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The Reaction of Dibenzylthiocarbamoyl Chloride with Sodium Nitrite

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Synopsis. The reaction of dibenzylthiocarbamoyl chloride with sodium nitrite in acetonitrile at room temperature yields *N*-nitrosodibenzylamine, dibenzylcarbamoyl chloride, bis(dibenzylcarbamoyl) disulfide, benzaldehyde, and benzyl isothiocyanate; possible mechanisms for the formation of these products are suggested.

The quantitative formation of *N*-nitrosodibenzylamine (**4**) from the nitrosative decarboxylation of dibenzylcarbamoyl chloride (**5**) with sodium nitrite in acetonitrile was recently reported.1) In the interest of exploring the use of related systems for the formation of nitrogen-nitrogen bonds, the study of the action of sodium nitrite in dibenzylthiocarbamoyl chloride (**1**) was undertaken.

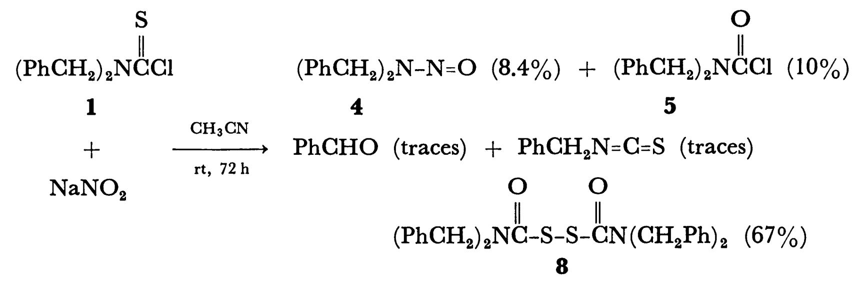
Although the NMR spectrum of the reaction mixture of equimolar amounts of **1** and sodium nitrite in dry acetonitrile indicated that the reaction was not as clean as that of **5** with sodium nitrite,1) the presence of benzaldehyde and *N*-nitrosodibenzylamine (**4**) in the crude reaction mixture was established; beside carbonyl bands at 1645, 1675, 1695 cm^{-1}, the IR spectrum displayed absorptions at 2180—2100 cm^{-1} which suggested the presence of a compound with a cumulative bond system. Chromatography of the mixture on silica gel led to the isolation and characterization on benzaldehyde, *N*-nitrosodibenzylamine, dibenzylcarbamoyl chloride (**5**) and the compound which displayed the absorption at 2180—2100 cm^{-1}; in addition an unknown soild, mp 132.5—133 °C, was isolated; its elemental analysis indicated the empirical formula to be $C_{15}H_{14}NOS$; the presence of a carbonyl group,2) its NMR and mass spectra,3) established the structure of bis(dibenzylcarbamoyl) disulfide (**8**). The compound displaying the strong absorption at 2180—2100 cm^{-1} was shown to be benzyl isothiocyanate (**6**) by comparison with an authentic sample.4) Once the identity of the products was established, the reaction was repeated and the yield of each product (except for **8** which was isolated and weighed) was determined by the integration of the NMR spectrum of the crude reaction product.

The formation of **8** may be understood in terms of an oxygen to sulfur migration of the nitroso group of **2**, followed by the loss of nitrogen monoxide from **3** and generation of the carbamoylthio radical (**7**) which could then dimerize to **8**. Although *N*-nitrosodibenzylamine (**4**) may be formed by loss of COS from **2** as anticipated, it could also arise from the action of nitrite ion on **3** and on **5**.1) However, control experiments showed that **8** did not react either with chloride or nitrite ions. A reaction run with a 1.4 excess of sodium nitrite for four days showed a dramatic increase in the yield of **4** (39%) with a concurrent decrease in the yield of **8** (43%); the yield of **5** was unchanged. The same reaction carried out overnight gave **8** as the major product (63%) with **4** and **5** being formed in only minor amounts. Similarly the formation of **5** could be rationalized by displacement of chloride ion on **3**. Although direct displacement of nitrite ion on **1** may account for the formation of benzyl isothiocyanate (Scheme 2, path a), an alternate path involves **2** as the intermediate which undergoes an internal displacement *via* a six-membered ring transition state leading to benzyl isothiocyanate (**6**) and benzyl nitrite (Scheme 2, path b); the latter compound is known to decompose to benzaldehyde;5) authentic benzyl nitrite reacted with chloride ion to give benzaldehyde. Scheme 3 summarizes the possible paths leading to the observed products.

