Reaction of Nitriles with Thionyl Chloride in the Presence of Hydrogen Chloride. Formation of Sulfinyl and Sulfenyl Chlorides and Phenyl Cyanosulfine

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Received July 26, 1974

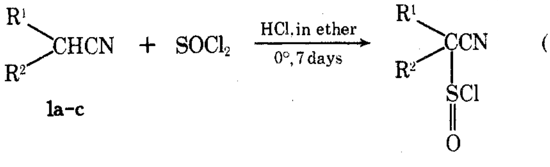
The reaction of nitriles with thionyl chloride in the presence of hydrogen chloride was investigated. The electrophilic attack of thionyl chloride occurred at the α carbon of nitriles rather than the nitrogen atom to give various products. 2-Methylpropionitrile and 2-methylbutyronitrile gave α-cyano-α-methylethane- and α-cyano-α-methylbutanesulfinyl chloride in 48 and 11% yield, respectively. α-Chlorophenylacetonitrile and 2-phenylpropionitrile gave the corresponding succinonitrile derivatives. On the other hand, some nitriles with two α hydrogens gave α-chloro-α-cyanoalkanesulfenyl chlorides in 4–44% yield. Phenylacetonitrile gave also *trans*-phenyl cyanosulfine in 5% yield when a smaller amount of hydrogen chloride was used. It was confirmed by H–D exchange experiment that nitriles were in equilibrium with α-chloroenamines under the reaction conditions. The reaction mechanisms were also discussed.

Reactions of nitriles with electrophiles in the presence of hydrogen chloride are generally initiated by the nitrogen attack of the electrophiles,[1] and there seem to be few examples which involve initial electrophilic attack at the α carbon atom.

In this paper we wish to report the reaction of nitriles with thionyl chloride in the presence of hydrogen chloride to give α-cyanosulfinyl and α-cyanosulfenyl chlorides and phenyl cyanosulfine via α carbon attack by thionyl chloride.

Results

Reaction of Nitriles Possessing one α Hydrogen. When 2-methylpropionitrile (**1a**) was allowed to react with thionyl chloride (3 equiv) in the presence of an excess of hydrogen chloride (ca. 6 equiv) at 0° for 7 days using diethyl ether as a solvent, α-cyano-α-methylethanesulfinyl chloride (**2a**) was obtained in 50% yield (based on the nitrile), and 37% of the starting nitrile was recovered.



$$R^1R^2CHCN + SOCl_2 \xrightarrow[0°, 7\,days]{HCl, in\ ether} R^1R^2C(CN)S(O)Cl \quad (1)$$

1a–c **2a–c**

a, $R^1 = R^2 = CH_3$
b, $R^1 = CH_3$; $R^2 = CH_3CH_2$
c, $R^1 = R^2 = CH_3CH_2$

Table I
Sulfinyl Chlorides 2a,b[a] and Sulfenyl Chlorides 7a–d

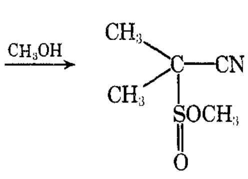
Compd	Yield (recovery of nitriles[b]), %	Bp, °C (mm)	NMR (CCl_4), δ, ppm
2a	50(37)	82–83(4)	1.80 (s, 1 H), 1.75 (s, 1 H)
2b	12(76)	73(3)	1.25 (t, 3 H)[d] 1.70 (s) and 1.75 (s) (total 3 H), 1.8–2.3 (m, 2 H)
7a	44(3)	94.5–95.5(0.7)	7.3–7.9 (m)
7b[c]	17(19)	116–116.5 (0.8)	7.4–7.9 (m)
7c	23(62)	45(5)	2.30 (s)
7d	4(80)	45–46(2)	1.35 (t, 3 H),[d] 2.10–2.65 (m, 2 H)

[a] All the sulfinyl chlorides **2a–c** showed a S=O stretching band at 1165 cm^{-1}. [b] Recovery of the starting nitriles was determined by NMR for **7a** and **7b** and by GLC for the others. [c] Mp 47–48°. [d] J = 6.8 Hz. Satisfactory analytical values (±0.3% for C, H, and N) were reported for all compounds in Table. Ed.

