Experimental Section

Elemental analyses were carried out in the Analytical Department of this laboratory under the supervision of Mr. A. F. Hamminga. Melting points were determined using a Reichert melting point apparatus with a microscope attachment. A Varian A-60D spectrometer, using chloroform-d_1 as solvent and Me_4Si as internal standard, was used for the NMR spectra and ir spectra were measured with a Unicam SP 200 instrument.

The starting materials I[12] and IIa–c[13] were prepared according to literature procedures.

Reaction of I with IIa–c. To a stirred solution of 4 mmol of II and 8 mmol of pyridine in 50 ml of chloroform was added 4 mmol of I over a period of 15 min at room temperature. After stirring for an additional 4–6 hr, the chloroform solution was extracted twice with 20 ml of water. The chloroform layer was dried over Na_2SO_4 and the solvent was evaporated. The reaction products were separated by preparative TLC, using silica gel 60 PF and dichloromethane as eluent.

The new compounds IVa–c and Vc are described below; the other reaction products were all identified by comparison (ir and NMR spectral data and, for solids, mixture melting points) with authentic samples. *tert*-Butylsulfonyl chloride (mp 91–93°, lit.[14] 95°) was prepared according to a literature procedure.[14]

Ethyl *N-tert*-Butylsulfonylcarbamate (IVa) was obtained in a yield of 35% after crystallization from benzene–petroleum ether (bp 60–80°) as a white solid: mp 84.5–86°; NMR δ 1.27 (t, J = 7 Hz, 2 H, CH_2), 1.47 [s, 9 H, $(CH_3)_3C$], 4.13 ppm (q, J = 7 Hz, ester CH_3); ir (Nujol) 3280 (NH), 1740 (CO), 1325, 1135 (SO_2), 1285 cm^{-1}.

Anal. Calcd for $C_7H_{15}NO_4S$: C, 40.18; H 7.22; N, 6.69; S, 15.32. Found: C, 39.76; H, 7.37; N, 7.17; S, 15.84.

Carbamate IVa was prepared independently in a yield of 35% by using a procedure analogous to that given by Cassidy et al.[15] and starting from 1.3 mmol of *tert*-butanesulfonamide. Ir and NMR spectral data were identical with those given above.

Methyl *N-tert*-Butylsulfonylcarbamate (IVb). This carbamate was obtained as described for IVa, yield 59%: white solid: mp 98–101°; NMR δ 1.48 [s, 9 H, $(CH_3)_3C$], 3.79 ppm (s, 3 H, CH_3); ir (CH_2Cl_2) 3280 (NH), 1740 (CO), 1330 and 1130 cm^{-1} (SO_2).

Methyl *N*-Methyl-*N-tert*-butylsulfonylcarbamate (IVc). Following the above procedure, this carbamate was isolated as a colorless oil: NMR δ 1.47 [s, 9 H, $(CH_3)_3C$], 3.26 (s, 3 H, NCH_3), 3.79 ppm (s, 3 H, OCH_3); ir (CH_2Cl_2) 1730 (CO), 1345, 1130 (SO_2), 1285, 990, 940, 890 cm^{-1}.

Conversion of IVb into IVc. A freshly prepared solution of diazomethane in ether (ca. 0.2 mmol ml^{-1}) was added at 0° to a solution of 0.092 g (0.47 mmol) of IVb in 10 ml of methanol until the yellow color remained. After stirring for an additional 1 hr at room temperature, the ether and surplus of diazomethane were evaporated to yield IVc in a yield of 90%.

Methyl *N*-methyl-*tert*-butylsulfonyloxycarboximidate (Vc) was a colorless oil, obtained in a yield of 11%: NMR δ 1.54 [s, 9 H, $(CH_3)_3C$], 3.38 (s, 3 H, NCH_3), 3.79 ppm (s, 3 H, OCH_3); ir (CH_2Cl_2) 1720 (C=N), 1345, 1145 (SO_2), 945, 840 cm^{-1}.

