

Dithiocarbaminates Are the Prospective Reagents for Metal Cations

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Abstract

Preparative method of dithiocarbaminates synthesis is improved. Suggested technique allows to shorten synthesis technological process. Anhydrous medium is proposed at this technique instead of aqueous or aqueous-alcohol mediums what are used in known technique. New dithiocarbaminates on the base of alkilen-diamanes are obtained by using suggested technique. Synthesised dithiocarbaminates on the base of alkilen-diamanes are sensitive reagents for Ag^+ , Cu^{2+} , Co^{2+} , Ni^{2+} , Pd^{2+} , Fe^{2+} cations.

Introduction

Dithiocarbaminates $\text{RNHC(S)S}^- \text{X}^+$ are wide used in organic synthesis for obtaining of thiosemicarbazides, S-thiocarbamoyl-thioacetic and S-thiocarbamoyl- β -thiopropionic acids and their cyclic derivatives - 2-thioxo-thiazolidones-4 and 2-thioxo-1,3-thiazanones-4¹⁻⁹.

Results and Discussion

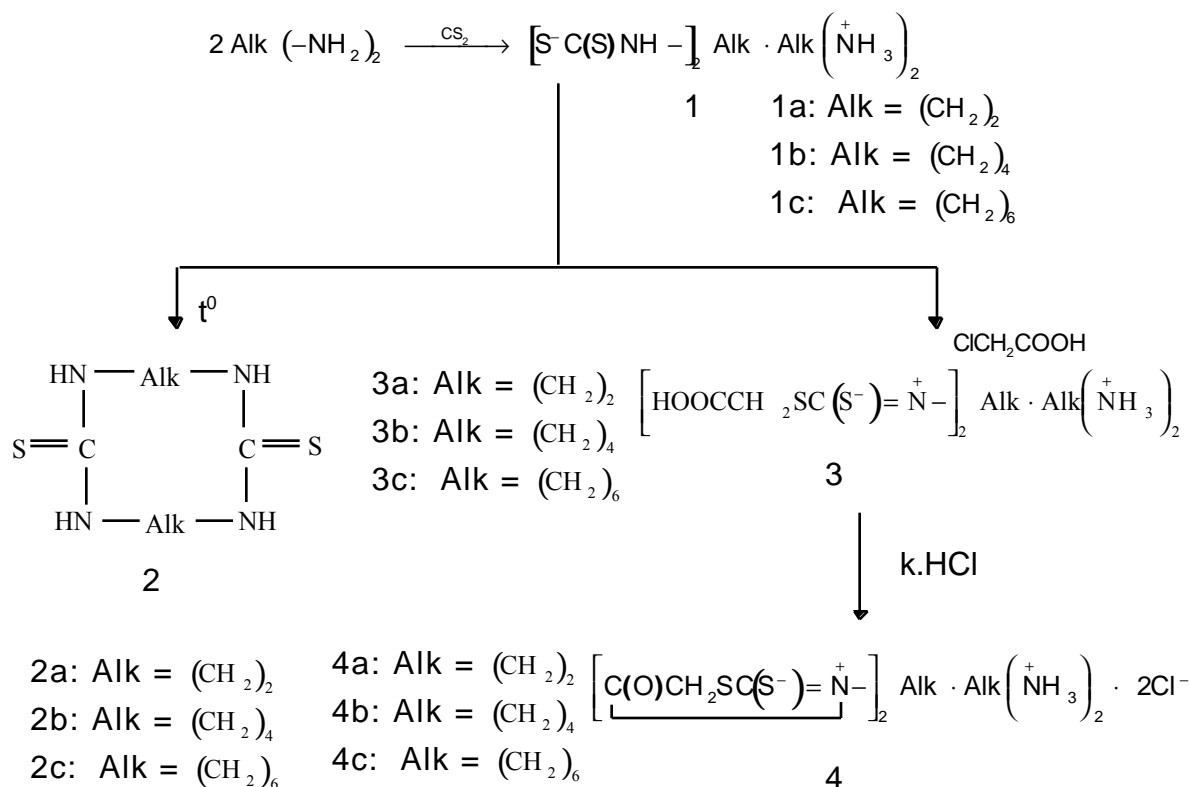
It is established that time of dithiocarbamate's synthesis may be shorten (to 5÷45 min.) and yield may be increased (from 40-60% to 80-90%). We used aqueous-free mediums (n-hexane, diethyl ether, benzol, etc.) instead of aqueous or aqueous-alcohol mediums. We obtained at the first time new dithiocarbaminates on the base of aliphatic diamines (1). Dithiocarbaminates synthesised on the base of aliphatic diamines in aqueous, aqueous-alkali or alcohol