The sulfinyl chloride was identified on the basis of its ir and NMR spectra and elemental analyses (Table I). The ir spectrum showed, in addition to a C≡N stretching band at 2230 cm^{-1}, a strong S=O stretching band at 1165 cm^{-1} characteristic of sulfinyl chlorides.[2] The NMR spectrum (CCl_4) showed two peaks at δ 1.80 and 1.75 with an area ratio of 1:1; the magnetic nonequivalence of the two methyl groups may be attributed to asymmetry at the sulfinyl sulfur.[3]

The structure of **2a** was further confirmed by converting it into sulfinate ester **3** according to the method of Douglass.[4]

2a



$$\mathbf{2a} \xrightarrow{CH_3OH} (CH_3)_2C(CN)S(O)OCH_3$$

3

The NMR spectrum of **3** measured in CCl_4 showed one singlet at δ 1.50 due to the two methyl groups attached to the α carbon atom. In benzene, however, two singlets were observed at δ 0.95 and 1.10 due to the magnetically nonequivalent two methyl groups.[3] The solvent effect is explained in terms of the anisotropy as in the case of methyl 2-propanesulfinate.[5]

The reaction was extended to some other nitriles with one α hydrogen in order to determine the scope and limitations as a route to sulfinyl chlorides. 2-Methylbutyronitrile (**1b**) and 2-ethylbutyronitrile (**1c**) gave the corresponding sulfinyl chlorides **2b** and **2c** in low yields (12% and trace, respectively) and most of the starting nitriles were recovered[6] (Table I). 2-Chloromethylpropionitrile (**1d**), however, did not afford the expected sulfinyl chloride and 78% of the starting nitrile was recovered. 2-Phenylpropionitrile (**1e**) gave, instead of the expected sulfinyl chloride, 2,3-dimethyl-2,3-diphenylsuccinonitrile (**4e**) in 16% yield (recov-

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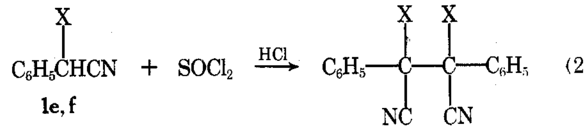


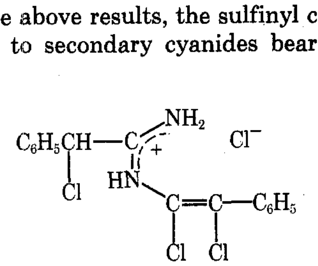
$$C_6H_5CHXCN + SOCl_2 \xrightarrow{HCl} C_6H_5C(X)(NC){-}C(X)(CN)C_6H_5 \quad (2)$$

1e,f 4e,f

e, X = CH_3
f, X = Cl

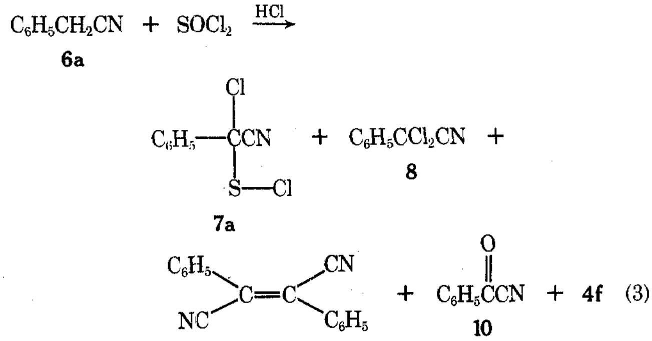
ery of 1e 75%) (eq 2). The nitrile 4e was found to be a mixture of meso and *dl* isomers (ratio 79:7) by NMR.[7] α-Chlorophenylacetonitrile (1f) gave only nitrile–hydrogen chloride adduct 5[8] in 40% yield under the same reaction conditions (recovery of 1f 27%). On the other hand, the reaction of 1f at 50° in chlorobenzene afforded a 5% yield of 2,3-dichloro-2,3-diphenylsuccinonitrile (4f) together with a 27% yield of 5 (recovery of 1f 43%). In this case, the diastereomer ratio was not determined.

In view of the above results, the sulfinyl chloride formation is limited to secondary cyanides bearing only alkyl substituents.