CIDNP Experiments. A quartz NMR tube containing 0.030 (0.3 mmol) of IIc and 0.050 g (0.6 mmol) of pyridine in 0.6 ml of chloroform-d_1 was placed in the NMR probe and the spectrum was recorded. Then a slight excess (ca. 0.33 mmol) of I was added and the tube was shaken once. The transitions shown in Figure 1 were obtained by recording the spectrum 15 sec after mixing. After 5 min all signals had obtained normal porportions and no further changes in the NMR spectrum were observed.

Acknowledgment. Stimulating discussions with Dr. R. Kaptein are gratefully acknowledged.

Registry No.—I, 31562-43-3; IIa, 589-41-3; IIb, 584-07-6; IIc, 6092-56-4; IVa, 56908-56-6; IVb, 56908-57-7; IVc, 56908-58-8; Vc, 56908-59-9; VIc, 6642-30-4; VIII, 10490-22-9; diazomethane, 334-88-3.

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Synthesis of $\Delta^{2,2'}$-Bis(1,3-benzodithiolidine) Derivatives and Complex Salts Therefrom with 7,7,8,8-Tetracyanoquinodimethane

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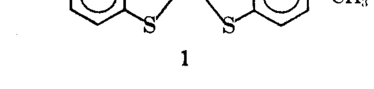
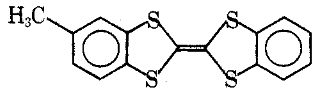
Sharp interest has recently been shown in the design and synthesis of some suitable organic metals[1] and prompts us to report our synthetic results. Several series of the charge-transfer salts including 1,3-dithiolidenes and related selenium analogues have been reported[2–5] and examined for their electrical properties.[2–7] Such charge-transfer salts of appropriate structure can afford organic solids with potential electrical conductivity.[1]

We have found that $\Delta^{2,2'}$-bis(5-methyl-1,3-benzodithiolidene) (1) and 5-methyl-$\Delta^{2,2'}$-bis(1,3-benzodithiolidine) (2)



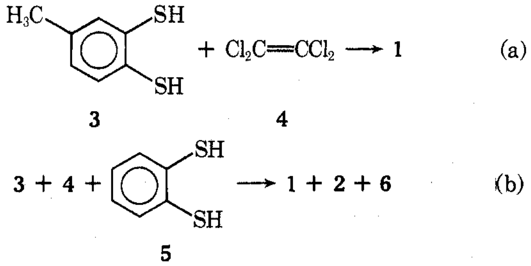
1

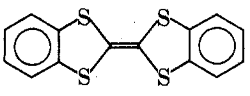


2

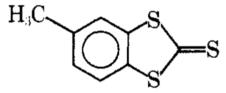
can be very conveniently prepared as shown in Scheme I in a and b, respectively. Although the yields are modest (33 and 15%, respectively) the procedure is *one step* and simple, and the starting materials are commercial. Heretofore, ready access to an *unsymmetrical* benzodithiolidine like **2** has not been published. In spite of the observation that the reaction mixture in b contains **1** and apparently **6** (via mass spectral analysis) it was possible to fractionally recrystallize out **2** from pyridine. To be sure, no physical or chemical property has permitted an unambiguous assignment of structure for **1** (the CH_3 groups could be in a syn or anti arrangement as in **1a** or **1b**) and a single-crystal x-ray examination seems the only alternative and is currently being investigated. A previous method involved a multistep process to give **1** in lower yield[8] (25% last step only) from **7** prepared by the condensation of **3** with CS_2 in aqueous sodium hydroxide. Desulfurization of **7** via heating with triethyl phosphite produced **1**.[8] Other conceivable approaches to **1** could involve deprotonation with tertiary amines of salts like **8**, potentially available from **7** via one of two published routes.[6,9] However, all attempts proved unfruitful for the preparation of **8**. A similar situation has been noted previously with certain other 1,3-dithiolium salts.[10,11]

