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Electrosynthesis of Hetero-Hetero Atom Bonds. I. A Direct Preparation of Bis(dialkylthiocarbamoyl) Disulfides from Dialkylamines and Carbon Disulfide

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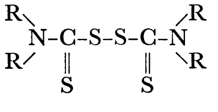
Synopsis. Bis(dialkylthiocarbamoyl) disulfides were synthesized directly from dialkylamines and carbon disulfide by electrolysis under constant voltage using an undivided cell. The electrochemical reaction was carried out effectively in a two-layer system of electrolysis solvents, *e. g.*, water-chloroform, water-dichloromethane, water-1,2-dichloroethane, and water-carbon disulfide. Likewise, the electrolysis could be performed in a homogeneous solution using dimethylformamide and/or acetonitrile.

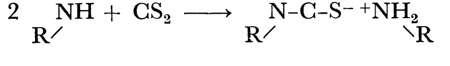
Bis(dialkylthiocarbamoyl) disulfides **1** are industrial chemicals of importance for use as vulcanization accelerators[1] and fungicides.[2] Two methods of preparation have been widely used, one involving



1: R=C_1-C_4

the oxidation of ammonium dialkyldithiocarbamates[3] and the other that of alkali dialkyldithiocarbamates.[4] Both methods require stoichiometric amounts of oxidizing agents which give rise to environmental problems. A clean process using few chemical reagents is desirable. We wish to report the direct electrosynthesis of **1** form dialkylamines and CS_2 by two methods, one involving a two-layer system for the continuous extraction of **1** and the other a homogeneous solvent system.[5]

For the two-layer system the following solvent combinations are used; water–chloroform, water–dichloromethane, water–1,2-dichloroethane, and water–CS_2. A schematic sketch of the apparatus for laboratory scale electrolysis is given in Fig. 1. Electrolysis was carried out in an aqueous solution (upper layer) containing the dithiocarbamates **2**,[3] prepared *in situ* by stirring a mixture of dialkylamines and CS_2, using an undivided cell fitted with platinum and/or carbon electrodes under a constant terminal voltage of 2.0 V (0.75—1.15 V *vs.* SCE).[6] The results are given in Table 1. Over 1.0—1.1 F/mol of electricity, the current becomes almost zero. During the course of the reaction,



$$2\ R_2NH + CS_2 \longrightarrow R_2N\text{-}C\text{-}S^{-}\ {}^{+}NH_2R_2 \qquad (2)$$

electrolysis efficient extraction of **1** with dichloromethane (lower layer) proceeds spontaneously. Removal of the extracting solvent afforded the solid material **1**(R=Me, Et, and Pr) in 76—99% yields (1, 2, 5, and 7). When electrolysis of **2**(R=Et) in an aqueous solution was carried out at 2 V without using the extracting solvents, the initial current was 27 mA/cm². Soon the platinum anode became covered with **1** as a pale yellow film and about 1 h later the passage of current stopped. Work-up of the electrolytic solution afforded **1** in 5—20% yields, indicating that the presence of extracting solvents in the lower layer contributes a great deal to the continuous electrolysis of **2**.

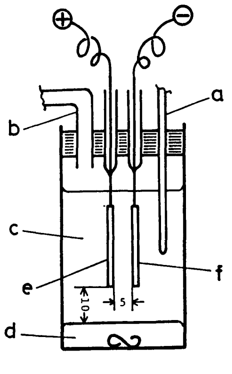


Fig. 1. Electrolysis cell.
a: Thermometer; b: gas lead pipe; c: aqueous layer; d: extraction layer; e: anode; f: cathode.

The electrolysis of a more bulky amine such as dibutylamine with CS_2 in a water dichloromethane system gave **1** in poor yield (9), because of the low solubility of **2** (R=Bu) in water, resulting in by-products.[7] However, electrolysis in a water–CS_2 system for 60 h afforded **1** (R=Bu) in 86% yield without pro-

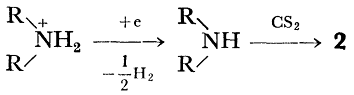
Table 1. Electrolysis of ammonium dialkyldithiocarbamates[a)]

