Found: C, 54.22; H, 4.17; N, 7.56; S, 8.45.

The solvolysis products from 6β-Cl were confirmed by comparison of TLC and IR data with those of authentic samples.

Thermal Isomerization of 5α-Cl and 5β-Cl in Me_2SO. Samples of 0.6 g of both penam chlorides, **5**α-Cl and **5**β-Cl, were dissolved in 20 mL of purified Me_2SO and kept at 100 °C for 1 h for complete isomerization. Next, the reaction mixture was poured into cold water and extracted twice with ethyl acetate. The organic layer was repeatedly washed with water to remove Me_2SO completely, dried over anhydrous magnesium sulfate, filtered, and condensed under reduced pressure to leave crude product mixtures from both chlorides, which showed three TLC spots of almost the same R_f values. Their NMR and IR spectra were also very similar, suggesting formation of the same products. Separation of both reaction mixtures on preparative TLC plates yielded **6**β-Cl as a major product (270 mg from **5**β-Cl and 310 mg from **5**α-Cl) and almost the same amounts of minor products **7** and **6**β-Cl (20–30 mg of **7** and 25 mg of **6**β-OH from both chlorides), confirming the formation of the same products from both. The formation of **6**β-OH could not be suppressed even by an attempted complete removal of water from the Me_2SO using an activated alumina column and molecular sieves. The structural elucidation of **7** and **6**β-OH was straightforward by comparison of melting point and spectral data with the reported values.[7,19] The structure of **6**β-Cl was previously reported by us.[9]

Methyl 6β-Phthalimido-2α,2β-bis(chloromethyl)penam-3-carboxylate (14). The oxidation of 0.6 mmol of **5**β-Cl (235 mg) with *m*-chloroperbenzoic acid by a conventional method afforded the *R* sulfoxide, which was successively subjected, without purification, to thermal sulfoxide rearrangement in the presence of equimolar amounts of acetyl chloride and pyridine, using a reported method.[9] After the usual workup, the resultant crude crystalline product was recrystallized from a solvent mixture of dichloromethane and ether to afford a pure sample of the title compound in an isolated yield of ca. 40% (102 mg): mp 106–108 °C; $[\alpha]^{24.5}{}_D$ +243.5 ± 4.7° (*c* 0.604, CH_3CN); IR ($CHCl_3$) 1798, 1780, 1730–1740 (two peaks) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.70 and 4.18 (AB q, 2, $C_{2\alpha}$-CH_2Cl, J = 11.5 Hz), 4.19 and 4.55 (AB q, 2, $C_{2\beta}$-CH_2Cl, J = 12.0 Hz), 3.83 (s, 1, $C_{3\alpha}$), 5.67 (d, 1, $C_{5\alpha}$), 5.75 (d, 1, $C_{6\alpha}$), 7.80 (m, 4, aromatic); mass spectrum, *m/e* 429 (M^+), 400, 392, 358, 341, 314, 242, 206, 187, 160, 146, 142. Anal. Calcd for $C_{17}H_{14}O_5N_2SCl_2$: C, 47.56; H, 3.29; N, 6.53; O, 18.63; Cl, 16.34. Found: C, 47.75; H, 3.64; N, 6.04; O, 18.48; Cl, 16.34.

The *R* sulfoxide derived from **5**α-Cl, having the cis S–O bond with respect to the C_2–CH_2Cl bond, did not produce **14** at all as reported by Spry[6] with similar systems having the acetoxy substituent in place of the chlorine.

Methyl 7β-Phthalimido-3α-(chloromethyl)-3β-hydroxycepham-4α-carboxylate (15). **14** (1 mmol, 429 mg) was dissolved in 25 mL of 80% aqueous Me_2SO containing an equimolar amount of $AgClO_4$ (207 mg) and kept at 45 °C for 3 h. After the same workup, except for filtration through a Celite layer, used in the thermal rearrangement of penam chlorides in Me_2SO, the resultant crude crystalline product was recrystallized from a mixed solvent of acetone and ether and gave a pure sample of **15** in 78.0% yield (320 mg): mp 189–190 °C; IR ($CHCl_3$) 1788, 1775, 1740, 1728 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.76, 3.56 (AB q, 2, C_2, J = 15.0 Hz), 3.73 (q, 2, $C_{3\alpha}$-CH_2Cl, J = 9.5 Hz), 3.82 (s, 3, CO_2CH_3), 4.80 (s, 1, $C_{4\alpha}$), 5.47 (d, 1, $C_{6\alpha}$), 5.67 (d, 1, $C_{7\alpha}$), 7.60–8.0 (m, 4, aromatic). Anal. Calcd for $C_{17}H_{15}N_2O_6SCl$: C, 49.70; H, 3.68; N, 6.82; S, 7.79; Cl, 8.63. Found: C, 49.82; H, 3.75; N, 6.62; S, 8.17; Cl, 8.33.