5

Reactions of Nitriles with Two α Hydrogens. When phenylacetonitrile (6a) was allowed to react with thionyl chloride in the presence of hydrogen chloride under the same conditions as described in the previous section, α-chloro-α-cyanophenylmethanesulfenyl chloride (7a) was obtained in 44% yield together with low yields of succinonitrile derivative 4f, α,α-dichlorophenylacetonitrile (8), *trans*-α,β-dicyanostilbene (9), and benzoyl cyanide (10) (recovery of 6a 3%) (eq 3).



$$C_6H_5CH_2CN + SOCl_2 \xrightarrow{HCl} C_6H_5C(Cl)(SCl)CN + C_6H_5CCl_2CN + \text{9} + C_6H_5COCN + \text{4f} \quad (3)$$

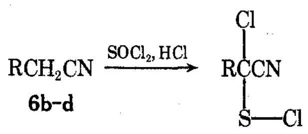
6a 7a 8 9 10

Sulfenyl chloride 7a was isolated by fractional distillation, and identified by its ir and NMR spectra and elemental analyses. The ir spectrum showed a C≡N and two S–Cl bands at 2240, 528, and 498 cm^{-1}, respectively. The NMR spectrum exhibited no peaks other than aromatic proton signals.

The sulfenyl chloride is thermally unstable and it was readily pyrolyzed at 145–150° under nitrogen to give a mixture of 4f (39%), 8 (39%), 9 (4%), and sulfur; this transformation also supports the sulfinyl chloride structure.

Products 8–10 were characterized by spectral and elemental analyses or by comparison with authentic samples (see Experimental Section).

In order to determine the scope and limitations of the reaction, the reaction of some other nitriles with two α hydrogens were also carried out under the same reaction conditions. *p*-Chlorophenylacetonitrile (6b), propionitrile (6c), and *n*-butyronitrile (6d) afforded the corresponding sulfenyl chlorides 7b–d in 17, 23, and 4% yield, respectively (eq 4) (Table I).



$$RCH_2CN \xrightarrow{SOCl_2, HCl} RC(Cl)(SCl)CN \quad (4)$$

6b-d 7b-d

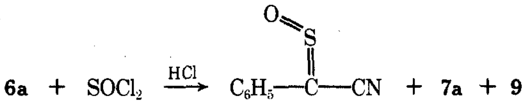
b, R = *p*-ClC_6H_4
c, R = CH_3
d, R = CH_3CH_2

Although the reaction of 6b yielded a fair amount of by-products, they were not characterized. In the case of 6c and 6d, only a small amount of tar was produced as a by-product and fair amounts of the starting nitriles were recovered (Table I).

Chloroacetonitrile (6e), 3-chloropropionitrile (6f), 3-phenylpropionitrile (6g), and ethyl cyanoacetate (6h) failed to give the corresponding sulfenyl chlorides. Nitrile 6e gave a nitrile–hydrogen chloride 2:3 adduct[8] in 71% yield. The reactions of both 6f and 6g resulted in a 70% recovery of the starting nitriles. Nitrile 6h afforded only an intractable tar (recovery of 6h 23%).

Thus, the sulfenyl chloride formation is limited to phenylacetonitriles and unsubstituted primary alkyl cyanides.

Formation of Phenyl Cyanosulfine. It is of much interest that a new type of sulfine, i.e., phenyl cyanosulfine (thiobenzoyl cyanide *S*-oxide, 11), was obtained in 5% yield together with *trans*-α,β-dicyanostilbene (9, 7%) and sulfenyl chloride 7a from the reaction of phenylacetonitrile (6a) with thionyl chloride (3 equiv) in the presence of a smaller amount of hydrogen chloride (3 equiv) at 0° for 3 days (eq 5); the recovery of the starting nitrile was 56%.



$$\text{6a} + SOCl_2 \xrightarrow{HCl} C_6H_5C(=S=O)CN + \text{7a} + \text{9} \quad (5)$$

11

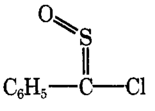
The reaction in the presence of 6 equiv of hydrogen chloride for both 3 and 6 days also yielded a trace amount of 11, the formation of which was confirmed by ir analyses of the reaction mixtures.

The structures of the sulfine was established by spectral and elemental analyses, and by its disproportionation reaction. The ir spectrum exhibited, in addition to the absorption at 767 and 682 cm^{-1} due to the monosubstituted benzene, two C≡N bands at 2215 and 2205 cm^{-1}, and C=S=O bands at 1140 and 998 cm^{-1}.[9,10] The mass spectrum showed the molecular ion peak at *m/e* 163 and the deoxygenated peak at *m/e* 147, and the NMR spectrum ($CDCl_3$) showed aromatic proton signals at δ 7.3–7.8 (m) and 8.1–8.4 (m) with relative areas of 3:2. In addition, by analogy to the behavior of some sulfines,[9,11] sulfine 11 decomposed gradually on heating with evolution of sulfur dioxide to give *trans*-α,β-dicyanostilbene (9). Thus, when a benzene solution of 11 was heated under reflux for 12 hr, a 54% yield of 9 was obtained together with benzoyl cyanide (10) (trace) and sulfur (recovery of the starting material 7%) (eq 6).