Scheme I

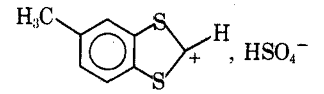




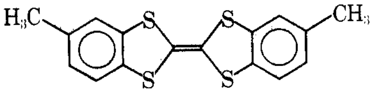
6



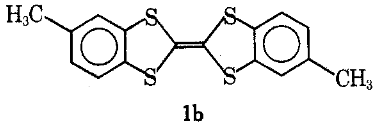
7



8



1a

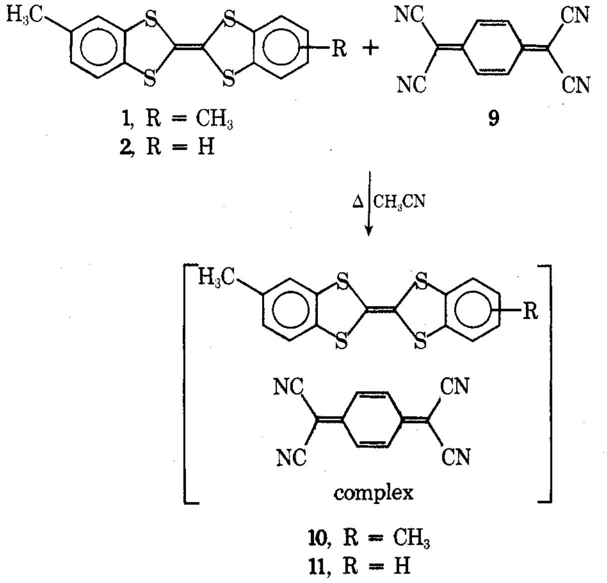


1b

Complexes of **1** and **2** were easily obtained by first dissolving either compound in boiling acetonitrile and filtering the solution. A hot, filtered solution of 7,7,8,8-tetracyanoquinodimethane (**9**) was then freshly prepared. Upon mixing the hot solutions of **1** (or **2**) and **9** there was formed a dark, blue green solution from which, upon cooling, dark crystals formed in good yield (Scheme II). All analytical data support a 1:1 complex for **10** (and **11**).

Preliminary dc conductivity measurements on compacted samples of **10** and **11** were found to give resistivities of 1.28×10^6 and 2.5×10^6 Ω cm, respectively, at room temperature and 1.8 Kbar pressure, well within the range of organic solid state semiconductors.[12,13] The conductance was electronic rather than electrolytic as evidenced by (a) the increase of conductivity with hydrostatic pressure, (b) independence of the conductivity to the direction of long-continued current flow, and (c) its independence of the number of coulombs passed.

Scheme II



Experimental Section

Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Microanalysis were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

The infrared data were recorded from spectra taken on a Beckman IRA spectrophotometer. KBr disks were used for all spectra. The intensity notations used are vs, s, m, w, b, and vw to indicate bands of very strong, strong, medium, weak, broad, and very weak intensities, respectively. All bands are recorded in wavenumbers (cm^{-1}).

Nuclear magnetic resonance spectra were measured on a Varian XL-100 (15) spectrometer. Tetramethylsilane was used as the internal standard. Chemical shifts are expressed in δ values. Electrical conductivity was determined by a previously reported procedure.[14]

Preparation of $\Delta^{2,2'}$-Bis(5-methyl-1,3-benzodithiolidene) (1). This compound was synthesized by a considerable modification of a procedure used for the synthesis of $\Delta^{2,2'}$-bis(1,3-benzodithiolidene) (**6**) (low yield) from *o*-benzenedithiol and tetrachloroethylene.[15,16] Several variations in procedure gave positive results but procedure A gave the highest yield most consistently.

A. 3,4-Dimercaptotoluene (**3**, 2 g, 0.012 mol), tetrachloroethylene (**4**, 1 g, 0.006 mol), and *N,N*-diisopropylethylamine (10 ml) were heated under reflux for 7 hr. The color of the reaction mixture changed to yellow after 0.5 hr of heating. After the mixture cooled, it was allowed to stand overnight. A yellow solid formed and was removed by filtration and dissolved in boiling pyridine (30 ml). This hot solution was filtered through a fluted filter paper. The latter contained about 100 mg of Nuchar activated carbon on the surface. Upon cooling, yellow crystals formed and were removed by filtration to weigh 0.7 g (33%).