Methyl 7β-Phthalimido-3-(chloromethyl)-3-cephem-4-carboxylate (16). To a benzene solution of 0.146 mmol of **15** (60 mg dissolved in 2 mL of benzene) and 0.438 mmol of pyridine was added 0.438 mmol of thionyl chloride dropwise at room temperature under stirring, and the mixture was heated at 80 °C for 10 min while gas evolution was observed. Next, the reaction mixture was quickly poured into cold 3% aqueous sodium bicarbonate solution, extracted with ethyl acetate twice, dried over magnesium sulfate, filtered, and condensed under reduced pressure, leaving an oily product mixture (58 mg) which showed two spots on TLC analysis. The preparative TLC separation of this mixture afforded a higher R_f fraction compound (12 mg, 19.1%), which was found to be **14** by comparison of its melting point and spectral data with those of the authentic sample, and also the pure lower R_f fraction compound (40 mg, 52.3%), which was determined to be **16** on the basis of the spectral and analytical data: mp 169–171 °C; $[\alpha]^{24.5}{}_D$ +5.1 ± 1.1° (*c* 0.396, CH_3CN); IR ($CHCl_3$) 1800, 1780, 1730 (two peaks) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.55 (AB q, 2, C_2, J = 18.0 Hz), 3.90 (s, 3, $COOCH_3$), 4.45 and 4.87 (AB q, 2, $C_{3\alpha}$-CH_2Cl, J = 11.0 Hz), 5.14 (d, 1, $C_{6\alpha}$), 5.80 (d, 1, $C_{7\alpha}$), 7.83 (m, 4, aromatic); mass spectrum, *m/e* 392 (M^+), 346, 329, 305, 270, 206, 187, 172, 160, 132, 104. Anal. Calcd for $C_{17}H_{13}N_2O_5SCl$: C, 51.99; H, 3.34; N, 7.13; S, 8.15; Cl, 9.03. Found: C, 51.79; H, 3.45; N, 7.06; S, 8.19; Cl, 9.11.

Acknowledgment. We thank Dr. T. Tsuji for helpful discussions.

Registry No. **5**α-Cl, 39067-79-3; **5**α-OEt, 73805-78-4; **5**β-Cl, 51415-59-9; **6**β-Cl, 40146-21-2; **6**β-OH, 51815-69-1; **6**β-OEt, 73816-18-9; **7**, 38584-05-3; **11**, 753-89-9; **12** (X = Cl), 931-78-2; **13A**, 73805-79-5; **14**, 73805-80-8; **15**, 73805-81-9; **16**, 73805-82-0; **17**-OH, 58346-65-9; **18**-OH, 54288-61-8.

Organic Semiconductors Based on Diaminodicyanothiophene and Diaminodicyanoselenophene

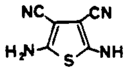
F. Wudl,* E. T. Zellers, and D. Nalewajek

Bell Laboratories, Murray Hill, New Jersey 07974

Received February 11, 1980

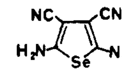
Several new derivatives of 2,5-diamino-3,4-dicyanothiophene (DAMCYT) as well as of the new compound 2,5-diamino-3,4-dicyanoselenophene (DAMCYS) are described. Conversions of a disulfinyl derivative and an *N,N*-bis(chlorothio) derivative to conducting polymers are reported.

In our continuing effort[1] to emulate polythiazyl[2] $[(SN)_x]$, we decided to prepare polymers with the backbone shown in Figure 1. These polymers could be envisioned as alternating sulfur diimides and diaminothiophenes (diaminoselenophenes). The latter are expected to be extremely unstable and have not been described in the literature. On the other hand, diaminodicyanothiophene (DAMCYT) is a known compound,[3] but DAMCYS (the



DAMCYT

1



DAMCYS

2

---

(1) F. Wudl, A. A. Kruger, and G. A. Thomas, *Ann. N. Y. Acad. Sci.*, **313**, 79 (1978).

(2) G. B. Street and W. D. Gill, *NATO Conf. Ser.*, [*Ser.*] *6*, 1, 301–326 (1979).

(3) W. J. Middleton, V. A. Engelhardt, and B. S. Fisher, *J. Am. Chem. Soc.*, **80**, 2822 (1958).

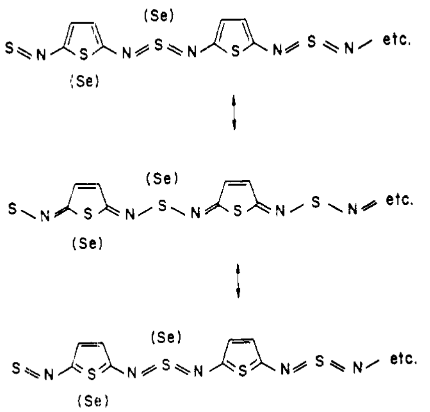
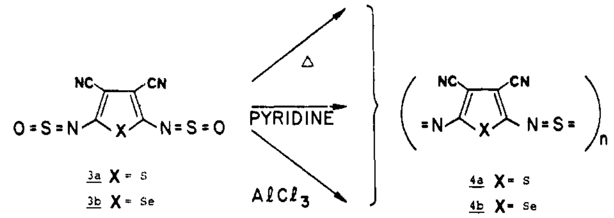


Figure 1.

Scheme I



selenophene analogue) is described for the first time in this publication. Presumably, the strong electron-withdrawing functional groups (CN) stabilize the overly electron-rich heterocycles.