$$11 \xrightarrow[\text{12 hr}]{\text{reflux in benzene}} 9 + 10 + SO_2 + S \quad (6)$$

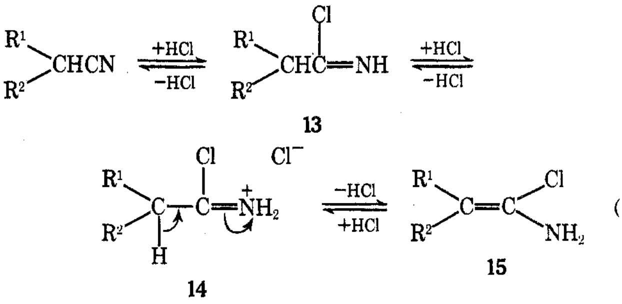
In view of the thermal instability of sulfine 11, *trans*-α,β-dicyanostilbene (9) in eq 5 must be formed through the decomposition of 11 during work-up.

If two substituents are different, it is possible for sulfines to exist in two geometrical isomers.[12] In the present case, cyanosulfine **11** probably has the trans configuration, i.e., the oxygen is trans to the cyano group, in view of the close resemblance of chemical shifts and patterns of its NMR signals to those of *trans*-phenyl chlorosulfine (**12**).[10,12]



12

H–D Exchange of the α Hydrogens of Nitriles in the Presence of Deuterium Chloride. Simchen and Krämer postulated that nitriles with at least one α hydrogen atom were in equilibrium with α-chloroenamine **15** in the presence of hydrogen chloride as shown in eq 7.[13]



(7)

Their postulation is based on the observation that α deuteriums of nitriles are replaced by hydrogens in the presence of hydrogen chloride.[13]

Since also in the present reactions the α-chloroenamine seemed to play an important role, the H–D exchange reaction of α hydrogens of nitriles was investigated to obtain mechanistic information.

Nitriles were treated with 3 equiv (for nitriles with one α hydrogen) or 6 equiv (for nitriles with two α hydrogens) of deuterium chloride in diethyl ether at 0° for 4 days. The degree of deuterium exchange was determined by NMR. Results are shown in Table II. It is obvious from the table that most nitriles examined except for **1c** are in equilibrium with the corresponding α-chloroenamine **15** under the reaction conditions.

Table II
H–D Exchange of α Hydrogens of Nitriles
Nitrile $R^1(R^2)CHCN$

Compd	R^1	R^2	% deuteration
1a	CH_3	CH_3	45
1b	CH_3	CH_3CH_2	18
1c	CH_3CH_2	CH_3CH_2	0
1d	CH_3	$ClCH_2$	82
1e	C_6H_5	CH_3	76
6a	C_6H_5	H	85
6c	CH_3	H	80
6f	$ClCH_2$	H	86

Whereas almost maximum deuterations (80–85%) were obtained for nitriles with two α hydrogens independent of the α substituents, deuterations of secondary cyanides varied significantly, depending on the nature of the α substituents.

For secondary alkyl cyanides, the extent of deuteration decreased dramatically on going from **1a** to **1c**, and this order is consistent with the order of the decrease in yields of the sulfinyl chlorides **2a–c**. However, it was difficult to generally correlate the deuterations with product yields.

