

unpaired electrons with increasing Mn concentration indicate that the overall features of the simple chemical bond scheme previously proposed<sup>4-6</sup> are essentially correct. The reduction from 4.0 unpaired electrons per Mn atom in the equiatomic NiMn, PdMn, and PtMn alloys to  $\sim 3.5$  in the case of IrMn presumably reflects the lowering of the Fermi level resulting from Ir having one valence electron less than Ni, Pd, and Pt.

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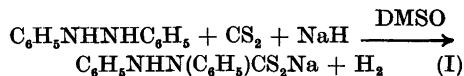
## *N,N'*-Diphenyldithiocarbazic Acid and Some Derived Compounds

LARS HENRIKSEN and  
OLE RICHARD JENSEN

*Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen Ø, Denmark*

Dithiocarbazates may generally be prepared from hydrazine or substituted hydrazines and carbon disulfide. This method fails, however, when the basicities of both nitrogen atoms in the hydrazine have been lowered by aromatic substituents. We now wish to report on the preparation of sodium *N,N'*-diphenyldithiocarbazate (I) by way of a synthetic method originally devised for the preparation of dithioic acids from carbon disulfide and CH-acidic compounds.<sup>1</sup> In addition, the properties of (I) and of some derived compounds have been investigated.

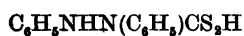
Compound (I) was obtained in good yield by the joint action of carbon disulfide and sodium hydride on hydrazobenzene in dimethyl sulfoxide solution.



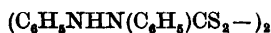
As the reaction between hydrazobenzene and sodium hydride was slow and incomplete, it was found convenient to add carbon disulfide at a rate such that the hydrazobenzene anion which formed was immediately consumed. The progress

of the reaction could easily be followed visually, the anion of hydrazobenzene being dark brown and the dithiocarbazate ion light orange in dimethyl sulfoxide solution.

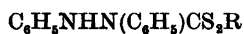
The free *N,N'*-diphenyldithiocarbazic acid (II) was obtained by acidification of an aqueous solution of (I) at 0°. This compound can be isolated as the dry solid, but reverts slowly to hydrazobenzene with the liberation of carbon disulfide. When II is dissolved in dipolar solvents the same reaction occurs. Thus we followed the decomposition in methanol at room temperature by TLC. The reaction was complete in less than one hour, and only hydrazobenzene was detected as decomposition product. The latter observation precludes a benzidine rearrangement during the acidification of (I).



II



III

IVa: R = CH<sub>3</sub>IVb: R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>

*S*-Substituted derivatives of II are, however, perfectly stable compounds. Oxidation of (I) with iodine in methanol gave bis-(*N,N'*-diphenyldithiocarbazoyl)-disulfide (III), and alkylation of (I) with alkyl halides led to *S*-alkyl esters. Thus, we have prepared *S*-methyl *N,N'*-diphenyldithiocarbazate (IVa) with methyl iodide and *S*-benzyl *N,N'*-diphenyldithiocarbazate (IVb) with benzyl chloride. The *S*-alkyl *N,N'*-diphenyldithiocarbazates are exceedingly unreactive towards nucleophilic reagents. Thus, IVa was recovered unchanged from a series of attempts to prepare 1,2-diphenylthiosemicarbazide. The reaction conditions employed during the attempts included heating with concentrated ammonia in ethanol, treatment with liquid ammonia (with and without added sodamide) and boiling with ammonium carbonate in phenol.

Treatment of an aqueous solution of (I) with a heavy-metal salt resulted in precipitation of the insoluble heavy-metal dithiocarbazates. The lead salt could

be recrystallized from chloroform; the nickel salt was soluble in acetone and could be crystallized by addition of 5 volumes of ether and 5 volumes of pentane to the cooled saturated acetone solution. The freshly prepared silver salt was soluble in dimethyl formamide, but was rapidly transformed into a completely insoluble substance. The latter product could not be dissolved in concentrated aqueous ammonia, nor did it react with nitric acid at room temperature. The insolubility of the silver salt makes electrometric titration with silver nitrate a feasible method for the quantitative estimation of (I), although the titration has to be performed in a neutral medium to avoid the formation and subsequent decomposition of II.

When the IR spectra of the derivatives of II are compared with the spectrum of hydrazobenzene, two conspicuous absorptions of the NCS<sub>2</sub>-group can be isolated. The first one is found as a strong band at 1295 cm<sup>-1</sup> in the spectrum of (I), shifted to 1340–1360 cm<sup>-1</sup> in the spectra of the heavy-metal salts and the compounds II, III, and IV. The second band appears at 985–1010 cm<sup>-1</sup> in the spectra of the salts and at 1055 cm<sup>-1</sup> in the spectra of compounds III and IV. The absorption at 1295–1360 cm<sup>-1</sup> can be assigned to a vibration containing mainly contributions from the C–N stretching. The high frequency is in agreement with the assumption that the C–N bond in thioamide structures has a partial double-bond character which is increased on the formation of metal complexes.<sup>2</sup> The absorption at 985–1055 cm<sup>-1</sup> is assigned to the ν<sub>as</sub>(CS<sub>2</sub>) vibration. Two medium-weak absorptions at ca. 800 and ca. 630 cm<sup>-1</sup>, respectively, are also present throughout the series of derivatives of II, but not in the spectrum of hydrazobenzene. The present material is insufficient to assign these absorptions to any particular vibration, although the lower frequency is close to the one assigned by Anthoni<sup>3</sup> to ν<sub>s</sub>(CS<sub>2</sub>) of dithiocarbazates with aliphatic *N*-substituents.