Two crystallizations from pyridine afforded pure **1** which melted at 260-262° (reported[8] mp 262°). The previous workers[8] recrystallized **1** from benzene, which proved unsatisfactory in our hands.

The infrared spectrum (KBr disk) of **1** showed absorptions at 3000 (vw), 2900 (vw), 1550 (w), 1445 (s), 1370 (w), 1250 (s), 1135 (w), 1115 (s), 1030 (b), 935 (w), 865 (w), 800 (vw), 780 (vs), 690 cm^{-1} (w). The nuclear magnetic resonance spectrum of **1** ($DCCl_3$) showed signals at the following δ values: 7.0-7.30 (6 H, multiplet, aromatic), 1.65 (6 H, sharp singlet, 2 CH_3).

B. 3,4-Dimercaptotoluene (**3**, 1 g, 0.006 mol) and tetrachloroethylene (**4**, 0.5 g, 0.003 mol) were heated under reflux in 15 ml of pyridine for 17 hr. The reaction mixture was allowed to stand at room temperature overnight and then diluted with 4 ml of water. A turbid solution resulted which was cooled in a refrigerator for 3–4 hr. Yellow crystals separated and were filtered and found to weigh 150 mg (15%, mp 255–258°). There was no depression in the melting point of this product after mixing it with a sample of **1** from procedure A. The infrared spectrum (KBr disk) of this product was also identical with that of the authentic sample of **1**.

C. 3,4-Dimercaptotoluene (**3**, 1.2 g, 0.007 mol) and tetrachloroethylene (**4**, 0.6 g, 0.0036 mol) were heated under reflux in 10 ml of dimethylformamide for 7 hr. The reaction mixture was cooled and kept at room temperature overnight. Dark brown needles were formed which were removed by filtration and washed with ethanol (3 × 10 ml). The dried crystals weighed 0.8 g (yield 63%) but melted at 240–250°. The above solid was dissolved in 40 ml of chloroform without warming and then the solution was filtered. The filtrate was cooled in a refrigerator to afford slightly impure 0.4 g of yellow crystals the properties of which were identical in all respects with those for **1** previously prepared. Repeated recrystallization lowered the yield to about that of procedure B.

Synthesis of 5-Methyl-$\Delta^{2,2'}$-bis(1,3-benzodithiolidene) (2). 3,4-Dimercaptotoluene (**3**, 1 g, 0.006 mol) and 1,2-benzenedithiol (**5**, 1 g, 0.007 mol) were added to 20 ml of *N,N'*-diisopropylethylamine and stirred for 2–3 min. To this was added tetrachloroethylene (**4**, 1 g, 0.006 mol) and the contents were again stirred for 2–3 min. The reaction mixture while being stirred was heated under reflux for 12 hr. Upon cooling, the mixture was allowed to stand at room temperature overnight. An orange solid formed which was removed by filtration and dried to weigh 0.9 g (mp 189–210°).

From NMR analysis ($DCCl_3$), it appeared that this solid (mp 189–210°) contained compounds **1** and **2**, the former being estimated at 10–13% in it. However, the mass spectrum indicated that this solid was a mixture of three components: **1** (*m/e* 332), **2** (*m/e* 318), and **6** (*m/e* 304). This mixture was recrystallized from pyridine as below.

The mixture (0.6 g) was dissolved in hot pyridine (30 ml) and then filtered. The filtrate was cooled to room temperature and allowed to stand for 1–2 hr. Fine needles formed and were removed by filtration. This solid contained considerable amount of **1** in it as indicated by its NMR spectrum.