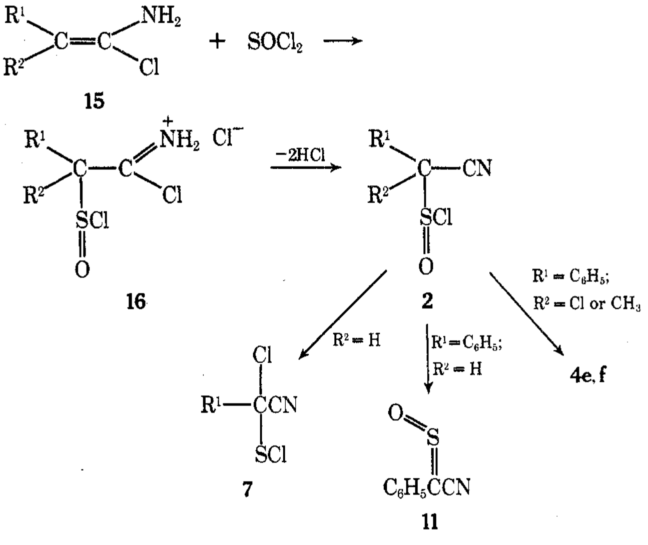
Discussion

Since the nitriles failed to react with thionyl chloride in the absence of hydrogen chloride, it is evident that hydrogen chloride plays a very important role in the present reactions. In other words, activated species derived from the reaction of nitriles with hydrogen chloride, i.e., nitrile–hydrogen chloride adducts **13–15**, take part in the reaction. Among them, α-chloroenamine **15** seems to be the most plausible species that is subjected to the electrophilic attack by thionyl chloride in view of the fact that the decrease in the yield of sulfinyl chlorides **2a–c** is in line with the decrease in percent deuteration of the starting nitriles **1a–c**. Nitriles **1d** and **1f**, however, failed to give the corresponding sulfinyl or sulfenyl chloride in spite of their high percent deuteration. This may be ascribed to low nucleophilicity of the β carbon of the corresponding α-chloroenamine **15** as a result of substitution of a chlorine atom on the adjacent saturated carbon atom.

The above speculation that α-chloroenamine **15** is attacked rather than **13** and **14** is reasonable in view of the resemblance of the present reactions to acid-catalyzed halogenation of ketones[14] and α-chlorosulfenylation of carboxylic acid chlorides and ketones,[15,16] in which enols (oxygen analogs of enamines) rather than ketones or acid chlorides themselves are subjected to the electrophilic attack.

The most plausible routes of the present reactions are depicted in Scheme I.

Scheme I



The reaction probably proceeds by the initial electrophilic attack of thionyl chloride at the β carbon of α-chloroenamine **15** to produce iminium salt **16**, followed by elimination of hydrogen chloride to give sulfinyl chloride **2** as the final product for nitriles **1a–c** or as the intermediate for nitriles **6a–d**. The succinonitrile derivatives **4e** and **4f** might also be produced via **2**. In the case of nitriles with two α hydrogens, the initially formed sulfinyl chloride further reacts with thionyl chloride to give the sulfenyl chloride **7** possibly via the Pummerer type reaction proposed by Krubsack et al. for the chlorosulfinylation of acid chlorides and ketones by thionyl chloride.[15,16]

In the case of phenylacetonitrile, phenyl cyanosulfine (**11**) is also produced, the yield of which is very low as a result of suppression of dehydrochlorination from sulfinyl chloride **2** (R^1 = C_6H_5; R^2 = H) when a large excess (6 equiv) of hydrogen chloride is used.

At a glance, sulfine **11** seems to be in equilibrium with sulfinyl chloride **2** (R^1 = C_6H_5; R^2 = H). If that is the case, sulfenyl chloride **7a** would be produced also from sulfine **11**. However, treatment of **11** with thionyl chloride in the presence of hydrogen chloride resulted in the almost quantitative recovery of the starting material. Thus, the sulfine is not in equilibrium with the sulfinyl chloride; this is consistent with the result of Strating et al.[17]

The present reaction is of synthetic use since sulfenyl or sulfinyl group is introduced into nitriles by one process under mild conditions.

Experimental Section[18]

General Procedure. Anhydrous HCl (ca. 11 g, 0.30 mol) was dissolved into a solution of a nitrile (0.05 mol) in anhydrous ether (30 ml) in a 115-ml glass tube under ice cooling, followed by addition of thionyl chloride (17.85 g, 0.15 mol). After sealing the tube, the mixture was allowed to stand at 0° for 7 days. After the gaseous products were purged, the solvent and other volatile materials were removed under reduced pressure (ca. 20 mm) at room temperature, then the resulting liquid was fractionally distilled to give a sulfinyl chloride or sulfenyl chloride. The distillation residue was chromatographed on either alumina or silica gel to give crystalline products.

In the case of α-chlorophenylacetonitrile (**1f**) and chloroacetonitrile (**6e**), the corresponding nitrile–hydrogen chloride adducts precipitated in the reaction mixture.

Sulfinate Ester 3. To a solution of **2a** (3.03 g, 0.02 mol) in anhydrous ether (10 ml) was added 1.0 g (0.031 mol) of methanol at −30° and the mixture was stirred for 30 min. After removal of the solvent, the resulting liquid was distilled under reduced pressure to give 2.53 g (86%) of **3** (colorless liquid): bp 88–89° (5 mm); ir (liquid film) 2230, 1460, 1160, 980, and 730 cm^{-1}; NMR (CCl_4) δ 1.50 (s, 6 H) and 3.85 (s, 3 H); NMR (C_6H_6) δ 0.95 (s, 3 H), 1.1 (s, 3 H), and 3.25 (s, 3 H).

