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Reaction of 4,5-Dichloro-1,2,3-dithiazolium Chloride with 2-(Phenylsulfonyl)acetonitrile

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Abstract: The reaction of 4,5-dichloro-1,2,3-dithiazolium chloride with 2-(phenylsulfonyl)acetonitrile (1 equiv) in the presence of pyridine (2 equiv) gave *S*-(3-chloro-5-cyanoisothiazol-4-yl)benzenesulfonothioate and (*Z*)-2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2-(phenylsulfonyl)acetonitrile in 19% and 23% yield, respectively. The compounds were fully characterized and the mechanistic rationale is proposed for the formation of the benzensulfonate.

Keywords: heterocycle; polyfunctionalized; 1,2,3-dithiazole; sulfone; isothiazole

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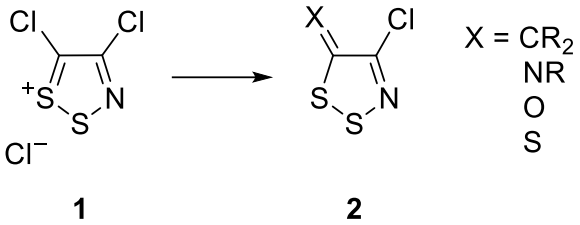
1. Introduction

Monocyclic 1,2,3-dithiazoles are sulfur-rich heterocycles that act as fungicides [1–3], antibacterials [4–6], antivirals [7,8] or anticancer agents [9–11]. Moreover, 1,2,3-dithiazolyls are potential organic magnets and/or conductors [12,13]. The field of monocyclic 1,2,3-dithiazoles took off over 35 years ago with the preparation of 4,5-dichloro-1,2,3-dithiazolium chloride **1** (aka Appel's salt, Scheme 1) [14], which has been used extensively for the preparation of many neutral 5*H*-1,2,3-dithiazoles **2** [15]. The chemistry and applications of 1,2,3-dithiazoles have been reviewed [16–19].

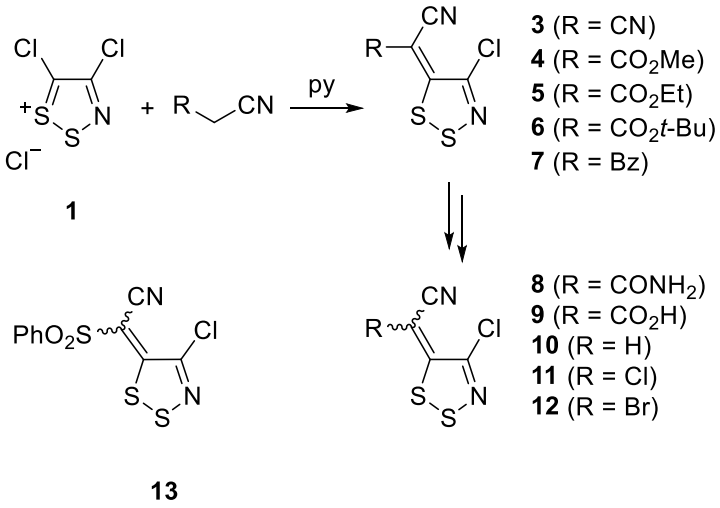


1 **2**

Scheme 1. Structure of Appel's salt **1** and its neutral 5*H*-1,2,3-dithiazoles **2**.

