evaporated and the crystals thus obtained filtered off and dried (m.p. 173-174°).

Anal. Calcd. for $C_8H_6BF_4IS_2$ (378.0): I, 33.4. Found: I, 32.5.

Di-(3-thienyl)iodonium Fluoride.

To 10 g. (0.030 mole) of di-(3-thienyl)iodonium chloride dissolved in 150 ml. of boiling water, a silver fluoride solution prepared from silver oxide dissolved in 25% hydrogen fluoride was added until no chloride ion was left. The disappearance of chloride ion was checked by adding a silver nitrate solution to an aliquot of the solution. The precipitated silver chloride was filtered off and the filtrate stored at room temperature for two days. It was then filtered and evaporated almost to dryness. The solid phase was filtered off, washed with ether and dried. Di-(3-thienyl)iodonium fluoride (7.1 g. 76%) (dec. slowly >170°) was obtained. Elemental analysis for iodine gave too low a value, possibly due to the presence of water of crystallization.

Symmetrical Difuryliodonium Chlorides. General Procedure.

2-Furyllithium (18) and 3-furyllithium (19) solutions were prepared from 0.60 mole of furan or bromofuran in 100 ml. of ether and 0.63 mole of commercial butyllithium in hexane. These solutions were cooled to -70° and slowly added to 0.30 mole of *trans*-chlorovinylidioso dichloride (8) in 400 ml. of dry toluene, also cooled to -70°, at such a rate as to avoid ring-opening of 3-furyllithium. The reaction mixture was stirred at -70° for 2-3 hours, whereupon the cooling bath was removed. After the temperature had risen to 0°, the mixture was poured into water. The solid phase was filtered off, washed with water, acetone and ether, dried and used directly for synthesis. Yields and analytical data are given in Table 1. For longer periods the salts were stored at

about -20° . Di-(2-furyl)iodonium chloride had, at times, a tendency to decompose at room temperature.

Symmetrical Diselenenyliodonium Chlorides. General Procedure.

2-Selenenyliithium (20) and 3-selenenyliithium (21) solutions were prepared from 0.10 mole of selenophene or 3-bromoselenophene (35) in 50 ml. of ether and 0.11 mole of commercial butyllithium in hexane. These solutions were cooled to -70° and added to 0.050 mole of *trans*-chlorovinylidioso dichloride (8) in 200 ml. of dry toluene, also cooled to -70° , at such a rate as to avoid ring-opening of 3-selenenyliithium. After stirring for 2-3 hours, the cooling bath was removed, and, after the temperature had risen to 0° , the mixture was poured into water. The solid phase was filtered off, washed with water, acetone and ether, dried and directly used for synthesis. Yields and analytical data are given in Table 1. To avoid decomposition, the salts were stored at about -20° .

Thiocyanothiophenes from Symmetrical Iodonium Chloride. General Procedure.

A solution of 0.030 mole of dithienyliodonium chloride, 0.15 mole of sodium thiocyanate and 200 ml. of *N,N*-dimethylformamide was stirred at $110-120^{\circ}$ for 3 hours. After cooling, the reaction mixture was poured into water and extracted with ether. The ether phase was washed with water and dried over magnesium sulfate. In the case of 3-methylthio-4-thiocyanothiophene, a pure product was not obtained directly upon distillation. The main fraction at $164-168^{\circ}/11$ mm. was contaminated by 3-iodo-4-methylthiothiophene. Therefore, this fraction was dissolved in boiling petroleum ether (b.p. $40-60^{\circ}$), and after the solution was cooled to -70° , pure 3-methylthio-4-thiocyanothiophene (m.p. $47.8-48.4^{\circ}$) precipitated in 15% yield. The same recrystallization procedure with the first fraction yielded another crop of 3-methylthio-4-thiocyanothiophene (m.p. $47.5-48.0^{\circ}$), raising the total yield to 23%. For the other thiocyanothiophenes, distillation gave pure products. The yields and analytical data for the thiocyanothiophenes are given in Table 2. Analytical samples were purified with preparative gas chromatography (BDS 20%, Chrom. A 60/80, $3/8'' \times 6'$). Columns: A, B.