Anal. Calcd for $C_5H_9NO_2S$: C, 40.80; H, 6.16; N, 9.52. Found: C, 40.76; H, 6.34; N, 9.95.

Reaction of 2-Phenylpropionitrile (1e). According to the general procedure, **1e** (6.55 g, 0.05 mol) was allowed to react with thionyl chloride. The liquid, obtained after removal of the volatile material, was distilled under reduced pressure to give 4.92 g (75%) of the starting nitrile. The distillation residue was chromatographed on alumina. Elution with CCl_4 gave 1.07 g (16%) of a mixture of *meso*- and *dl*-2,3-dimethyl-2,3-diphenylsuccinonitrile (**4e**), which was recrystallized from benzene to give colorless prisms: mp 234–235°; ir (KBr) 2230, 1500, 1450, 1230, 1805, 790, 745, and 695 cm^{-1}; NMR ($CDCl_3$) δ 1.80 (s, CH_3 of meso isomer) and 2.08 (s, CH_3 of *dl* isomer)[7] (area ratio 79:7); mass spectrum (70 eV) *m/e* (rel intensity) 260 (M^+), 130 (100, $M^+/2$), 103 (50), and 77 (30).

Anal. Calcd for $C_{18}H_{16}N_2$: C, 83.05; H, 6.20; N, 10.76. Found: C, 83.04; H, 6.26; N, 10.99.

Reaction of α-Chlorophenylacetonitrile (1f) at 50° in Chlorobenzene. Anhydrous HCl (0.80 g, 0.022 mol) was dissolved into **1f** (4.55 g, 0.03 mol) in a 80-ml Pyrex tube, and then a mixture of thionyl chloride (10.7 g, 0.09 mol) and chlorobenzene (6 ml) was added. After sealing the tube, the mixture was heated at 50° for 2 days on an oil bath. The precipitates formed were filtered, washed with a small portion of ether, and dried in vacuo to give 1.53 g (27%) of **5**, which was identified by comparison with an authentic sample.[8] The filtrate was concentrated and distilled under reduced pressure to give 1.94 g (43%) of **1f**. The distillation residue was chromatographed on silica gel. Petroleum ether–benzene (4:1 v/v) eluted 0.4 g (5%) of 2,3-dichloro-2,3-diphenylsuccinonitrile (**4f**), which was recrystallized from benzene to give colorless prisms: mp 188–189°; ir (KBr) 1495, 1445, 1180, 1000, 845, 795, 725, and 690 cm^{-1}; NMR ($CDCl_3$) δ 7.1–7.8 (m); mass spectrum (70 eV) *m/e* (rel intensity) 300 (M^+), 265 ($M^+ - Cl$), 230 (100, $M^+ - 2Cl$), 215 (32), 203, and 150 (60, $M^+/2$).

Anal. Calcd for $C_{16}H_{10}N_2Cl_2$: C, 63.81; H, 3.35; N, 9.30; Cl, 23.54. Found: C, 63.88; H, 3.15; N, 9.62; Cl, 23.82.

Reaction of Phenylacetonitrile (6a) in the Presence of 6 Equiv of HCl. Phenylacetonitrile (**6a**, 5.85 g, 0.05 mol) was allowed to react according to the general procedure. The liquid obtained after removal of the volatile materials was fractionally distilled to give 2.53 g of a forerun and 4.85 g (44%) of α-chloro-α-cyanophenylmethanesulfenyl chloride (**7a**, a yellow liquid). The forerun was a mixture of **6a**, **7a**, **8**, and **10**. Nitriles **8** (ir 1500, 1457, 1200, 1022, 870, 797, 727, and 688 cm^{-1}) and **10** (ir 2320 and 1690 cm^{-1}) were identified by comparison of the GLC retention time and ir spectrum with those of authentic samples.[19,20] The distillation residue was chromatographed on silica gel. Sulfur (0.05 g), 2,3-dichloro-2,3-diphenylsuccinonitrile (**4f**, 0.32 g, 4%), and a trace amount of α,β-dicyanostilbene (**9**) were eluted with petroleum ether–benzene (4:1 v/v) and petroleum ether–benzene (1:1 v/v), respectively. Dicyanostilbene **9** was recrystallized from EtOH to give colorless needles: mp 160–162°; ir (KBr) 2200 ($C\equiv N$), 1495, 1250, 755, and 690 cm^{-1}. The mixture melting point of **9** and an authentic sample[21] showed no depression.