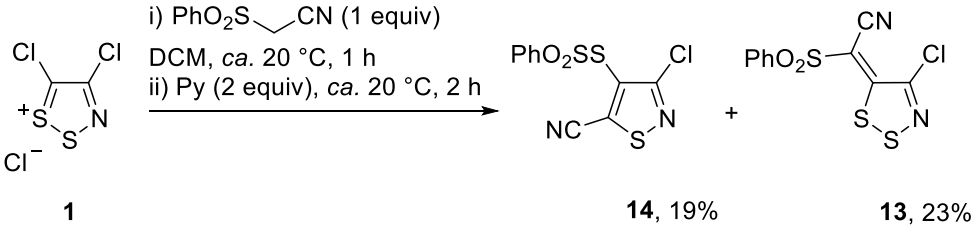
2. Results and Discussion

Recently, we investigated the biological activity of (5*H*-1,2,3-dithiazol-5-ylidene)-2-acetonitriles and required access to analogues that can be prepared from the condensation of Appel's salt **1** with active methylenes [14,20,21]. While preparations for ylidene-acetonitriles **3**–**7** [14,20–23] and their derivatives **8**–**12** [24] are reported and the compounds are fully characterized, little is known about the only sulfone analogue **13** (Scheme 2). This compound was reported by Rees in 1992, quoting a low yield (exact number not reported) [25], but the reaction conditions or any characterization data of the product were not reported. We therefore repeated this synthesis to obtain and characterize the desired product **13**. Interestingly, the carbonyl-containing (5*H*-1,2,3-dithiazol-5-ylidene)-2-acetonitriles **4**–**7** were assigned as the *Z* isomers due to stabilizing "non-bonding" interactions between the carbonyl oxygen and the dithiazole [26].



Scheme 2. Synthesis of dithiazole ylidenes.

The reaction of Appel's salt **1** with 2-(phenylsulfonyl)acetonitrile (1 equiv) in DCM, for 1 h, followed by the addition of pyridine (2 equiv) and further stirring for 2 h gave two main products, the colorless *S*-(3-chloro-5-cyanoisothiazol-4-yl)benzenesulfonothioate (**14**) in 19% yield and the yellow colored (*Z*)-2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2-(phenylsulfonyl)acetonitrile (**13**) in 23% yield (Scheme 3).



Scheme 3. Reaction of Appel's salt **1** with 2-(phenylsulfonyl)acetonitrile.

Product **14** was isolated as colorless needles, m.p. 146–147 °C (from *c*-hexane). FTIR spectroscopy showed a cyano ν(C≡N) stretch at 2236 cm^{-1} along with sulfone ν(S=O) stretches at 1335 and 1148 cm^{-1}, while mass spectrometry revealed a molecular ion [M + Na$^+$] peak of *m/z* 339 (100%) along with a [M + Na$^+$ +2] peak at 341 (45%), which supported the presence of a single chlorine. ^{13}C NMR spectroscopy showed the presence of three CH resonances and five quaternary carbon resonances (see Supplementary Materials for the complete spectra), while a correct elemental analysis (CHN) was obtained for the molecular formula $C_{10}H_5ClN_2O_2S_3$. Structural support was also provided by single-crystal X-ray diffraction studies (Figure 1).

Product **13** was isolated as yellow needles, m.p. 181–183 °C (from *c*-hexane). UV–vis spectroscopy supports an intact dithiazole ring (λ_{max} 433 nm, log ε 4.26). FTIR spectroscopy showed a cyano ν(C≡N) stretch at 2197 cm^{-1} along with sulfone ν(S=O) stretches at 1315 and 1144 cm^{-1}, while mass spectrometry revealed a molecular ion [M + Na$^+$] peak of *m/z* 339 (100%) along with a [M + Na$^+$ +2] peak at 341 (44%) that supported the presence of a single chlorine. ^{13}C-NMR spectroscopy showed the presence of three CH resonances and five quaternary carbon resonances (see Supplementary Materials for the complete spectra), while a correct elemental analysis (CHN) was obtained for the molecular formula $C_{10}H_5ClN_2O_2S_3$. We tentatively assigned the alkene geometry as *Z* owing to steric and electronic repulsion between the C-4 chloride and the sulfonyl group, while a "non-bonding" interaction between the sulfonyl oxygen and the dithiazole S1 is also possible [26].