Sulfur diimides are generally prepared from sulfinylamines,[4] from amines and sulfur tetrachloride,[4] and from the dimerization of thionitrosyl compounds.[5] Sulfur-nitrogen multiply bonded compounds can also be prepared according to eq 1.[6] Scheme I summarizes reactions dis-

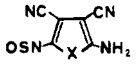
$$R_2S{=}O + TsN{=}C{=}O \rightarrow R_2S{=}NTs + CO_2 \quad (1)$$

covered by Kresze for *N*-sulfinyl sulfonamides and applied to our problem. The bis(sulfinylamino) compounds 3 could be prepared by published procedures.[4]

Results

Both diaminodicyano heterocycles were prepared from tetracyanoethylene and hydrogen sulfide or selenide by the procedure which was published for the sulfur derivative.[3] The course of the reaction was slightly different for the selenophene than the thiophene (cf. Experimental Section).

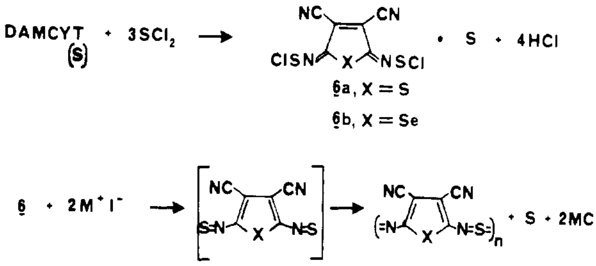
Prolonged reaction between the heterocycles and neat thionyl chloride produced the bis(sulfinylamino) compounds. When methylene chloride was used as solvent and pyridine as base, compound **3b** could be isolated in good yield. The disulfinyl derivatives were, not unexpectedly, very moisture sensitive; this was particularly true for the DAMCYS derivative. Exposure to atmospheric moisture produced only the partial hydrolysis products **5a,b**. Thus,



5a X = S
5b X = Se

attempted recrystallization from hot toluene in an open Erlenmeyer flask produced pure **5a**. Whereas **5a** and **5b** had superimposable IR spectra, a correct elemental analysis for **5b** could not be obtained. Presumably the stability of **5** to further hydrolysis under these conditions is due to "push-pull"; i.e., the electrophilicity of the N=S=O linkage is greatly diminished by the resonance electron donation from the amino group in the 5-position. Complete (exothermic) hydrolysis back to DAMCYT (DAMCYS) occurred in moist dimethylformamide. Incidentally, the sequence shown in eq 2 constitutes an excellent method to purify DAMCYT(S) from persistent colored impurities.

Scheme II



$$\text{DAMCYT(S)} + \text{SOCl}_2 \rightarrow \text{DAMCYT(SO)}_2 \xrightarrow[\text{H}_2\text{O}]{\text{DMF}} \text{DAMCYT(S)} \quad (2)$$

Reaction of the bis(sulfinylamino) compounds with pyridine was relatively rapid at room temperature. The homogeneous, dark yellow solutions slowly became darker and eventually solidified. The reaction mixture consisted of acetonitrile soluble (blue-black solutions) and insoluble fractions. Evaporation of the solvent afforded a blue-black gum which was not characterized further. The insoluble fraction was a black powder which had incorporated pyridine as determined by elemental analysis. It exhibited a strong, broad solid-state ESR signal with $g = 2.0027$ G and a room-temperature compressed-pellet resistivity of 700 Ω cm. An analogous reaction with **3b** afforded a solid with $g = 2.0025$ G and a pellet resistivity of 3000 Ω cm.

Attempted polymerization of the bis(sulfinylamino) compounds via $AlCl_3$ produced only black, intractable materials which could not be separated from aluminum salts.

Since the pyridine-catalyzed polymerization had incorporated pyridine and the other polymerizations based on disulfinyl precursors failed, we attempted to generate a bis(thionitrosyl) intermediate which would polymerize[5] to the desired product according to the reactions depicted in Scheme II.

Reaction of DAMCYT with excess sulfur dichloride (for the reaction of nitrile-containing sulfur heterocycles with SCl_2, see ref 7) afforded beautiful red crystalline platelets whose elemental analysis was correct for **6a** but whose IR spectrum exhibited a very low intensity absorption in the C≡N region, inconsistent with the above formulation. More confusion was cast on the problem by the following: (a) the mass spectrum of **6a** was as expected; (b) the solution molecular weight of **6a** was much higher than expected (see Experimental Section), but the solution molecular weight of **6b** was the same as the calculated value (see Experimental Section); (c) spectroscopically (IR), **6a** and **6b** were identical, and the mass spectra were correct for the above structures, but the results of elemental analyses were consistently high for chlorine in the case of **6b**; (d) recrystallization of **6a** from ethylene chloride with and without chlorine gas afforded completely different morphologies, yet the elemental analyses were identical.

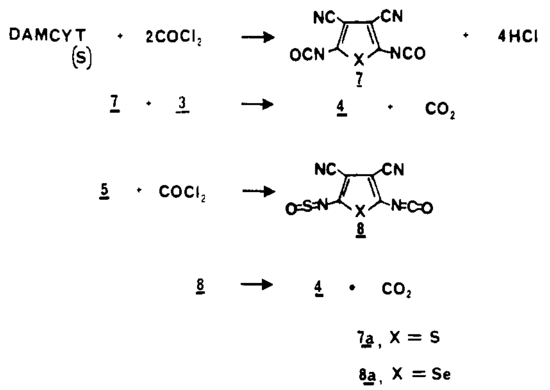
---

[4] G. Kresze and W. Wucherpfennig, *Angew. Chem., In. Ed. Engl.*, 6, 149 (1967).

[5] R. Mayer, S. Bleisch, and G. Domschke, *Z. Chem.*, 18, 323 (1978).