Pyrolysis of 7a. Sulfenyl chloride **7a** (8.72 g, 0.04 mol) was placed in a 15-ml two-necked flask equipped with a gas inlet tube and a gas outlet tube and it was heated on an oil bath at 145–150° for 3 hr. A continuous stream of nitrogen was passed through the reaction mixture during the pyrolysis. The precipitates formed were filtered, washed with a small portion of ether, and dried in vacuo to give a mixture of sulfur, **4f**, and **9**. The filtrate was distilled under reduced pressure to give 2.88 g (39%) of **8**, bp 82.5–83° (3.5 mm). The mixture obtained by filtration and the distillation residue were combined and chromatographed on silica gel. Sulfur (0.5 g), **4f** (2.36 g, 39%), and **9** (0.17 g, 4%) were eluted with petroleum ether, petroleum ether–benzene (9:1 v/v), and petroleum ether–benzene (1:1 v/v), respectively.

Reaction of Phenylacetonitrile (6a) with Thionyl Chloride in the Presence of 3 Equiv of HCl. A solution of **6a** (5.85 g, 0.05 mol) in 30 ml of anhydrous ether was placed in a 115-ml glass tube, then anhydrous HCl (5.6 g, 0.15 mol) was dissolved into the solution, followed by the addition of thionyl chloride (17.85 g, 0.15 mol). After sealing the tube, the mixture was allowed to stand at 0° for 3 days. After removal of the volatile materials, the residual oil was distilled under reduced pressure to give two fractions, the first 3.45 g (55–85°, 0.1 mm) and the second 1.60 g (85–95°, 0.1 mm). The second fraction partially solidified when it was left standing at room temperature. The solid that formed was filtered, washed with a small portion of *n*-hexane, and dried in vacuo to yield 0.5 g (6%) of *trans*-phenyl cyanosulfine (**11**, a yellow powder), which was recrystallized from *n*-hexane–CCl_4 (10:3 v/v) to give fine yellow needles: mp 69.5–70°; ir (Nujol)[22] 2215, 2205, 1592, 1583, 1445, 1283, 1190, 1140, 1110, 1604, 998, 767, and 682 cm^{-1}; NMR ($CDCl_3$) δ 7.3–7.8 (m, 3 H) and 8.1–8.4 (m, 2 H); mass spectrum (70 eV) *m/e* (rel intensity) 163 (100, M^+), 147 (38, $M^+ - 0$), 135 (42), and 115 (30); λ_{max} (CH_3CN)[23] (log ε) 227 (3.78), 273 (3.43), and 341 nm (4.07).

Anal. Calcd for C_8H_5NOS: C, 58.80; H, 3.09; N, 8.58; S, 19.65. Found: C, 58.64; H, 2.99; N, 8.52; S, 19.27.

The filtrate of the second fraction and the first fraction were combined, and percent recovery of the starting nitrile was determined by NMR to be 56%.

Pyrolysis of *trans*-Phenyl Cyanosulfine (11). A solution of sulfine **11** (335 mg, 2.1 mmol) in 2 ml of benzene was heated under reflux for 12 hr on an oil bath (bath temperature 110–120°). The solvent was removed under reduced pressure (ca. 20 mm) at room temperature and the residue was chromatographed on silica gel. Elution with petroleum ether gave 25 mg of sulfur, and further elution with petroleum ether–benzene (2:1 v/v) gave a trace amount of benzoyl cyanide (**10**), 23 mg (7%) of *trans*-phenyl cyanosulfine (**11**), and 128 mg (54%) of *trans*-α,β-dicyanostilbene (**9**), successively.