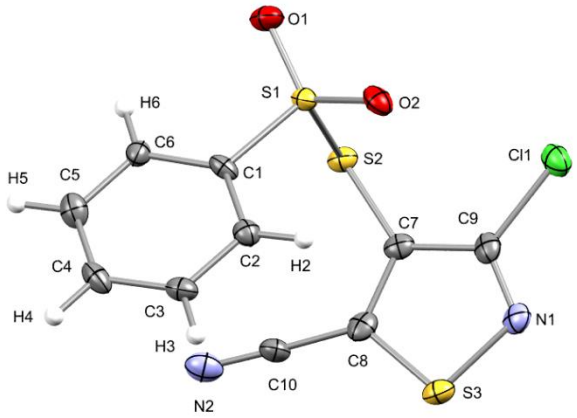
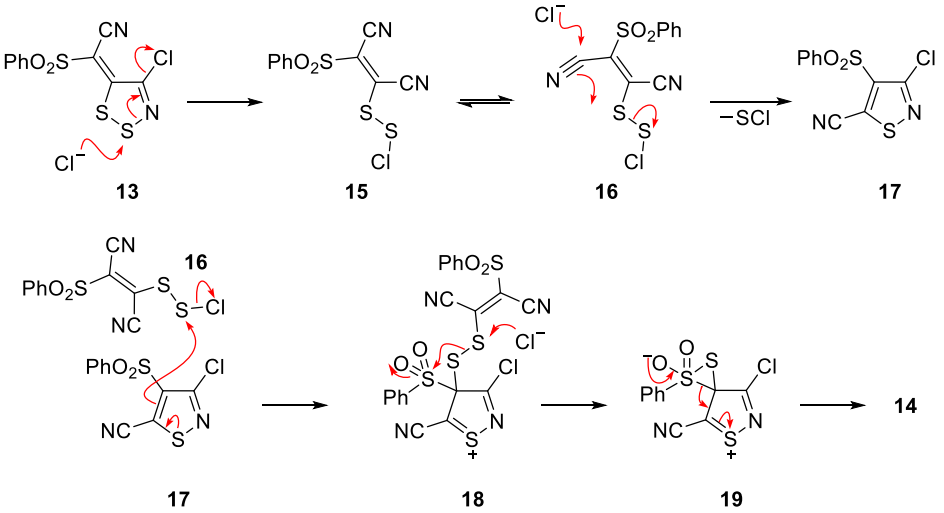


Figure 1. Geometry of *S*-(3-chloro-5-cyanoisothiazol-4-yl)benzenesulfonothioate (**14**) in the crystal; crystallographic atom numbering. Thermal ellipsoids at 50% probability.

The formation of isothiazole **14**, which is a structural isomer of ylidene **13**, is mechanistically interesting. The conversion of (5*H*-1,2,3-dithiazol-5-ylidene)-2-acetonitriles to isothiazoles occurs in the presence of catalytic chloride [20] or anhydrous HCl or HBr [24], while isothiazoles can also be formed from the reaction of Appel's salt **1** with enamines [21,27,28]. Tentatively, the reaction herein proceeds via the thiophilic attack of chloride at the S-1 position of dithiazole **13** to form the ring-opened disulfide **15** (Scheme 4). Rotation of the double bond in disulfide **15** enabled by resonance can give the more stable *E* alkene **16**, which can then add chloride to the nitrile and cyclize onto sulfur to give isothiazole **17** with elimination of 'SCl'. While isothiazole **17** was not observed, we propose that once formed it rapidly reacted its C-4 position with the electrophilic sulfur of either disulfide **15** or **16** to give intermediate **18**. Subsequent attack by chloride on the disulfide group can lead to the stepwise migration of the phenylsulfone unit onto the sulfur via the spirocycle **19** and the formation of isothiazole **14**. A few examples of such migrations leading to benzenesulfonothioates have been reported and include a thermal rearrangement of aziridines [29], a chlorotropic rearrangement [30] and a photochemical reaction of diphenyl sulfone [31].



Scheme 4. Mechanistic rationale of the formation of isothiazole **14**.