The filtrate was diluted with water until a faint turbidity appeared. This was boiled to clear solution and filtered, and the solution was allowed to stand at room temperature overnight. Orange crystals formed which were removed by filtration and dried. Two more crystallizations afforded 0.2 g (15% yield) of compound **2** which begins to shrink at 190° and melts at 207–210°.

Anal. Calcd for $C_{15}H_{10}S_4$: C, 56.61; H, 3.14; S, 40.25. Found: C, 56.54; H, 3.16; S, 40.46.

The infrared spectrum (KBr disk) shows absorptions at 3000 (vw), 1600 (vw), 1430 (s), 1360 (w), 1260 (w), (w), 1250 (w), 1140 1110 (s), 1020 (w), 930 (w), 875 (w), 800 (s), 770 (s), 750 (s), 690 (w), and 670 cm^{-1} (w).

An NMR spectrum ($DCCl_3$) has signals at the following δ values: 6.80–7.35 (7 H, multiplet, aromatic), 2.30 (3 H, sharp singlet, CH_3).

Synthesis of 5-Methyl-1,3-benzodithiole-2-thione (7). This compound was synthesized by a modification of a previous procedure[15] used for the synthesis of 2-thio-1,3-benzodithiole from the sodium salt of *o*-benzenedithiol. 3,4-Dimercaptotoluene (**3**, 1 g, 0.006 mol) was added to a solution obtained by dissolving sodium hydroxide (0.6 g, 0.015 mol) in 30 ml of water. To this was added carbon disulfide (2.0 g, 0.027 mol), and the reaction mixture was heated at reflux for 4 hr, cooled, and then let stand at room temperature overnight. A yellow solid formed and was filtered. The dried solid weighed 1.2 g and melted at 75–85°. Two recrystallizations from 95% ethanol afford 1.0 g (79% yield) of yellow needles which melted at 85–86° (reported[17] mp 84°).

The NMR spectrum ($DCCl_3$) of **7** (previously unreported) supported its structure with signals at δ 7.08–7.47 (3 H, multiplet, aromatic) and 2.38 (3 H, singlet, CH_3 aromatic). All attempts to convert **7** to **8** by general procedures in the literature[6,9] gave only very complex dark mixtures.

Synthesis of *o*-Benzenedithiol (5). Compound **5** was synthesized according to a previous procedure[18] except for the following modification.

Cuprous oxide was obtained from 100 g (0.40 mol) of $CuSO_4 \cdot 5H_2O$ according to a previous procedure.[19] The solid was washed with water (2 × 100 ml) and ethanol (2 × 100 ml), followed by decantation. This Cu_2O was filtered under suction and was immediately transferred to a 1-l., round-bottomed flask containing 500 ml of 95% ethanol. To this was added 1-butanethiol (22 g, 0.24 mol) in one lot and the mixture, while being stirred, was heated at reflux for 72 hr. It was filtered to afford 44.4 g of cuprous *n*-butyl mercaptide, slightly wet.

Cuprous *n*-butyl mercaptide (37 g, 0.24 mol) and 1,2-dibromobenzene (24 g, 0.10 mol) were heated in a mixture of quinoline (100 ml) and pyridine (40 ml) for 3.5 hr at 150–170°. The contents, while at 100°, were poured into 1000 g of ice and 200 ml of concentrated HCl. A yellow material formed and the mixture was stirred for 3 hr; then the water was decanted. The remaining mass was extracted with ether (3 × 100 ml.). It was allowed to stand at room temperature overnight and then the ether layer was separated by decantation. The ether layer was washed with 10% HCl (3 × 100 ml), water (3 × 100 ml), concentrated NH_4OH (2 × 100 ml), and then water (2 × 100 ml). After this, the ether layer was dried (K_2CO_3) overnight. The drying agent was filtered and the filtrate was concentrated (rotary evaporation). A yellow oil remained and was distilled at 127–130° (0.35 mm). Light yellow 1,2-bis(*n*-butylthio)benzene weighed 14.2 g (yield 55%) [reported[18a] bp 123–124° (0.3 mm)].