Entry	Amine[b)] R	Amine[b)] mmol	CS_2 mmol	Solvent[c)] (ml)	Current mA/cm²	Temp °C	Time[d)] h	Yield[e)] %
1	Me	6.0	3.0	CH_2Cl_2-H_2O (3/20)	27—0.1	3— 5	26	99
2	Me	6.0	3.0	CH_2Cl_2-H_2O (3/20)	13—0.7	14—16	20	76[f)]
3	Me	6.0	3.0	CH_2ClCH_2Cl-H_2O (5/20)	17—0.7	24—26	22	97
4	Me	6.0	3.0	$CHCl_3$-H_2O (3/20)	20—0.7	23—25	22	87
5	Et	5.3	2.6	CH_2Cl_2-H_2O (3/20)	23—0.1	19—21	8	99
6	Et	3.0	excess	CS_2-H_2O (3/20)	15—0.2	17—20	9	99
7	Pr	4.0	2.0	CH_2Cl_2-H_2O (3/20)	9—0.1	15—18	23	80
8	Pr	3.0	excess	CS_2-H_2O (3/20)	7—0.03	18—20	48	96
9	Bu	3.0	1.5	CH_2Cl_2-H_2O (3/20)	1—0.03	16—17	17	28
10	Bu	2.0	excess	CS_2-H_2O (3/20)	1—0.07	17—18	60	86
11	Me	9.0	3.0	MeCN (20)	19—13	12—14	3	79
12	Et	6.0	3.0	MeCN (20)	22—6	10—12	1.7	99
13	Et	6.0	3.0	DMF (20)	13—3	10—11	3.5	99
14	Pr	6.0	3.0	DMF (20)	8—0.4	10—13	6	99
15	Bu	6.0	3.0	DMF (20)	9—0.2	9—12	5	100

a) Carried out under voltage of 2 V using Pt foil electrodes (3 cm²). b) Aqueous 50% Me_2NH used. c) Containing 160 mg of NH_4Cl (1—10) or 100 mg of Et_4NClO_4 (11—15). d) 1.01—1.05 F/mol passed. e) Isolated yields based on CS_2 (1—5, 7, 9, and 11—15) or amines (6, 8, and 10). f) Carbon electrodes (3 cm²) used.

ducing by-products (10).

Choice of CS_2 for diethylamine, dipropylamine, and dibutylamine as an extracting solvent was found suitable, since electrolysis could be carried out without preparing **2** by adding appropriate amines to the aqueous solution, product **1** moving smoothly into the lower layer. Upon concentration of the CS_2 fraction, disulfides **1** were obtained in 86—99% yields as fine crystals (6, 8, and 10). It is well known that dithiocarbamate ion, upon one electron oxidation on the anode followed by the coupling of the thio radical, gives **1**.[8] In the course of electrolysis of **2**, dialkylammonium ions, upon discharge on the cathode, liberate dialkylamines, which can react with CS_2 to regenerate **2**. Consequently, most of the dialkylamines used (6, 8, and 10) could be converted into **1**.



$$R_2\overset{+}{N}H_2 \xrightarrow[-\frac{1}{2}H_2]{+e} R_2NH \xrightarrow{CS_2} \mathbf{2}$$

We further investigated the direct synthesis of **1** from dialkylamines and CS_2 in a homogeneous solvent using MeCN and/or DMF. Electrolysis of a solution of two parts of diethylamine and one part of CS_2 in MeCN was carried out by using platinum electrodes at 2 V in the presence of tetraethylammonium perchlorate as a supporting electrolyte (12). After 1.05 F/mol of electricity had been passed, work-up of the solution afforded **1** in 99% yield.

Experimental

All melting points are uncorrected. Carbon-13 NMR spectra (CMR) were taken at 25.05 MHz in the Fourier mode using a JEOL FX-100 spectrometer. Samples were dissolved in $CDCl_3$ containing Me_4Si as an internal standard.