3. Materials and Methods

The reaction mixture was monitored by TLC using commercial glass-backed thin-layer chromatography (TLC) plates (Merck Kieselgel 60 F_{254}). The plates were observed under UV light at 254 and 365 nm. The melting point was determined using a PolyTherm-A, Wagner & Munz, Kofler—Hotstage Microscope apparatus (Wagner & Munz, Munich,

Germany). The solvent used for recrystallization is indicated after the melting point. The UV–vis spectrum was obtained using a Perkin-Elmer Lambda-25 UV-vis spectrophotometer (Perkin-Elmer, Waltham, MA, USA) and inflections are identified by the abbreviation "inf". The IR spectrum was recorded on a Shimadzu FTIR-NIR Prestige-21 spectrometer (Shimadzu, Kyoto, Japan) with Pike Miracle Ge ATR accessory (Pike Miracle, Madison, WI, USA) and strong, medium and weak peaks are represented by s, m and w, respectively. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 machine at 500 and 125 MHz, respectively, (Bruker, Billerica, MA, USA). Deuterated solvents were used for homonuclear lock and the signals are referenced to the deuterated solvent peaks. Attached proton test (APT) NMR studies were used for the assignment of the ^{13}C peaks as *C*H$_3$, *C*H$_2$, *C*H and *C*q (quaternary). The matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrum (+ve mode) was recorded on a Bruker Autoflex III Smartbeam instrument (Bruker). 4,5-Dichloro-1,2,3-dithiazolium chloride (**1**) was prepared according to the literature procedure [14].

Reaction of Appel's Salt **1** *with 2-(Phenylsulfonyl)acetonitrile.*

To a stirred suspension of 4,5-dichloro-1,2,3-dithiazolium chloride (**1**) (104.3 mg, 0.50 mmol) in DCM (2 mL) was added 2-(phenylsulfonyl)acetonitrile (90.6 mg, 0.50 mmol) and the reaction mixture was stirred at *ca.* 20 °C for 1 h. Pyridine (81 µL, 1.00 mmol) was then added and the reaction mixture was stirred for another 2 h. The mixture was then adsorbed onto silica and chromatographed (*n*-hexane/DCM 50:50) to give *S*-(3-chloro-5-cyanoisothiazol-4-yl)benzenesulfonothioate (**14**) (30.7 mg, 19%) as colorless needles, m.p. 146–147 °C (from *c*-hexane); R_f 0.33 (*n*-hexane/DCM 50:50); (found: C, 38.02; H, 1.70; N, 8.65. $C_{10}H_5ClN_2O_2S_3$ requires C, 37.91; H, 1.59; N, 8.84%); λ_{max}(DCM)/nm 252 (log ε 4.36), 294 (4.31); υ_{max}/cm^{-1} 2236w (C≡N), 1454m, 1447m, 1335s (S=O), 1314w, 1294m, 1190m, 1148s (S=O), 1076m, 997w, 959w, 827w, 758m, 718s; δ_H(500 MHz; $CDCl_3$) 7.76-7.71 (3H, m, Ar C*H*), 7.58 (2H, dd, *J* 8.4, 7.5, Ar C*H*); δ_C(125 MHz; $CDCl_3$) 165.1 (*C*q), 143.9 (*C*q), 142.7 (*C*q), 135.2 (*C*H), 130.0 (*C*H), 129.0 (*C*q), 127.5 (*C*H), 108.1 (*C*q); *m/z* (MALDI-TOF) 357 (M + K$^+$+2, 40%), 355 (M + K$^+$, 48), 341 (M + Na$^+$+2, 45), 339 (M + Na$^+$, 100), 298 (22), 274 (40), 180 (18), 153 (15), 133 (18). Further elution (*n*-hexane/DCM 25:75) gave (*Z*)-2-(4-chloro-5*H*-1,2,3-dithiazol-5-ylidene)-2-(phenylsulfonyl)acetonitrile (**13**) (36.8 mg, 23%) as yellow needles, mp 181–183 °C (from *c*-hexane); R_f 0.37 (*n*-hexane/DCM 25:75); (found: C, 38.09; H, 1.42; N, 8.61. $C_{10}H_5ClN_2O_2S_3$ requires C, 37.91; H, 1.59; N, 8.84%); λ_{max}(DCM)/nm 267 (log ε 4.16), 283 inf (3.78), 433 (4.26); υ_{max}/cm^{-1} 2197m (C≡N), 1481m, 1470s, 1447m, 1315m (S=O), 1294m, 1190m, 1144s (S=O), 1082m, 1045m, 997w, 916w, 860s, 799w, 760m, 721s; δ_H(500 MHz; $CDCl_3$) 8.03 (2H, dd, *J* 8.6, 1.3, Ar C*H*), 7.76 (1H, ddd, *J* 7.6, 7.6, 1.2, Ar C*H*), 7.63 (2H, dd, *J* 7.9, 7.9, Ar C*H*); δ_C(125 MHz; $CDCl_3$) 158.7 (*C*q), 143.6 (*C*q), 138.1 (*C*q), 135.2 (*C*H), 129.7 (*C*H), 128.0 (*C*H), 112.1 (*C*q), 103.1 (*C*q); *m/z* (MALDI-TOF) 357 (M + K$^+$+2, 9%), 355 (M + K$^+$, 22), 341 (M + Na$^+$+2, 44), 339 (M + Na$^+$, 100), 319 (MH$^+$+2, 5), 317 (MH$^+$, 17), 133 (35).