1,2-Bis(*n*-butylthio)benzene (5.1 g, 0.02 mol) was reduced with sodium (1.85 g, 0.08 g-atom) in 80 ml of liquid ammonia as described previously.[17] It afforded *o*-benzenedithiol (**5**) which weighed 1.5 g (51% yield) and distilled at 96–98° (5 mm) [reported[18b] bp 95° (5 mm)]. Solidification of yellow *o*-benzenedithiol occurred when kept in a refrigerator overnight. It melted at 28–29° (reported[20,21] mp 27–28°).

Synthesis of Charge-Transfer Complex 10. $\Delta^{2,2'}$-Bis(5-methyl-1,3-benzodithiolidene) (**1**, 30 mg, 9×10^{-5} mol) was dissolved by boiling in 110 ml of acetonitrile. The solution was filtered. In another flask, 7,7,8,8-tetracyanoquinodimethane (**9**, 50 mg, 24×10^{-5} mol) was dissolved in 15 ml of acetonitrile by heating and the solution was filtered.

The above filtered solutions of compound **1** and **9** were mixed together while hot. A green solution formed and was allowed to cool to room temperature and then kept at room temperature overnight. Dark needles appeared which were carefully filtered and washed several times with acetonitrile and dried. The yield of **10** was 40 mg (82% yield), mp 291–292°.

Anal. Calcd for $C_{28}H_{16}S_4N_4$: N, 10.44; S, 23.91. Found: N, 10.73; S, 24.27.

The infrared spectrum (KBr disk) of the compound shows absorptions at 3000 (vw), 2240 (s), 1575 (w), 1500 (w), 1425 (w), 1360 (broad), 1160 (s), 1130 (vw), 1100 (s), 855 (vw), 828 (s), 800 (s), 780 (s), 700 (w), 685 cm^{-1} (s). Unfortunately, the low solubility of **10** in all solvents examined prevented ^1H NMR analysis.

Synthesis of Charge-Transfer Complex 11. Compound **2** (20 mg, 9×10^{-5} mol) was dissolved in 50 ml of acetonitrile by boiling and then this solution was filtered. Compound **9** (60 mg, 29×10^{-5} mol) was dissolved in 30 ml of acetonitrile by boiling and then the solution was filtered. Both of these filtered, hot solutions were mixed together in one lot. The mixture was heated gently for 2–3 min and then allowed to stand at room temperature overnight. Blue crystals formed, were filtered, and were washed with acetonitrile (3 × 10 ml). The dried crystals of **11** weighed 30 mg (51% yield) and melted at 272–275°.

Anal. Calcd for $C_{27}H_{14}S_4N_4$: N, 10.64; S, 24.52. Found: N, 10.91; S, 24.75.

The infrared spectrum (KBr disk) showed absorptions at 3000 (vw), 2190 (s), 1575 (w), 1550 (s), 1450 (b), 1390 (b), 1180 (m), 1110 (m), 830 (m), 800 (m), 770 (m), 745 (s), 710 (w), 690 (w), 670 cm^{-1} (w). Again low solubility in all common solvents prevented a ^1H NMR examination.

Acknowledgment. We gratefully acknowledge support of this work by a grant from the 3M Co.

Registry No.—**1**, 41638-48-6; **2**, 57031-43-3; **3**, 496-74-2; **4**, 127-18-4; **5**, 17534-15-5; **7**, 54199-61-0; **9**, 1518-16-7; **10**, 54928-15-3; **11**, 57031-44-4; 1-butanethiol, 109-79-5; 1,2-dibromobenzene, 583-53-9; 1,2-bis(*n*-butylthio)benzene, 53663-38-0.