An SH-absorption at 2550 cm<sup>-1</sup> is found in the spectrum of II, showing that this compound, at least in part, exists in the SH-form contrary to the dithiocarbazates with aliphatic *N*-substituents, which are reported to be purely zwitterionic.<sup>3</sup>

*Experimental.* Sodium *N,N'*-diphenylthiocarbazate (I). Dimethyl sulfoxide was dried by distillation from calcium hydride. Sodium hydride (3.2 g; 50 % suspension in oil) was suspended in the dry dimethyl sulfoxide (200 ml) in a nitrogen atmosphere. Subsequently, hydrazobenzene (12.2 g) was dissolved in the mixture and carbon disulfide (5.4 g) was added at a rate such that a dark coloured reaction mixture was just maintained. At the end of the reaction the resulting orange solution was washed with ether containing 10 % pentane, and then the solvent was removed *in vacuo*. The residual oil was washed with ether containing 10 % chloroform and crystallized upon cooling. The crystals were washed thoroughly with chloroform. Yield 16.5 g (75 %). Recrystallization from 1-propanol containing 10 % of water and then from acetone afforded (I) as a trihydrate. (Found: C 46.24; H 4.97; S 19.15; M.W. 336 (by titration with silver nitrate). Calc. for  $C_{13}H_{17}N_4NaO_3S_2$ : C 46.42; H 5.09; S 19.07; M.W. 336).

*N,N'*-Diphenylthiocarbazic acid (II). Compound (I) (100 mg) was dissolved in a little water and mixed with 5 ml of 1 M hydrochloric acid at 0°. Precipitated material was filtered off, washed with a few ml of 0.1 N hydrochloric acid and immediately thereupon dried over  $P_2O_5$  and NaOH at 1 mm Hg. (Found: C 60.22; H 4.66; S 23.88. Calc. for  $C_{13}H_{11}N_2S_2$ : C 59.99; H 4.65; S 24.59). After 14 days at room temperature, the sulfur content had decreased to ca. 1.5 %.

*Bis(N,N'*-diphenylthiocarbazoyl)-disulfide (III). Compound (I) (0.4 g) was dissolved in methanol (20 ml) and iodine (0.13 g) dissolved in a few ml of methanol was added. Precipitated material was filtered off and recrystallized once from chloroform-methanol. Yield 0.18 g (60 %), m.p. 203–205°. For analysis, the product was also recrystallized from toluene. (Found: C 60.20; H 4.45; N 10.63. Calc. for  $C_{26}H_{22}N_4S_4$ : C 60.22; H 4.27; N 10.80).

*S-Methyl N,N'*-diphenylthiocarbazate (IVa). To (I) (0.5 g) dissolved in methanol was added methyl iodide (0.26 g). The reaction mixture was left at room temperature overnight and then diluted with water. Precipitated material was isolated by filtration, dried, and recrystallized from ether.

Yield 0.25 g (62 %). For analysis the product was also recrystallized from methanol. M. p. 155.5–156.5°. (Found: C 61.35; H 5.28; N 9.96. Calc. for  $C_{14}H_{12}N_2S_2$ : C 61.26; H 5.14; N 10.21).

*S-Benzyl N,N'*-diphenylthiocarbazate (IVb) was prepared by an analogous procedure using benzyl chloride. The crude product was recrystallized from ethanol. Yield 0.24 g (60 %), m.p. 168.5–170°. (Found: C 68.35; H 5.33; N 7.83. Calc. for  $C_{20}H_{16}N_2S_2$ : C 68.55; H 5.18; N 7.99).

*Lead N,N'*-diphenylthiocarbazate was precipitated from an aqueous solution of (I) (0.34 g) with 0.5 ml of 1 M lead nitrate. Isolated material was washed with water, dried, and recrystallized from chloroform. Yield 0.23 g (64 %), m.p. ca. 210° (decomp.). (Found: C 42.74; H 3.08; N 7.68. Calc. for  $C_{26}H_{22}N_4PbS_4$ : C 43.02; H 3.06; N 7.72).

*Nickel N,N'*-diphenylthiocarbazate was prepared in an analogous way using nickel chloride. The crude, dried product was treated with boiling chloroform and yielded after filtration from the hot solvent 0.20 g (70 %), m.p. ca. 215° (decomp.). (Found: C 54.10; H 3.86; N 9.70. Calc. for  $C_{26}H_{22}N_4NiS_4$ : C 54.08; H 3.84; N 9.70). A crystalline sample of this compound was obtained by dissolution of the crude material in a small volume of acetone, followed by addition of 5 volumes of ether and 5 volumes of pentane and cooling to –40°.

*Silver N,N'*-diphenylthiocarbazate was prepared in an analogous way using silver nitrate. Yield 0.30 g (82 %), m.p. ca. 190° (decomp.). (Found: C 40.72; H 2.94; N 7.34. Calc. for  $C_{13}H_{11}AgN_2S_2$ : C 42.52; H 3.10; N 7.62).

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