H-D Exchange of α Hydrogens of Nitriles. DCl was prepared by dropping D_2SO_4 (96–98%) into a mixture of dried NaCl and DCl solution (20%) in D_2O and it was dried by passing through a P_2O_5 column. DCl was dissolved into diethyl ether and two DCl–ether solutions of different concentration, solution A (3.04 mmol DCl/ml) and solution B (5.60 mmol DCl/ml), were prepared. Solutions A and B were used for nitriles with one α hydrogen and for those with two α hydrogens, respectively. A mixture of a nitrile (10 mmol) and 10 ml of the DCl–ether solution in a 20-ml sealed glass tube was allowed to stand at 0° for 4 days. After removal of the solvent, the residual liquid was distilled at ordinally or reduced pressure to give a mixture of undeuterated and deuterated nitriles. The percent deuteration was determined by NMR analysis of the mixture.[24]

Registry No.—**1a**, 78-82-0; **1b**, 18936-17-9; **1e**, 1823-91-2; **1f**, 22259-83-2; **2a**, 56630-18-3; **2b**, 56630-19-4; **3**, 56630-20-7; *meso*-**4e**, 16510-37-5; *dl*-**4e**, 16510-36-4; **4f**, 52819-60-0; **6a**, 140-29-4; **6b**, 140-53-4; **6c**, 107-12-0; **6d**, 107-74-0; **7a**, 56630-21-8; **7b**, 56630-22-9; **7c**, 56630-23-0; **7d**, 56630-24-1; 8, 40626-45-7; **9**, 2450-55-7; **10**, 613-90-1; **11**, 56630-25-2; thionyl chloride, 7719-09-7; methanol, 67-56-1.

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Chemical Purity and the Electrical Conductivity of Tetrathiafulvalinium Tetracyanoquinodimethanide

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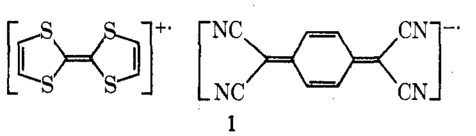
Received March 6, 1975

A critical evaluation using high-pressure liquid chromatography is made of three purification techniques for the neutral precursors of the highly conducting organic charge-transfer salt TTF-TCNQ (1). The purification techniques examined are (a) recrystallization, (b) sublimation, and (c) gradient sublimation. It is demonstrated that for the compounds studied gradient sublimation offers no significant advantage over more conventional sublimation techniques, and in fact is less efficient than simpler methods. Direct current conductivity data for crystals obtained from TTF^0 and TCNQ^0 of the varying purity are also presented. Only in extremely dirty samples do we see any significant change in electrical conductivity. We conclude that for impurity concentrations likely to be achieved routinely in most laboratories, crystal perfection rather than chemical purity chiefly determines the sample-dependent conductivity of TTF-TCNQ.

The best organic conductors of electricity known are the charge-transfer salt TTF-TCNQ (tetrathiafulvalinium tetracyanoquinodimethanide, 1), first prepared in these laboratories,[2–8] and several of its derivatives[9] and analogs.[10,11] The chain-like structures[5] of these materials lead to conductivities which are highly anisotropic, but metallic in magnitude along the chain axis. Since the propagation of conduction electrons is thus restricted effectively to one dimension, it is natural to expect chemical impurities and lattice defects to influence transport more profoundly here than in conventional three-dimensional metals.



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Interest in the problem of purification has sharpened with the observation[2,12–14] that the conductivity of TTF-TCNQ is strongly sample dependent. Although it now appears that early reports[12] of truly giant conductivities in occasional crystals were overstated,[15–17] the variation among specimens is still large enough that the intrinsic conductivity of TTF-TCNQ remains in some doubt. Compounding the uncertainty are claims by at least one laboratory[12,13,18] of extreme chemical purity, based solely upon accounts of the methods of purification and care employed in synthesis.

Toward a resolution of these questions, we have undertaken to evaluate the methods currently used by various laboratories for purification of the neutral molecules TTF^0 and TCNQ^0. Using newly available techniques of high-pressure gel permeation chromatography, we obtain separations of 4000–5000 theoretical plates, and by differential ultraviolet detection we are able to monitor impurity concentrations as low as 1 ppm. We find that conventional techniques of recrystallization and sublimation are sufficient to reduce impurity levels in TTF^0 below the sensitivity of our instruments. The same is true of TCNQ^0 except for a tendency to complex weakly with acetonitrile. The acetonitrile is removed upon formation of the TTF-TCNQ salt. The gradient sublimation technique introduced by McGhie et al.[18] offers no improvement for TTF^0 or TCNQ^0. The conductivities of TTF-TCNQ crystals of maximum purity are the same as reported previously,[2,14,15] and not significantly different from those of deliberately contaminated samples. The latter, however, appear more susceptible to inhomogeneous current distributions which give rise to spurious giant apparent conductivities.[15,16] We conclude that most of the variation in conductivity among samples of TTF-TCNQ is due to lattice imperfections rather than chemical purity.