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Chemistry in Hydrogen Fluoride. Preparation of Aromatic Amides and Thioamides

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The electrophilic substitution reactions of aromatic compounds using a wide variety of substrates, electrophiles, and catalysts have been extensively investigated.[1] The direct introduction of the amide or thioamide moiety into an aromatic ring by electrophilic substitution has received little attention. Gattermann[2] observed formation of aromatic amides by the aluminum chloride catalyzed reaction of aromatic compounds with carbamoyl chloride.[3] More recently, Russian workers[4] observed the formation of aromatic amides in the reaction of aromatic hydrocarbons with alkali metal cyanate in concentrated sulfuric acid in the presence of aluminum chloride.[5] In this note the direct amidation and thioamidation of aromatic compounds with potassium cyanate or potassium thiocyanate using anhydrous hydrogen fluoride as solvent and catalyst are reported.

Aromatic amides were obtained by treating aromatic compounds with dry potassium cyanate in liquid HF at temperatures of 25–100°. The results are presented in Table I. In all cases the only organic materials observed were the monoamides and unreacted substrate with no tar formation. Control experiments demonstrated that the change in isomer ratio with temperature in the case of toluene was not due to isomerization of initially formed species at the higher temperature. With the more reactive aromatic compounds, anisole and toluene, replacement of the cyanate salt with potassium thiocyanate resulted in thioamide formation in high yield and moderate conversion (Table II).

A possible mechanism for the reaction is outlined in Scheme I. In a first step the cyanate salt reacts with HF to generate carbamoyl fluoride (1). Generation of the relative unstable carbamoyl fluoride (1, X = O) from reaction of KOCN with HF has been previously reported.[5] Subsequent acylation of the aromatic by 1 affords the observed products. The ability of HF to function as a Friedel–Crafts catalyst is well known.[1] Alternatively, partial amidation may occur via one or more intermediates in the reversible[5] for-

Scheme I

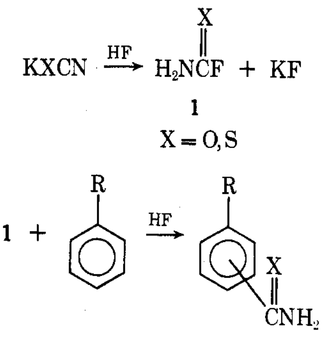

Table I
Reaction of Aromatic Compounds with Potassium Cyanate in HF

Substrate (mol)	Registry no.	KOCN, (mol)	Temp, °C	Conversion,[a] %	Product	Registry no.
Toluene (0.14)	108-88-3	0.030	100	70	45% *o*-toluamide [b]	527-85-5
					18% *m*-toluamide	618-47-3
					37% *p*-toluamide	619-55-6
Toluene (0.054)		0.040	25	50	26% *o*-toluamide [b]	
					74% *p*-toluamide	
Benzene (0.17)	71-43-2	0.030	100	63	Benzamide[c]	55-21-0
Anisole (0.74)	100-66-3	0.050	25	42	34% *o*-anisamide [d]	2439-77-2
					66% *p*-anisamide	3424-93-9
Naphthalene (0.05)	91-20-3	0.040	25	51	89% 1-naphthamide [e]	2243-81-4
					11% 2-naphthamide	2243-82-5
Chlorobenzene (0.08)	108-90-7	0.040	100	9	Chlorobenzamide[f]	619-56-7
Fluorobenzene (0.08)	462-06-6	0.040	100	20	*p*-Fluorobenzamide[g]	824-75-9
Pyridine (0.10)	110-86-1	0.050	100			
Aniline (0.05)	62-53-3	0.050	100			
Benzotrifluoride (0.06)	98-08-8	0.05	100			

[a] Based on KOCN. [b] Analyzed by GLC (6 ft × 0.125 in. 10% SE-30 on Chromosorb W column at 175°). [c] Mp 127–128° (lit.[7] mp 132.5–133.5°). [d] Analyzed by NMR, ratios by integration of methoxy singlets. [e] Isomer distribution by GLC analysis (10 ft × 0.25 in. 10% Carbowax on Chromosorb W at 150°) of the methyl esters formed by acid hydrolysis of the crude product, followed by diazomethane. Unreacted naphthalene (3.7 g) was recovered. [f] Mostly para (by NMR), not quantitatively analyzed. [g] Mp 150–152° (lit.[8] mp 152–153°).