X-ray crystallographic studies on S*-(3-chloro-5-cyanoisothiazol-4-yl)benzenesulfonothioate* (**14**).

Data were collected on an Oxford-Diffraction Supernova diffractometer, equipped with a CCD area detector utilizing Cu-Kα radiation (λ = 1.5418 Å). A suitable crystal was attached to glass fibers using paratone-N oil and transferred to a goniostat where they were cooled for data collection. Unit cell dimensions were determined and refined by using 2397 ($4.159^\circ \leq \theta \leq 71.800^\circ$) reflections. Empirical absorption corrections (multi-scan based on symmetry-related measurements) were applied using CrysAlis RED software [32]. The structures were solved by direct method and refined on F^2 using full-matrix least squares using SHELXL97 [33]. Software packages used: CrysAlis CCD [32] for data collection, CrysAlis RED [32] for cell refinement and data reduction, WINGX for geometric calculations [34], and DIAMOND [35] for molecular graphics. The non-H atoms were treated anisotropically. The hydrogen atoms were placed in calculated, ideal positions and refined as riding on their respective carbon atoms.

Crystal refinement data for S-*(3-chloro-5-cyanoisothiazol-4-yl)benzenesulfonothioate (***14***):* isolated as colorless needles (from DCE/*n*-pentane vapor diffusion), $C_{10}H_5ClN_2O_2S_3$, M = 316.79, orthorhombic, space group Pna2l, a = 14.6146(12) Å, b = 15.4871(8) Å, c = 5.3576(3) Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, V = 1212.63(14) Å^3, Z = 4, T = 100(2) K, ρ_{calcd} = 1.735 g·cm^{-3}, θ_{max} = 71.800°. Refinement of 163 parameters on 1529 independent reflections out of 2397 measured reflections (R_{int} = 0.0358) led to R_1 = 0.0431 (I > 2σ(I)), wR_2 = 0.1141 (all data), and S = 1.211 with the largest difference peak and hole of 0.357 and −0.367 e·Å^{-3}, respectively. (CCDC: 2132438).

Supplementary Materials: The following are available online: mol file, ^{1}H and ^{13}C NMR spectra.

Author Contributions: A.S.K. and P.A.K. conceived the experiments; A.S.K. designed the experiments; K.P. performed the experiments and collected the data; P.A.K. grew the X-ray crystals; A.K. collected the X-ray crystallography data; A.S.K. wrote the paper; A.S.K. and P.A.K. edited the manuscript. All authors have read and agreed to the published version of the manuscript.

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