

# Reactions of Hydrazidoyl Chlorides with Sodium *N,N*-Dialkyldithiocarbamates

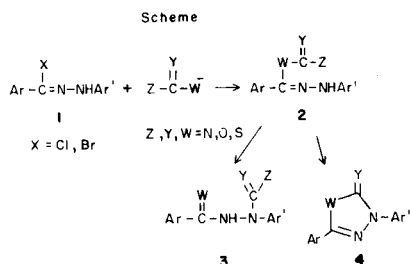
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The reaction of *N*-arylbzenzhydrazidoyl chlorides (**1**) with sodium *N,N*-dialkyldithiocarbamates yields the hydrazone derivatives **2**, which react further to form **4** unless the reaction sites are sterically crowded.

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Several types of reactions of *N*-arylbzenzhydrazidoyl halides (**1**) with nucleophiles such as *O*-alkyldithiocarbamates (1), thiourea (2), acetates (3), thioacetates (4,5), and dithiocarbamates (6) lead to rearranged (**3**) or cyclic (**4**) products. In these reactions an initial intermediate (**2**) has been postulated to be formed from the nucleophilic displacement of the halide. Depending on the nature of Z, either **3** or **4** is formed as the isolatable product (Scheme).



However, we have not found any reports of the isolation of an intermediate of type **2** (7). Therefore we wish to describe the first such isolation, specifically from the reactions of *N*-arylbzenzhydrazidoyl chlorides with sodium *N,N*-dialkyldithiocarbamates.

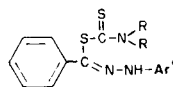
Four of the reactions gave **2** stable enough for characterization, one reaction gave **2** which could be isolated,

but not characterized, and three reactions gave **4**. Structure and stability observations are summarized in the Table. Examination of this table reveals that the stability of **2** is determined by the branching of the alkyl groups in the dithiocarbamate fragment and by the ortho substitution in the hydrazone aryl group. The enhanced stability of **2d** over its lower homologs can be explained by the steric hindrance of the thiocarbonyl carbon of **2d** due to the twelve atoms in the six position (8). Electronic effects do not seem to have a major influence (**2g** and **2h**) although this was not investigated in detail. A judicious combination of the two steric effects can then lead to a range of stabilities for **2**.

Since we have demonstrated that **2** are intermediates in the reaction of **1** to **4**, the very closely related displacements with other nucleophiles (1-5) can be safely postulated to follow the same pathway.

The structures of **2** were established by the <sup>13</sup>C nmr spectra for **2d**, **2f**, and **2g**. The compounds had only one C=S at δ 186.8, 185.6, and 186.2, respectively. In addition, **2f** and **2g** showed nine carbons in the δ 112 to 141 region, as expected for structure **2**, but not for **3**. Compound **2d** showed only eight carbons in this region in the decoupled spectrum, but the resonance at δ 127.5 was shown to con-

Table  
Stability of Dithiocarbamates **2**



Compound No.	Ar'	R	Stability at Ambient Temperature
<b>2a</b>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	not stable; cyclizes during reaction
<b>2b</b>	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	not stable; cyclizes during reaction
<b>2c</b>	C <sub>6</sub> H <sub>5</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	not stable; cyclizes during reaction
<b>2d</b>	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	stable
<b>2e</b>	2,4,6-Cl <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	CH <sub>3</sub>	can be isolated; cyclizes upon standing
<b>2f</b>	2,4,6-Cl <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	CH <sub>2</sub> CH <sub>3</sub>	stable; cyclizes at 40°
<b>2g</b>	2,4,6-Cl <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	stable
<b>2h</b>	2,6-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	stable

tain overlapping signals by off-resonance decoupled and fully coupled spectra.

## EXPERIMENTAL

### General.

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. The  $^{13}\text{C}$  nmr spectra were recorded in deuteriochloroform on a Varian CFT-20 spectrometer with tetramethylsilane as internal standard.

The sodium dithiocarbamates were prepared in methanol from equimolar amounts of sodium methoxide or sodium hydroxide, the appropriate dialkylamine, and a slight excess of carbon disulfide and were used *in situ*.

### Preparation of 2d.

To the sodium diisobutylidithiocarbamate prepared from 6.46 g. (50.0 mmoles) of diisobutylamine in 100 ml. of methanol was added 11.53 g. (50.0 mmoles) of *N*-phenylbenzhydrazidoyl chloride (9). The reaction mixture was heated on a steam bath for 5 minutes. On cooling, 18.0 g. (90.2%) of product was obtained. The analytical sample, m.p. 125-126°, was obtained after recrystallization from ethyl acetate;  $^{13}\text{C}$  nmr:  $\delta$  18.43, 24.42, 26.40, 60.20, 112.15, 119.52, 125.04, 126.26, 126.50, 127.49, 136.22, 141.66, 186.83.

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{29}\text{N}_3\text{S}_2$ : C, 66.12; H, 7.31; N, 10.52; S, 16.05. Found: C, 66.47; H, 7.05; N, 10.72; S, 16.42.

### Preparation of 2e and 4e.

To 5.36 g. (30.0 mmoles) of dimethyldithiocarbamate sodium salt dihydrate in 300 ml. of methanol was added 10.0 g. (30.0 mmoles) of *N*-(2,4,6-trichloro)phenylbenzhydrazidoyl chloride (10) and the mixture was stirred for 2 hours. The solids were filtered and chromatographed on 300 g. of silica gel with benzene to give a white solid which liquified upon standing overnight. Recrystallization from benzene/cyclohexane gave 6.30 g. (56.2%) of 2-phenyl-4-(2,4,6-trichlorophenyl)- $\Delta^2$ -1,3,4-thiadiazoline-5-thione (4e), m.p. 165-166°.