[6] C. King, *J. Org. Chem.*, 25, 352 (1960).

Scheme III



Nevertheless,[9] reaction of **6a** with excess tetrabutylammonium iodide afforded complete dechlorination and reduction to a radical anion [g = 2.0025 G, broad (4.7 G), strong signal] with tetrabutylammonium as counterion (eq 3 and 4).

$$\text{DAMCYT} + SCl_2 \rightarrow C_6N_4S_3Cl_2 \qquad (3)$$

$$C_6N_4S_3Cl_2 + Bu_4NI \rightarrow [C_{22}N_{17}S_9]^-Bu_4N^+ \qquad (4)$$

This material, amorphous by appearance, had a lower room temperature compaction resistivity (260 Ω cm) than that of the pyridine containing polymer. The conductivity could be improved considerably (19 Ω cm) by metathesis reaction with $(TTF)_3(BF_4)_2$ which resulted in complete exchange of Bu_4N^+ for TTF^+ with a concomitant change in stoichiometry.

Similar reactions were attempted by starting with DAMCYS and sulfur dichloride, but the dechlorination products were ill defined.

Since, once again, a reagent involved in the polymerization reaction (i.e., Bu_4N^+) was incorporated in the final product, there remained at least two more approaches to the desired polymers, summarized in Scheme III.

Since DAMCYT is very insoluble in all common solvents (including acetonitrile), it was not surprising that several attempts to generate the diisocyanate **7a** failed, with the isolable product being isocyanopolyurea as determined by infrared spectroscopy. Reaction of **5a** with phosgene afforded complex mixtures which showed (via IR spectroscopy) that the N=S=O function had been destroyed; absorptions due to urea were also observed, and consequently, **8** was not formed. Finally, heating thionylaniline (PhNSO) with phenyl isocyanate in either acetonitrile or toluene overnight resulted in no visible reaction, i.e., no CO_2 evolution or disappearance of starting materials (IR).

Discussion

When we set out to prepare the polymers **4**, we envisioned that conductivity would occur via the CNS spine in analogy to $(SN)_x$. In addition, we thought that more charge carriers might be generated by a donor–acceptor interaction between the $\ddot{N}=\ddot{S}=\ddot{N}$ and the N≡C—C=C—C≡N moieties of the polymer. However, incorporation of pyridine and reduction by iodide would indicate that either the $\ddot{N}=\ddot{S}=\ddot{N}$ function (contrary to the behavior observed with $(SN)_x$) is a poor donor or that it was not generated under the reaction conditions. Inspection of the infrared spectrum revealed that there were some broad peaks in the region where N=S=N is expected to absorb. Tetrasulfur tetranitride (S_4N_4) and our "polymer" had strong absorptions in the same IR frequency range: S_4N_4 (KBr) 1230, *1195*, 1042, *1005*, *922*, *725*, *695* cm^{-1}; "pyridine polymer" (KBr) 1480, 1355, 1300, *1200*, *1095*, *1010*, *910*, *700* cm^{-1}.

The compaction conductivity of the TTF derivative is sufficiently high to indicate that if this material were to be produced as a single crystal, its conductivity may be as high as that of doped polyacetylene. Also, the fact that the tetrabutylammonium precursor to this TTF derivative conducts electricity indicates that the radical anion is responsible for transport properties and that it may constitute an anionic counterpart to polyacetylene.

If the above assumption that multiply bonded sulfur–nitrogen or sulfur–oxygen functional groups are strongly electron withdrawing is correct,[8] then **3** would be expected to form charge-transfer complexes. Indeed, **3** reacts with donors in solution. When **3a** was slightly contaminated with chloride (not enough to be detected by elemental analyses), a highly conducting TTF derivative was formed. On the other hand, scrupulously purified **3a** afforded only semiconducting TTF derivatives (ρ = 1000 Ω cm). That the contaminant was not thionyl chloride was shown by the fact that admixture of traces of this reagent to the donor–acceptor reaction mixture produced only insulating to semiconducting products with TTF.

Conclusion

While we have yet to produce a neutral $(CN=S=N)_n$ polymer, we found an unexpected, potentially interesting result: the N=S=N functional group, when incorporated into an electron-deficient framework, is strongly electron withdrawing.[10]

After the fact, this should not have been surprising since it was recently shown[8] that N=S=O enhances the acidity of hydrogens attached to the carbon bearing this functional group. However, since nitrogen is more electropositive than oxygen, N=S=N was still expected to be a weak donor. After all, O=S=O is a reducing agent, and S_4N_4 reacts exothermally with bromine.[2]

Our result indicates that if one were to produce $(=C—N=S=N)_n$ in thin-film form, it could be doped with weak donors and thus be a complement to $(CH)_x$ which is dopable with weak acceptors but only with very strong donors (Na^0, etc.).

Experimental Section

All elemental analyses (mostly duplicate and several times quadruplicate) were performed by Schwarzkopf Analytical Laboratory. Electrical conductivity measurements were two-probe measurements on pressed pellets of ca. 1.5-mm diameter and 0.5-mm thickness. No special precautions were observed during electrical measurements.