mediums under heat transform into cyclic thioureas (2). With polar solvent in thiol form above-mentioned dithiocarbaminates react with monochloroacetic acids and form corresponding S-thiocarbamoylthioacetic acids (3). Synthesised S-thiocarbamoylthioacetic acids in concentrated hydrochloric acid are cyclised to corresponding thiazolidones-4 (4). Synthesised dithiocarbaminates and products of their transformations (1-4) were investigated as analytic reagents for metal cations. It is established that synthesised dithiocarbaminates on the base of aliphatic diamines are sensitive reagents for Ag^+ , Cu^{2+} , Co^{2+} , Ni^{2+} , Pd^{2+} cations. They form crystal precipitates and color solutions. Cyclic thioureas, N,N'-alkilen-bis(S-thiocarbamoyl-thioacetic) acids and products of their cyclisation - bicyclic noncondensed thiazolidones-4 are sensitive reagents for Pd^{2+} cations. Reaction sensitivity is $0.16 \div 0.40$ mg/ml.

Experimental Section

Synthesis of the most sensitive reagents is described below. Elemental analysis of all new compounds and calculated values (C, H, N, S ± 0.3) have satisfactory agreements. Synthesised compounds structures are confirmed by IR-spectroscopy (UR-20 spectrometer, Carl Zeiss, Iena, Germany). ¹HNMR spectra were recorded at 100MHz on a Bruker WP-100 SY spectrometer in DMSO-d₆ or CDCl₃ using tetramethylsilane as an internal standard (0.00 ppm), and chemical shifts are expressed as δ values. Coupling constants (j) are given in hertz.

Scheme

**1,2-Ethylene-bis(dithiocarbamate) of ethylenediamine (1a).**

15.2g (0.2 mole) of CS₂ in 50ml of dioxane were added to cooled (5-8°C) 70% aqueous solution of ethylenediamine (17.1g, 0.2 mole). The mixture were mixed 45 min. Received precipitate was filtered and dried. Yield - 87%. Melting point - 194-195°C (from water).

¹HNMR (DMSO-d₆) 2.83 (4H, t, J=7.7, NCH₂ × 2), 3.46 (4H, d, J=7.0, NCH₂ × 2), 6.28 (6H, s, NH₃ × 2), 7.69 (2H, s, SH × 2), 8.38 (2H, t, NH × 2).

1,6-Hexamethylene-bis(dithiocarbaminates) of hexamethylene diamanes (1c).

7.6g (0.1 mole) of CS₂ were added to cooled (5-8°C) solution of 5.8g (0.05 mole) of hexamethylenediamine in 50ml of diethyl ether. Received precipitate was filtered and dried. Yield - 94%. Melting point - 168-170°C (from water).

¹HNMR (DMSO-d₆) 1.30 (16H, t, J=3.8, NCH₂CH₂CH₂ × 2, NCH₂CH₂CH₂ × 2), 2.77 (4H, t, J=7.7, NCH₂CH₂CH₂ × 2), 3.33 (4H, d, J=7.0, NCH₂CH₂CH₂ × 2), 6.40 (6H, s, NH₃ × 2), 7.63 (2H, s, SH × 2), 8.36 (2H, t, NH × 2).

1,4-Tetramethylene-bis(dithiocarbamate) of tetramethylenediamine (1b).

By analogous way it was received 1,4-tetramethylene-bis(dithiocarbamate) of tetra-methylenediamine. Yield - 81%. Melting point - 168-170°C (from water).

¹HNMR (DMSO-d₆) 1.39 (8H, t, J=3.7, NCH₂CH₂ × 2, NCH₂CH₂ × 2), 2.81 (4H, t, J=7.8, NCH₂CH₂ × 2), 3.38 (4H, d, J=7.0, NCH₂CH₂ × 2), 6.34 (6H, s, NH₃ × 2), 7.65 (2H, s, SH × 2), 8.37 (2H, t, NH × 2).