Di-(3-thienyl)iodonium Chloride and Sodium Thiocyanate in the Presence of Copper Sulfate.

Di-(3-thienyl)iodonium chloride (1.7 g., 5.2 mmoles) and 1.3 g. (16 mmoles) of sodium thiocyanate were reacted at $70-110^{\circ}$ in *N,N*-dimethylformamide or dimethylsulfoxide in the presence of varying amounts of anhydrous copper sulfate. Besides 3-iodothiophene, which was formed in all reactions, combined vpc-mass spectrometry indicated that the addition of copper sulfate favored the formation of 3-chloro- and 3-isothiocyanothiophene, lowering the yield of 3-thiocyanothiophene obtained in the uncatalyzed reaction.

3-Thiocyanofuran.

To 7.3 g. (0.090 mole) of sodium thiocyanate and 100 ml. of *N,N*-dimethylformamide, 9.0 g. (0.030 mole) of di-(3-furyl)iodonium chloride was added at 110° . After stirring for 2 hours at $110-120^{\circ}$, 75 g. of anhydrous sulfolane was added and the main part of the *N,N*-dimethylformamide distilled off, as the first fraction, at reduced pressure (12 mm.). The next fraction ($52-140^{\circ}/12$ mm.) of about 10 g. was collected for further purification. This fraction contained, according to vpc, 3-thiocyanofuran and *N,N*-dimethylformamide together with small amounts of 3-iodofuran and sulfolane. One further distillation gave two fractions. The first fraction at $53-71^{\circ}/12$ mm. contained

3-iodofuran, *N,N*-dimethylformamide and a small amount of 3-thiocyanofuran, and the second at $71-79^{\circ}/12$ mm. contained *N,N*-dimethylformamide and 3-thiocyanofuran. Preparative gas chromatography (BDS 20%, Chrom. A 60/80, $3/8'' \times 6'$) gave pure 3-thiocyanofuran. Column: A. For nmr data, cf. Table 2.

3-Thiocyanoselenophene.

Thirteen g. (0.031 mole) of di-(3-selenenyl)iodonium chloride, 12 g. (0.15 mole) of sodium thiocyanate and 300 ml. of *N,N*-dimethylformamide were stirred at 110° for 3 hours. The mixture was poured into water and extracted with ether. The combined phases were washed with water and dried over magnesium sulfate. Distillation gave 2.8 g. (48%) of 3-thiocyanoselenophene at $131-137^{\circ}/15$ mm. Column: A. For analytical and nmr data, cf. Table 2.

Phenyl-3-thienylsulfone.

A solution of 10.0 g. (30 mmoles) of di-(3-thienyl)iodonium chloride and 20 g. (120 mmoles) of sodium phenylsulfinate in 300 ml. of *N,N*-dimethylformamide was stirred at $120-130^{\circ}$ for 7 hours. After cooling, the reaction mixture was poured into water and extracted with ether. The combined ether phases were washed with water and dried over magnesium sulfate. The ether was evaporated and some hexane was added to the solid residue which dissolved the 3-thiothiophene. The mixture was filtered and the residue recrystallized from ethanol, yielding 1.9 g. (28%) of phenyl-3-thienylsulfone, m.p. $119-120^{\circ}$; lit. value (25) m.p. $117.5-119^{\circ}$. Column: B.

Phenyl-(4-methyl-3-thienyl)sulfone.

From 10.0 g. (27 mmoles) of di-(4-methyl-3-thienyl)iodonium chloride, 20 g. (120 mmoles) of sodium phenylsulfinate and 300 ml. of *N,N*-dimethylformamide, 1.4 g. (22%) of the title compound was obtained, m.p. $81-82^{\circ}$, after 5 hours at $120-130^{\circ}$ and after the same work up as described above. Column: B.

Anal. Calcd. for $C_{11}H_{10}O_2S_2$: C, 55.4; H, 4.23; S, 26.9. Found: C, 55.5; H, 4.23; S, 26.6.

Phenyl-(4-methylthio-3-thienyl)sulfone.