Preparation of 2,5-Diamino-3,4-dicyanoselenophene (2). A solution of 24.9 g (0.194 mol) of tetracyanoethylene in 300 mL of acetone and 300 mL of carbon disulfide was cooled to 3 °C in

---

[7] B. A. Carlson, L. S. Guggenberger, R. C. Gearhart, and M. D. Gordon, Abstracts, ACS/CSJ Chemical Congress, Honolulu, HI, Apr 1979, No. ORGN 159.

[8] F. M. Schell, J. P. Carter, and C. Wiaux-Tamar, *J. Am. Chem. Soc.*, **100**, 2894 (1978).

[9] Results of X-ray crystallography by the Molecular Structure Corp. confirm structure **6a** for $C_6N_4Cl_2S_3$. Details of this structure and that of the selenium analogue (which turned out to be $C_6N_4Cl_4S_2Se$) will be the subject of future publications.[12]

[10] Geevers and Trompen[11] found that the following reaction is very facile: NCC(Cl)=NSCl + Cl^- ⇄ NCC(Cl)=N^- + SCl_2. If reaction of **6a** with iodide proceeds in analogy to this reaction rather than (or in addition to) the proposed second reaction in Scheme II, then the product may have incorporated $(NC)_2C=C(CN)C(S)N=S$ units resulting from ring opening and loss of SClI from **6a**. This moiety should be very susceptible to further reduction to a stable radical anion. We are currently attempting to substantiate this conjecture.

[11] J. Geevers and W. P. Trompen, *Tetrahedron Lett.*, 1687 (1974).

[12] F. Wudl and E. T. Zellers, *J. Am. Chem. Soc.*, **102**, 4283 (1980); F. Wudl and E. T. Zellers, *ibid.*, in press.

an ice–water bath. Hydrogen selenide gas was passed through the stirred mixture for 30 min, resulting in the formation of an orange precipitate. Then 100 mL of pyridine was added, and the precipitate turned gray-green in color (prolonged stirring did not dissolve the precipitate). Hydrogen selenide was passed through for another 30 min, with no apparent change occurring in the reaction mixture. After the system was purged thoroughly with N_2, the mixture was filtered. The dark blue solid obtained was washed with acetone and dried under N_2. Extraction with dimethylformamide (300 mL) gave a deep orange solution. This solution was cooled to 3 °C, and water was added slowly (temperature kept at <25 °C) until the product precipitated. Washing with acetone and drying yielded 34.53 g (84%) of light tan crystals: IR (CsI) 3400 (s), 3310 (s), 2195 (s), 1610 (s), 1560 (s), 1530 (s), 1390 (m), 1342 (s), 1250 (m), 1180 (w), 1150 (m), 100 (m) cm^{-1}.

Anal. Calcd for $C_6H_4N_4Se$: C, 34.12; H, 1.90; N, 26.54; Se, 37.44. Found: C, 34.07; H, 2.22; N, 25.87; Se, 37.64.

Preparation of 2,5-Bis(sulfinylamino)-3,4-dicyanothiophene (3a). A mixture of 1.64 g (0.01 mol) of **1** and 10 mL of distilled thionyl chloride was refluxed for 4 h and allowed to cool. Filtration yielded a dark gray solid (1.73 g) which was washed with toluene and dried under a N_2 stream. Recrystallization from 50 mL of thionyl chloride gave 1.15 g (45%) of gold needles which turn red on prolonged exposure to the atmosphere: the ^{13}C NMR spectrum (THF-d_8) showed three singlets of nearly equal intensity at δ 149.6, 111.1, and 107.8 relative to Me_4Si; IR (KBr) 2230 (s), 1440 (m), 1379 (m), 1298 (w), 1270 (s), 1231 (w), 1205 (w), 1165 (s) cm^{-1}.

Anal. Calcd for $C_6N_4O_2S_3$: C, 28.12; N, 21.88; O, 12.50; S, 37.50. Found: C, 28.46; N, 21.92; O, 12.76; S, 37.39.

Preparation of 2,5-Bis(sulfinylamino)-3,4-dicyanoselenophene (3b). To a vigorously stirred mixture of 100 mL of dry methylene chloride, 6.5 mL of pyridine, and 3.2 mL of freshly distilled thionyl chloride was added 4.22 g (0.014 mol) of **2**. The orange-gold product which formed after 24 h was filtered and washed with 5 mL of methylene chloride to yield 5 g of product.

The crude product was transferred to a flask containing 100 mL of methylene chloride, 6 mL of pyridine, and 3 mL of thionyl chloride. After the mixture was stirred for 1 h, the golden yellow crystals were filtered and washed with 5 mL of methylene chloride: yield 4.2 g (69%) of pure **3b**; IR (KBr) 2230 (m), 1500 (m) 1457 (m), 1413 (m), 1375 (w), 1250 (m), 1150 (s), 1015 (w), 910 (w), 750 (w) cm^{-1}.

Anal. Calcd for $C_6N_4O_2S_2Se$: C, 23.77; N, 18.48; S, 21.15; Se, 26.04. Found: C, 24.18; N, 18.56; S, 21.52; Se, 26.31.

Preparation of 2-Amino-3,4-dicyano-5-(sulfinylamino)-thiophene (5a). To 750 mg (2.93 mmol) of **3a** was added 400 mL of toluene. The mixture was heated to reflux for 1 h and allowed to cool. Shiny red crystals (220 mg, 36%) were isolated, washed with cold toluene, and dried under a N_2 stream: IR (KBr) 3380 (s), 3280 (s), 3175 (s), 2225 (s), 1625 (s), 1510 (s), 1465 (s), 1440 (w), 1318 (s), 1139 (s), 1020 (m), 940 (m) cm^{-1}.