2,7-Dithioxo-1,3,6,8-tetraazacyclodecane (2a).

2.72g (0.01 mole) of 1,2-Ethylene-bis(dithiocarbamate) of ethylenediamine was boiled in 50ml of butanole 3 hours. Reaction mixture was cooled and precipitate was filtered. Yield - 78%. Melting point - 165-166°C (from butanole).

¹HNMR (DMSO-d₆) 3.42 (8H, s, J=7.0, NCH₂ × 4), 5.20 (2H, s, SH × 2), 7.46 (4H, s, NH × 4).

2,9-Dithioxo-1,3,8,10-tetraazacyclotetradecane (2b).

By analogous way it was received 2,9-dithioxo-1,3,8,10-tetraazacyclotetradecane. Yield - 69%. Melting point - 128-131°C (from butanole).

$^1\text{HNMR}$ (DMSO- d_6) 1.40 (8H, s, $J=3.8$, $\text{NCH}_2\text{CH}_2 \times 4$), 3.38 (8H, s, $J=7.0$, $\text{NCH}_2\text{CH}_2 \times 4$), 5.18 (2H, s, SH $\times 2$), 7.46 (4H, s, NH $\times 4$).

2,11-Dithioxo-1,3,10,12-tetraazacyclooctadecane (2c).

By analogous way it was received 2,11-Dithioxo-1,3,10,12-tetraazacyclooctadecane.. Yield - 82%. Melting point - 106-108°C (from DMFA/water).

$^1\text{HNMR}$ (DMSO- d_6) 1.31 (16H, d, $J=3.7$, $\text{NCH}_2\text{CH}_2\text{CH}_2 \times 4$), 3.31 (8H, s, $J=7.8$, $\text{NCH}_2\text{CH}_2\text{CH}_2 \times 4$), 5.13 (2H, s, SH $\times 2$), 7.44 (4H, s, NH $\times 4$).

N,N'-Ethylene-bis(S-thiocarbamoylthioacetic) acid's ethylenediamine (3a).

2.72g (0.01 mole) of 1,2-Ethylene-bis(dithiocarbamate) of ethylenediamine was added to 10ml of aqueous solution of monochloroacetic acid (2.82g, 0.03 mole) and is mixed 30 min. 50 ml of dioxane was added to mixture. Oily substance that precipitated was separated and rinsed by dioxane to crystallisation. Yield - 40%. Melting point - 192-195°C (from water/acetone).

3360-3330 cm^{-1} (ν_{NH}), 2970-2940 cm^{-1} (ν_{NH}^+), 3200-3000 cm^{-1} (ν_{OH}), 3000-2800 cm^{-1} (ν_{CH}), 2960-2940 cm^{-1} (ν_{asCH_2}), 2880-2860 cm^{-1} (ν_{sCH_2}), 1625-1615 cm^{-1} ($\nu_{\text{C=N}}$), 1520-1500 cm^{-1} (δ_{NH}^+), 1390-1340 cm^{-1} (ν_{CN}), etc.

N,N'-Hexamethylene-bis(S-thiocarbamoylthioacetic) acid's hexamethylenediamine (3b).

By analogous way it was received N,N'-hexamethylene-bis(S-thiocarbamoylthioacetic) acid's hexamethylenediamine. Yield - 44%. Melting point - 138°C (from water/dioxane). The substance is characterised by similar absorption frequency in IR spectrum range.

1,2-Ethylene-bis(2-mercapto-4-oxo-3-yl-thiazolin-2) of ethylenediamine's dichloride (4a).

15.2g (0.2 mole) of CS_2 in 50ml of dioxane were added to cooled (5-8°C) 70% solution of ethyldiamine (17.1g, 0.2 mole). The mixture were mixed 30 min. Received precipitate was filtered and dissolved in aqueous solution of monochloroacetic acid (18.9g, 0.2 mole). After precipitate dissolving mixture was blend with 100ml of HCl and was heated on boiled water 30 min. The received precipitate was filtered and dried. Yield - 48%. Melting point - 182-184°C (from water/acetone).