*Preparation of **1** from Dialkylamines and Carbon Disulfide in a Two-layer Solution.* A typical procedure is as follows: A mixture of aqueous 50% Me_2NH (0.80 ml, 6.0 mmol) and CS_2 (0.18 ml, 3.0 mmol) in water (20 ml) was stirred for *ca.* 1 h at room temperature. To this solution were added NH_4Cl (160 mg) and CH_2Cl_2 (3 ml), Pt electrodes (3 cm^2) being immersed in the aqueous layer. The mixture was electrolysed at 2 V (0.79—0.90 V *vs.* SCE) at 3—5 °C for 26 h. The current densities varied from 27 to 0.1 mA/cm^2 during the course of electrolysis. The CH_2Cl_2 layer (lower layer) was separated, washed with brine, and dried (Na_2SO_4.) Removal of the solvent afforded **1** (R=Me, 357 mg, 99%): mp 143—145 °C from EtOH (lit,[4e] mp 145—146 °C); CMR ($CDCl_3$) δ 193.3 (s, C=S), 47.4, 42.2 (q, CH_3).

The reaction conditions and results are given in Table 1, 1—10. Physical and spectral data of **1** (R=Et, Pr, and Bu) are as follows.

Compound **1** (R=Et): Mp 69—70.5 °C from EtOH (lit,[4e] mp 69.5—70.5 °C); CMR ($CDCl_3$) δ 192.4 (s, C=S), 52.0, 47.6 (t, CH_2), 13.4, 11.4 (q, CH_3).

Compound **1** (R=Pr): Mp 48.5—49.5 °C from EtOH (lit,[4e] mp 49—50.5 °C); CMR ($CDCl_3$) δ 193.2 (s, C=S), 59.2, 55.1 (t, CH_2N), 21.7, 19.6 (t, CH_2), 11.3 (q, CH_3).

Compound **1** (R=Bu):[4e] CMR ($CDCl_3$) δ 192.9 (s, C=S), 57.4, 53.2 (t, CH_2N), 30.2, 28.1 (t, C_β), 20.1 (t, C_γ), 13.8 (q, CH_3).

*Preparation of **1** from Dialkylamines and Carbon Disulfide in Acetonitrile.* A mixture of Et_2NH (0.62 ml, 6.0 mmol), CS_2 (0.18 ml, 3.0 mmol), and Et_4NClO_4 (100 mg) in MeCN (20 ml) was electrolyzed at 2 V (0.75—1.10 V *vs.* SCE) at 10—12 °C using Pt electrodes (3 cm^2). After a current of 3.15×10^{-3} F had been passed for 1.7 h, the mixture was concentrated *in vacuo.* The residue was worked up to give **1** (R=Et, 99%): Mp 69—70.5 °C from EtOH (lit,[4e] mp 69.5—70.5 °C). Similarly, DMF was used for the preparation of **1** (R=Et, Pr, and Bu). The conditions and results are given in Table 1, 11—15.

*Electrolysis of Diethylammonium Diethyldithiocarbamate **2** (R=Et) in Water.* A mixture of Et_2NH (0.62 ml, 6.0 mmol), CS_2 (0.18 ml, 3.0 mmol), and NH_4Cl (160 mg) in water (20 ml) was stirred at 14 °C for 1 h to give a homogeneous solution of **2** (R=Et).[3c] The aqueous solution was electrolyzed at 2 V (0.75—0.85 V *vs.* SCE) at 13—15 °C with Pt electrodes (3 cm^2). At the beginning of the reaction the current density was 27 mA/cm^2. After 10 min, pale yellow precipitates were deposited on the anode. After 1 h the anode was covered with the precipitates as a film and the current was reduced to almost zero. Electrolysis was continued for further 2.5 h (total 0.3×10^{-3} F). After the usual work-up 35 mg (8%) of **1** (R=Et) was obtained.

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5) A similar attempt involving electrolysis of an aqueous solution of sodium dithiocarbamates using an alternating current has been reported. However, the low solubility of **1** for water along with the low current efficiency (12.5%) gives rise to difficulties: J. A. Gardner, U. S. Pat., 2385410 (1945).

6) Change in the cell voltage did not affect product selectivity and yields.

7) In the course of electrolysis of **2** in water–CH_2Cl_2, methylene bis(dialkyldithiocarbamate) was obtained as a by-product (R=Me, Et, <1%; R=Pr, 5—10%; R=Bu, 65—70%). Formation of the by-product could be surpressed by use of carbon disulfide as an extracting solvent. Methylene bis(dimethyldithiocarbamate) has been prepared from CH_2Cl_2 and sodium dimethyldithiocarbamate: T. Nakai and M. Okawara, *Chem. Lett.*, **1974**, 731.

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