From 5.0 g. (12 mmoles) of di-(4-methylthio-3-thienyl)iodonium chloride, 8.2 g. (50 mmoles) of sodium phenylsulfinate and 200 ml. of *N,N*-dimethylformamide, 1.5 g. (46%) of the title compound was obtained, m.p. $170-171^{\circ}$ after 5 hours at 120° and the same work-up as above, except for the extraction for which chloroform was used as the product was difficultly soluble in ether. Column: B.

Anal. Calcd. for $C_{11}H_{10}O_2S_3$: C, 48.9; H, 3.73; S, 35.6. Found: C, 48.8; H, 3.77; S, 35.8.

3-Thienylphenyl Ether.

A solution of 20 g. (0.061 mole) of di-(3-thienyl)iodonium chloride, 28 g. (0.30 mole) of phenol, 12 g. (0.30 mole) of sodium hydroxide and 600 ml. of water was stirred at reflux for 20 hours. More water was added and the water phase extracted with ether. The combined ether phases were washed with water, dilute sodium hydroxide solution and water. After drying over magnesium sulfate, distillation gave 2.5 g. (23%) of 3-thienylphenyl ether at $133-134^{\circ}/15$ mm. An analytical sample was further purified by preparative gas chromatography (OV17, 15%, Chrom. A 60/80, $3/8'' \times 6'$). Column: A. Nmr (deuteriochloroform): Two quartets from the thiophene protons centered at $\delta = 6.49$ ppm for the 2-hydrogen and at $\delta = 6.78$ ppm for the 4-hydrogen. The thiophenic 5-hydrogen and the phenyl hydrogens were not resolved

(centered at 7.0 ppm). $J_{24} = 1.5$ Hz, $J_{25} = 3.2$ Hz, $J_{45} = 5.3$ Hz.

Anal. Calcd. for $C_{10}H_8OS$: C, 68.2; H, 4.58; S, 18.2. Found: C, 68.1; H, 4.52; S, 18.2.

3-Bromo- and 3-Iodothiophene in the Reaction with Sodium Phenoxide.

To 100 ml. of anhydrous methanol was added 6.0 g. (0.26 mole) of sodium. When the hydrogen gas evolution had finished, 26 g. (0.26 mole) of phenol was added followed by 15 g. (0.092 mole) of 3-bromothiophene (34), 3.8 g. (0.048 mole) of copper(II) oxide and 0.10 g. (0.60 mmole) of potassium iodide. After stirring at reflux for 96 hours, the reaction mixture was analyzed by vpc. It was, however, found that only about 2% of the 3-bromothiophene had been converted to 3-thienylphenyl ether. The same reaction in *N,N*-dimethylformamide at 50-60° using sodium hydride instead of sodium hydroxide as base gave, after 112 hours, no 3-thienylphenyl ether. The use of 3-iodothiophene (22) instead of 3-bromothiophene did not lead to any improvement. Column: A.

3-Thienylphenyl Sulfide.

A solution of 20.0 g. (0.0609 mole) of di-(3-thienyl)iodonium chloride, 29.0 g. (0.260 mole) of thiophenol, 10.5 g. (0.260 mole) of sodium hydroxide and 300 ml. of water was stirred at reflux for 4.5 hours. After cooling, the reaction mixture was extracted with ether. The combined ether phases were washed with water, dilute sodium hydroxide solution and water, dried and distilled giving 3.0 g. (26%) of 3-thienylphenyl sulfide at 167-169°/1 mm; lit. values: 88-94°/0.3 mm. (25) and 100-103°/0.3 mm. (36). Column: B. Nmr (deuteriochloroform): δ_4 = centered at 7.00 ppm. $J_{24} = 1.8$ Hz, $J_{45} = 4.8$ Hz; other couplings badly resolved.

2-Methoxyfuran.

A. To 11 g. (0.20 mole) of sodium methoxide in 300 ml. of anhydrous methanol, 50 g. (0.28 mole) of 1,1-diphenylethylene was added, followed by 21 g. (0.071 mole) of di-(2-furyl)iodonium chloride. After reflux for 1.5 hours, the reaction mixture was poured onto ice and extracted several times with ether. The combined ether phases were washed with water and dried over magnesium sulfate. Distillation gave 1.4 g. (20%) of 2-methoxyfuran at 113-116° (lit. value (37): 110-111°), containing about 10% of 2-iodofuran. Column: A.