Anal. Calcd for $C_6H_2N_4OS$: C, 34.29; H, 0.95; N, 26.67; O, 7.60; S, 30.40. Found: C, 34.55; H, 1.23; N, 26.54; O, 7.79; S, 30.24.

Preparation of **5b**, the analogous selenium compound, was similar.

Reaction of 2,5-Bis(sulfinylamino)-3,4-dicyanothiophene (3a) with Pyridine. In a dry flask, under N_2, were combined 480 mg (1.88 mmol) of **3a** and 6 mL of dry pyridine (stored over 4-Å molecular sieves). The mixture was stirred for 15 min until the solid had dissolved. The stirring bar was removed and the mixture allowed to stand overnight. The next day, the solidified contents of the flask were washed copiously with pyridine followed by acetonitrile and then dried under a N_2 stream. The product, a black amorphous solid, had a room-temperature compressed-pellet resistivity of 700 Ω cm. Its IR spectrum (KBr) showed a broad conducting band with a poorly defined spectrum superimposed on it: 2190 (s), 1610 (s), 1570 (m), 1480 (s), 1355 (s), 1300 (m), 1200 (m), 1095 (m), 1010 (m), 910 (m), 700 (s) cm^{-1}.

Anal. Calcd for $C_{41}H_{22}N_{18}O_5S_8$: C, 44.64; H, 1.99; N, 22.86; O, 7.26; S, 23.23. Found C, 44.61; H, 2.03; N, 23.63; O, 7.27; S, 23.49.

Reaction of 2,5-Bis(sulfinylamino)-3,4-dicyanoselenophene (3b) with Pyridine. In a dry flask, under N_2, were combined 325 mg (1.07 mmol) of **3b** and 5 mL of dry pyridine. The mixture was stirred for 5 min until the solid had dissolved. The stirrer bar was removed and the mixture allowed to stand for 42 h in the dark. Most of the mixture had solidified. The excess pyridine was evaporated at reduced pressure. The solid remaining was washed with acetonitrile (500 mL) until the washings were only faintly colored and then dried under N_2, yielding 112 mg of black amorphous solid: compressed-pellet resistivity 3000 Ω cm; IR (KBr) 2195 (m), 1612 (s), 1570 (m), 1485 (s), 1360 (s), 1300 (m), 1200 (m), 1095 (w), 1010 (m), 875 (w), 815 (w), 768 (m), 710 (m), 700 (m) cm^{-1}.

Anal. Calcd for $C_{31}H_{16}N_{14}S_4Se_4$: C, 36.18; H, 1.56; N, 19.07; S, 12.45; Se, 30.74. Found: C, 36.01; H, 1.56; N, 18.85; S, 13.61; Se, 30.83.

Reaction of 2,5-Diamino-3,4-dicyanothiophene (1) with Sulfur Dichloride. To 45 mL of sulfur dichloride (distilled over PCl_5) was added 1.0 g (6.0 mmol) of **1** in a dry flask. The mixture was swirled gently, and a fine stream of gas was evolved. The mixture was allowed to stand overnight, and shiny red crystals formed. These were filtered, washed with hexane, and dried under N_2, yielding 895 mg (50%) of **6a**: UV–vis (CH_2Cl_2) 282 nm (sh, ϵ 5880), 297 (7720), 400 (4680), 507 (22700); IR (KBr) 2230 (w, 1530 (s), 1500 (s), 1345 (s), 1240 (w), 892 (s), 841 (s), 820 (m) cm^{-1}; mass spectrum, *m/e* 296 $[(P + 2)^+]$, 294 $[(C_6Cl_2N_4S_3)^+]$, 259 $[(P - Cl^+]$, 224 $[(P - Cl_2)^+]$, 192 $[(P - SCl_2)^+]$, 146 $[(P - NSCl_2)^+]$, etc.; molecular weight calcd for $C_6Cl_2N_4S_3$ 295, found 381, 409; $E_{1/2}{}^{P} = -0.32, -0.77, -1.1$ vs. SCE, CH_2Cl_2, $Bu_4N^+BF_4^-$ as supporting electrolytes. The first two waves are reversible, the last is not. Solutions color deeply during these experiments.

Anal. Calcd for $C_6Cl_2N_4S_3$: C, 24.41; Cl, 24.07; N, 18.98; S, 32.54. Found: C, 24.21; Cl, 23.93; N, 18.66; S, 32.83.

Reaction of 2,5-Diamino-3,4-dicyanoselenophene (2) with Sulfur Dichloride. To 20 mL of sulfur dichloride (distilled over PCl_5) was added 1.0 g (4.7 mmol) of **2**. The mixture was swirled and heated slightly until gas evolution was noted. When the mixture was allowed to stand overnight, crystals formed. These were filtered, washed with hexane, and dried under N_2, yielding 1.64 g (84%) of siny brown crystals of **6b**: UV–vis (CH_2Cl_2) 296 nm (ϵ 6270), 400 (6840), 427 (10 200), 454 (15 200), 511 (10 900); IR (KBr) 2225 (w), 1520 (m), 1490 (s), 1330 (s), 1227 (w), 849 (m), 812 (s) cm^{-1}; mass spectrum, *m/e* 344 $[(P + 2)^+]$, 342 $[(C_6Cl_2N_4S_2Se)^+]$, 307 $[(P - Cl)^+]$, 272 $[(P - Cl_2)^+]$, etc.; solution molecular weight calcd for $C_6Cl_4N_4S_2Se$ 413, found 403, 422.