$^1\text{HNMR}$ (DMSO- d_6) 2.81 (4H, t, $J=7.7$, $\overset{+}{\text{NCH}}_2 \times 2$), 3.98 (4H, d, $J=7.3$, $\overset{+}{\text{NCH}}_2 \times 2$), 4.32 (4H, t, $J=7.3$, $\overset{+}{\text{NCH}}_2 \times 2$), 4.32 (4H, s, $\text{O}=\overset{+}{\text{C}}-\text{CH}_2-\text{S}-\times 2$), 8.23 (6H, s, $\overset{+}{\text{NH}}_3 \times 2$).

1,4-Tetramethylen-bis(2-mercapto-4-oxo-3-yl-thiazolin-2) of tetramethylenediamane's dichloride (4b).

By analogous way it was received 1,4-tetramethylen-bis(2-mercapto-4-oxo-3-yl-thiazolin-2) of tetramethylenediamane's dichloride by using diethyl ether as reaction medium. Yield - 42%. Melting point - 160-161°C (from water/acetone).

$^1\text{HNMR}$ (DMSO- d_6) 1.38 (4H, q, $J=3.7$, $\overset{+}{\text{NCH}}_2\text{CH}_2 \times 2$), 1.59 (4H, t, $J=3.5$, $\overset{+}{\text{NCH}}_2\text{CH}_2 \times 2$), 2.77 (4H, t, $J=7.8$, $\overset{+}{\text{NCH}}_2\text{CH}_2 \times 2$), 3.91 (4H, t, $j=7.1$, $\overset{+}{\text{NCH}}_2\text{CH}_2 \times 2$), 4.3 (4H, s, $\text{O}=\overset{+}{\text{C}}-\text{CH}_2-\text{S}-\times 2$), 8.16 (6H, s, $\overset{+}{\text{NH}}_3 \times 2$).

1,6-Hexamethylene-bis(2-mercapto-4-oxo-3-yl-thiazolin-2) of hexamethylenediamine's dichloride (4c).

By analogous way it was received 1,6-hexamethylene-bis(2-mercapto-4-oxo-3-yl-thiazolin-2) of hexamethylenediamine's dichloride. Yield - 53%. Melting point - 160-161°C (from water/butanole).

$^1\text{HNMR}$ (DMSO- d_6) 1.34 (8H, q, $J=3.8$, $\overset{+}{\text{N}}\text{CH}_2\text{CH}_2\text{CH}_2 \times 2$), 1.56 (8H, t, $J=3.3$, $= \overset{+}{\text{N}}\text{CH}_2\text{CH}_2\text{CH}_2 \times 2$), 2.75 (4H, t, $J=7.8$, $\overset{+}{\text{N}}\text{CH}_2\text{CH}_2\text{CH}_2 \times 2$), 3.87 (4H, t, $j=7.0$, $\overset{+}{\text{N}}\text{CH}_2\text{CH}_2\text{CH}_2 \times 2$), 4.28 (4H, s, $\text{O}=\overset{\text{O}}{\underset{|}{\text{C}}}-\text{CH}_2-\text{S}- \times 2$), 8.10 (6H, s, $\overset{+}{\text{N}}\text{H}_3 \times 2$).

References

1. A. P. Grystchuk, I. P. Barylak, *Pharm. J. Ukraine*, 1964, **3**, pp.51-53.
2. L. Y. Ladna, E. M. Protsenko, *Chem. Pharm. J. USSR*, 1968, **5**, pp.24-27.
3. M. M. Orlynski, *J. Org. Chem. USSR*, 1996, **32**, 144-145.
4. M. M. Orlynski, B. S. Zimenkowski, W. R. Stets, *Chem. Pharm. J. USSR*, 1994, **4**, pp.27-29.
5. Y. M. Paskevitch, *Pharm. J. Ukraine*, 1961, **1**, 8-12.
6. L. I. Petlychna, W. M. Wwedenskij, M. M. Thurkevitch, *Pharm. J. Ukraine*, 1967, **4**, pp.7-9.
7. M. M. Thurkevitch, I.P.Barylak, *Pharm. J. Ukraine*, 1973, **6**, pp.18-21.
8. M. M. Thurkevitch, Y. M. Paskevitch, *J. Gen. Chem. USSR*, 1961, **33**, pp.3718-3721.
9. E. V. Vladzimirskaya, I. I. Samulak, *Pharm. J. Ukraine*, 1964, **3**, pp.51-53.