B. To 8.1 g. (0.15 mole) of sodium methoxide and 3.0 g. (0.030 mole) of cuprous chloride in 200 ml. of anhydrous methanol, 9.0 g. (0.030 mole) of di-(2-furyl)iodonium chloride was added. After reflux for 1 hour, the reaction mixture was, after cooling, poured into water and extracted several times with ether. The combined ether phases were washed with water and dried over magnesium sulfate. The ether phase was concentrated to 30-40 ml. In addition to ether, this residue contained 2-methoxy- and 2-iodofuran. After cooling to -70°, 0.79 M ethyllithium in ether was added until the 2-iodofuran was consumed as checked by vpc. Protonation was performed with methanol. After pouring into water, the mixture was extracted with ether. The combined ether phases were dried over magnesium sulfate. Distillation gave 0.3 g. (10%) of pure 2-methoxyfuran at 108-110°; lit. value (37): 110-111°. Column: A.

3-Thienyl-1-hexyl Ether.

To 200 ml. of 1-hexanol, 5.7 g. (0.25 mole) of sodium was added. When the evolution of hydrogen gas had finished, 7.9 g. (0.049 mole) of anhydrous copper sulfate was added followed by 16 g. (0.049 mole) of di-(3-thienyl)iodonium chloride. After stirring at 110° for 1.5 hours, the reaction mixture was poured

into water and extracted with ether. The combined ether phases were washed with water and dried over magnesium sulfate. Distillation gave 2.1 g. (23%) of 3-thienyl-1-hexyl ether at 119-123°/16 mm. Column: A. Nmr (deuteriochloroform): $\delta_2 = 6.25$ ppm, $\delta_4 = 6.75$ ppm, $\delta_5 = 7.15$ ppm, $\delta_{O-CH_2} = 3.93$ ppm, $\delta_{(CH_2)_4} = 1.36$ ppm, $\delta_{CH_3} = 0.90$ ppm. $J_{24} = 1.5$ Hz, $J_{25} = 3.1$ Hz, $J_{45} = 5.2$ Hz, $J_{O-CH_2-CH_2} = 6.0$ Hz; other couplings were not resolved.

Anal. Calcd. for $C_{10}H_{16}OS$ (184.3): C, 65.2; H, 8.75; S, 17.4. Found: C, 65.3; H, 8.77; S, 16.7.

3-Chlorothiophene.

Fifteen g. (0.046 mole) of di-(3-thienyl)iodonium chloride, 14 g. (0.24 mole) of sodium chloride, 7.4 g. (0.046 mole) of anhydrous copper sulfate, and 250 ml. of *N,N*-dimethylformamide were stirred at 110° for 3 hours. After cooling, the reaction mixture was poured into water and worked up as above. Distillation gave 2.9 g. (53%) of 3-chlorothiophene at 136-142°; lit. value (17): 133-135°.

3-Furyl-phenyl Ether.

To 11 g. (0.12 mole) of phenol, 4.8 g. (0.12 mole) of sodium hydroxide, 4.0 g. (0.040 mole) of cuprous chloride and 200 ml. of methanol, 12 g. (0.040 mole) of di-(3-furyl)iodonium chloride was added. After stirring at reflux for 1 hour and subsequent cooling, the reaction mixture was filtered, poured into water and extracted with ether. The combined ether phases were washed with dilute sodium hydroxide solution, water and dried over magnesium sulfate. Distillation gave 0.1 g. (2%) of ca. 90% pure 3-furyl-phenyl ether at 92-96°/11 mm. Column: A. Nmr (deuteriochloroform): Furan hydrogens centered at $\delta = 6.24$ ppm, $\delta = 7.05$ ppm and $\delta = 7.15$ ppm. Phenyl protons centered at $\delta = 7.24$ ppm. Couplings were badly resolved.

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