Anal. Calcd for $C_6Cl_2N_4S_2Se$: C, 21.05; Cl, 20.76; N, 16.37; S, 18.70; Se, 23.09. Found: C, 19.22; Cl, 28.11; N, 15.11; S, 15.26; Se, 22.03.

Reaction of 6a with Tetrabutylammonium Iodide. To a warm solution of 258 mg (0.875 mmol) of **6a** in 50 mL of dry CH_2Cl_2 was added 967 mg (2.62 mmol) of tetrabutylammonium iodide. Upon addition the solution turned from red to green. The mixture was swirled gently and allowed to stand for 2 days. The precipitate which had formed was filtered under N_2, washed with CH_2Cl_2, and dried under N_2, yielding 153 mg of amorphous black solid: compressed-pellet resistivity 260 Ω cm; IR (KBr) 2195 (m), 1360 (s), 1320 (s), 1200 (s), 905 (w), 835 (m), 760 (w), 700 (m) cm^{-1}.

Anal. Calcd for $C_{38}H_{36}N_{18}S_9$: C, 44.18; H, 3.48; N, 24.41; S, 27.91. Found: C, 44.38; H, 3.45; N, 24.01; S, 28.35.

Reaction of 6b with Tetrabutylammonium Iodide. To a warm solution of 413 mg of **6b** in CH_2Cl_2 was added 1.51 g (4.08 mmol) of tetrabutylammonium iodide, resulting in an immediate color change from red to green. The mixture was swirled and allowed to stand in the dark for 2 days under Ar. The black crystals (68 mg) which resulted were isolated, washed with CH_2Cl_2, and dried under a N_2 stream: IR (KBr) 2195 (m), 1330 (s), 1200 (m), 1020 (w), 910 (w), 830 (w), 740 (w), 700 (m) cm^{-1}.

Anal. Calcd for $C_{25}H_{25}N_{10}S_9Se_9$: C, 20.49; H, 1.70; N, 9.56; S, 19.67; Se, 48.56. Found: C, 19.35; H, 1.65; N, 9.05; S, 19.68; Se, 46.13.

Reaction of $(C_{22}N_{17}S_9)^-Bu_4N^+$ with $(TTF)_3(BF_4)_2$. A mixture of **7a** (90 mg) and $(TTF)_3(BF_4)_2$ (137 mg, 0.17 mmol) in distilled CH_3CN (40 mL) was stirred for 5 days at room temperature. A black amorphous solid was isolated, washed with CH_3CN, and dried under N_2 (93 mg). The product gave a compressed-pellet resistivity of 19 Ω cm and a strong, broad ESR signal (g = 2.0071 G) in the solid state. Its IR spectrum (KBr) gave a typical broad conducting band with poorly resolved peaks: 2100 (m), 1365 (s), 1318 (s), 1210 (s), 910 (w), 835 (m), 700 (m) cm^{-1}.

J. Org. Chem. 1980, 45, 3215–3227

Anal. Calcd for $C_{18}H_4N_8S_8$: C, 36.73; H, 0.68; N, 19.05; S, 43.54. Found: C, 35.02; H, 0.64; N, 19.22; S, 43.66.

Reaction of 3a with TTF. A solution of **3a** (0.15 g, 5.8×10^{-4} mol) and TTF (0.239 g, 1.17×10^{-3} mol) was prepared by dissolving the respective compounds in 25 mL of CH_3CN. When the reactants were mixed, shiny black platelets were deposited. After being allowed to stand at ambient temperature for 8 h, the mixture was filtered and continuously washed with CH_3CN until the filtrate was colorless. The nonstoichiometric complex (see below) exhibited a compressed-pellet resistivity of 1000 Ω cm.

On the basis of the results of the analytical data, a molecular formula of $C_{27}H_{15}N_{10}O_5S_{12}$ was calculated. Varying the molar ratio of TTF had no effect on this formulation.

Anal. Calcd for $C_{27}H_{15}N_{10}O_5S_{12}$: C, 34.34; H, 1.60; N, 14.83; O, 8.47; S, 40.68. Found: C, 34.49; H, 1.59; N, 14.59; O, 8.52; S, 41.26.

Acknowledgment. Special thanks go to D. J. Freed and A. Mujsce for mass spectroscopy and S. Vincent for qualitative X-ray fluorescence analysis.

Registry No. 1, 17989-89-8; 2, 74007-35-5; **3a**, 74007-36-6; **3b**, 74007-37-7; **5a**, 74007-38-8; **6a**, 74007-39-9; **6b**, 74007-40-2; **7a**, 74019-23-1; tetracyanoethylene, 670-54-2; carbon disulfide, 75-15-0.