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_7\text{Cl}_3\text{N}_3\text{S}_2$ : C, 44.99; H, 1.89; Cl, 28.46; N, 7.50; S, 17.16. Found: C, 45.25; H, 1.68; Cl, 28.66; N, 7.22; S, 17.00.

### Preparation of 2e and 4e.

To 5.36 g. (30.0 mmoles) of dimethyldithiocarbamate sodium salt dihydrate in 300 ml. of methanol was added 10.0 g. (30.0 mmoles) of *N*-(2,4,6-trichloro)phenylbenzhydrazidoyl chloride (10) and the mixture was stirred for 2 hours. The solids were filtered and chromatographed on 300 g. of silica gel with benzene to give a white solid which liquified upon standing overnight. Recrystallization from benzene/cyclohexane gave 6.30 g. (56.2%) of 2-phenyl-4-(2,4,6-trichlorophenyl)- $\Delta^2$ -1,3,4-thiadiazoline-5-thione (4e), m.p. 165-166°.

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_7\text{Cl}_3\text{N}_3\text{S}_2$ : C, 44.99; H, 1.89; Cl, 28.46; N, 7.50; S, 17.16. Found: C, 45.25; H, 1.68; Cl, 28.66; N, 7.22; S, 17.00.

### Preparation of 2f.

To the sodium dithiocarbamate prepared from 3.70 g. (50.0 mmoles) of diethylamine in 100 ml. of methanol was added 16.7 g. (50.0 mmoles) of *N*-(2,4,6-trichloro)phenylbenzhydrazidoyl chloride (10) in 175 ml. of tetrahydrofuran. After 2 hours at room temperature the solvent was removed, the residue taken up in methylene chloride, washed with water, dried over sodium sulfate, the solvent evaporated, and the residue recrystallized from ethyl acetate to yield 10.0 g. (44.8%) of 2f, m.p. 117-122°;  $^{13}\text{C}$  nmr:  $\delta$  11.52, 13.18, 48.35, 49.37, 124.91, 126.93, 127.34, 128.17, 128.58, 128.89, 133.22, 135.66, 137.31, 185.64.

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{18}\text{Cl}_3\text{N}_3\text{S}_2$ : C, 48.38; H, 4.06; N, 9.40. Found: C, 48.43; H, 4.10; N, 9.67.

The solution used for  $^{13}\text{C}$  nmr showed only 4e and no 2f (tlc) upon being held in the nmr probe at 40° overnight.

### Preparation of 2g.

To the sodium dithiocarbamate prepared from 2.52 g. (25.0 mmoles) of dipropylamine in 50 ml. of methanol was added 8.35 g. (25.0 mmoles) of *N*-(2,4,6-trichloro)phenylbenzhydrazidoyl chloride (10) in 75 ml. of tetrahydrofuran. After 1 hour at room temperature the solvent was removed and the residue was chromatographed on silica gel with 1:1 Skellysolve B/benzene to yield 8.90 g. (74.9%) of product, which was recrystallized from ether/Skellysolve F to yield the analytical sample, m.p. 65-66°;  $^{13}\text{C}$  nmr:  $\delta$  11.03, 19.38, 21.28, 55.61, 56.23, 124.64, 126.73, 126.95, 128.17, 128.58, 128.89, 133.31, 135.60, 137.32, 186.24.

*Anal.* Calcd. for  $\text{C}_{20}\text{H}_{22}\text{Cl}_3\text{N}_3\text{S}_2$ : C, 50.58; H, 4.67; Cl, 22.40; N, 8.85; S, 13.50. Found: C, 50.76; H, 4.43; Cl, 22.15; N, 8.71; S, 13.36.

### Preparation of 2h.

To the sodium dithiocarbamate prepared from 0.394 g. (3.90 mmoles) of dipropylamine in 10 ml. of methanol was added 1.00 g. (3.90 mmoles) of *N*-(2,6-dimethyl)phenylbenzhydrazidoyl chloride, and the solution was allowed to stand for 6 days. The solvent was removed on a rotary evaporator and the residue was chromatographed on 60 g. of silica gel with 2:1 benzene/Skellysolve B to yield 0.70 g. (44.9%) of the product as an oil.

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{29}\text{N}_3\text{S}_2$ : C, 66.12; H, 7.31; N, 10.52. Found: C, 65.85; H, 7.56; N, 10.19.

### Preparation of 4a.

To the sodium diisopropylidithiocarbamate prepared from 2.52 g. (25.0 mmoles) of diisopropylamine in 50 ml. of methanol was added 5.75 g. (25.0 mmoles) of *N*-phenylbenzhydrazidoyl chloride (9) in 50 ml. of tetrahydrofuran. After 1.5 hours the solids were filtered and recrystallized from benzene/Skellysolve B to yield 4.50 g. (66.6%) of 2,4-diphenyl- $\Delta^2$ -1,2,4-thiadiazoline-5-thione, m.p. 151-152° [lit. (1) m.p. 151-152°].

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{10}\text{N}_4\text{S}_2$ : C, 62.19; H, 3.73; N, 10.36; S, 23.72. Found: C, 62.58; H, 3.48; N, 10.07; S, 23.72.

### Acknowledgement.

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