Unidirectional Dieckmann Cyclizations on a Solid Phase and in Solution

John I. Crowley[1] and Henry Rapoport*

Department of Chemistry, University of California, Berkeley, California 94720

Received January 28, 1980

Dieckmann cyclization of 2% divinylbenzene–copolystyrene resin alkyl pimelates and analogous benzyl alkyl pimelates is reported. The use of uniquely single-labeled dioate esters has allowed analysis of the direction of closure via decarboxylation of the keto ester products. The influence of steric factors on the competition between enolate condensation and transesterification and upon the direction of closure of the cyclization has been evaluated, and the conditions for achieving >99% regioselective closure are described. Modifications in the conditions of solid-phase peptide synthesis required for successful high-temperature enolate cyclization have been developed and the results are compared to solution reactions of benzyl alkyl esters under similar conditions. The resin attachment afforded a clear benefit over the benzyl models and greatly simplified isolation and purification of the resulting β-keto esters.

Introduction

Success in the synthesis of carbocyclic compounds from open-chain precursors is dependent upon the competitive interplay of a number of factors, among the most important of which is ring size.[2] Entropy effects dictate a decreased rate of closure with increasing probability of separation of the terminal C-α and C-β carbons. On the other hand, the summed effects of interactions occurring as the atoms in the chain assume the cyclic transition state is an enthalpy effect and is a complex function of ring size. The resultant of these two effects affords maximum rates of formation for five- and six-membered carbocycles and minimum rates for nine- and ten-membered rings.

An α,ω-bifunctional molecule can lead to cyclization and/or polymerization, depending upon the relative rates of intra- and intermolecular condensations. Recognition that the cyclization rate has a first-order, while polymerization has a second-order, dependence upon concentration led to introduction of the high-dilution principle.[3] Useful yields of ring compounds containing 12 or more carbons have been obtained; however, for nine- or ten-membered rings, this relative advantage has been insufficient to provide practical synthetic processes.[4] A further technique, restriction of the mobility of the reacting termini by adsorption on a surface which effects cyclization,[5] was applied successfully to the preparation of nine- and ten-membered carbocycles in the acyloin reaction.[6,7]

An ideal cyclization will possess the following characteristics: (1) cyclization should be the fastest reaction taking place; (2) competitive polymerization should be prevented, e.g., by high dilution,[2,3] immobilization,[6,7] or some equivalent technique; (3) closure should lead to a single or predominate carbocycle, easily separable from other products. Solid-phase synthesis[8,9] appeared to offer a superior technique for the development of a cyclization method which meets a number of these criteria. Preliminary reports[10] have appeared of the solid-phase cyclization of pimelates and of the less successful cyclization of sebacate analogues. Also, solid-phase organic synthesis, including cyclization, has been the subject of several comprehensive reviews, and experimental ambiguities in this field have been critically examined.[11]

We now describe the detailed experimental conditions required to achieve Dieckmann closures of resin-bound pimelate esters and benzylic model compounds and the synthetic utility of mixed-ester substrates. Dieckmann

---

[1] IBM Research Laboratory, San Jose, CA.

[2] Sicher, J. In "Progress in Stereochemistry"; de la Mare, P. B. D., Klyne, W., Eds.; Butterworth: Washington, 1962; Vol. 3, p 222.

[3] (a) Ruggli, P. *Justus Liebigs Ann. Chem.* **1912**, *392*, 92. (b) Ziegler, K.; Eberle, H.; Ohlinger, H. *Ibid.* **1933**, *504*, 94.

[4] Leonard, N. J.; Schimelpfenig, C. W., Jr. *J. Org. Chem.* **1958**, *23*, 1708.

[5] Hansley, V. L. U.S. Patent 2 226 268, 1941.

[6] Stoll, M.; Rouve, A. *Helv. Chim. Acta* **1934**, *17*, 1283.

[7] (a) Prelog, V.; Frenkiel, L.; Kobelt, M.; Barman, P. *Helv. Chim. Acta* **1947**, *30*, 1741. (b) Bloomfield, J. J.; Owsley, D. C.; Nelke, J. M. *Org. React.* **1976**, *23*, 259.

[8] (a) Merrifield, R. B. *Adv. Enzymol.* **1969**, *32*, 221. (b) Erickson, B. W.; Merrifield, R. B. "The Proteins", 3rd ed.; Neurath, H., Hill, R. L., Eds.; Academic Press: New York, 1976; Vol. 2. (c) Wieland, T.; Birr, C.; Frodl, R.; Lochinger, W.; Stahnke, G. *Justus Liebigs Ann. Chem.* **1972**, *757*, 136.

[9] Stewart, J. M.; Young, J. D. "Solid Phase Synthesis"; W. H. Freeman: San Francisco, 1969.

[10] (a) Crowley, J. I.; Rapoport, H. *J. Am. Chem. Soc.* **1970**, *92*, 6363. (b) Crowley, J. I.; Harvey, T., III; Rapoport, H. *J. Macromol. Sci., Chem.* **1973**, *A7*, 1118.

[11] (a) Leznoff, C. C. *Chem. Soc. Rev.* **1974**, *3*, 65. (b) Pitman, C. U., Jr.; Evans, G. O. *CHEMTECH* **1973**, 560. (c) Overberger, C. G.; Sannes, K. N. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 159. (d) Crowley, J. I.; Rapoport, H. *Acc. Chem. Res.* **1976**, *9*, 135. (e) Neckers, D. C. *CHEMTECH* **1978**, 108. (f) Leznoff, C. C. *Acc. Chem. Res.* **1978**, *11*, 327. (g) Maxur, S.; Jayalekshmy, P. *J. Am. Chem. Soc.* **1979**, *101*, 677.

0022-3263/80/1945-3215$01.00/0