Experimental

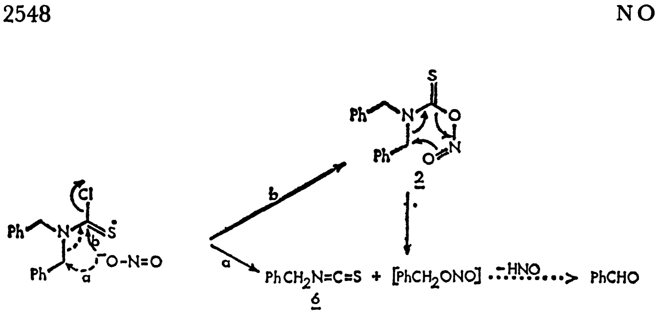
All mps and bps are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Infracord and NMR spectra were determined on CCl_4 or $CDCl_3$ on a R-24 Hitachi-Perkin Elmer Spectrometer using TMS as an internal standard. Mass spectra were obtained at Chemical Spectrometry Laboratory of Massachusetts Institute of Technology and taken on Varian Mat 44 mass spectrometer. A low energy (50 eV) spectrum was obtained on a Hitachi-Perkin Elmer mass spectrometer model RMU-6L.

Dibenzylthiocarbamoyl Chloride (1). To a solution of 85% (w/w) thiophosgene (10.5 g, 77 mmol) in anhydrous ether (75 ml) at −5 °C, was added a solution of dibenzylamine (30.5 g, 155 mmol) in anhydrous ether (75 ml) with a mechanical stirring. An additional 50 ml of anhydrous ether was added, and the mixture was stirred at ambient temperature overnight. The precipitated dibenzylamine hydrochloride was collected, and the filtrate was evaported to dryness at room temperature *in vacuo*. The solid residue

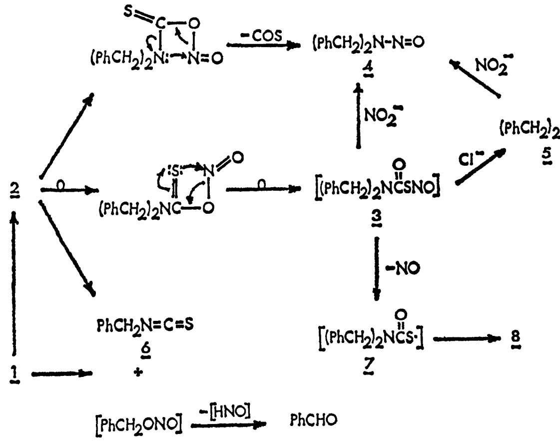


$$\underset{\mathbf{1}}{(\mathrm{PhCH_2})_2\mathrm{N}\overset{\mathrm{S}}{\overset{\|}{\mathrm{C}}}\mathrm{Cl}} + \mathrm{NaNO_2} \xrightarrow[\text{rt, 72 h}]{\mathrm{CH_3CN}} \underset{\mathbf{4}}{(\mathrm{PhCH_2})_2\mathrm{N{-}N{=}O}}\ (8.4\%) + \underset{\mathbf{5}}{(\mathrm{PhCH_2})_2\mathrm{N}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Cl}}\ (10\%) + \mathrm{PhCHO}\ (\text{traces}) + \mathrm{PhCH_2N{=}C{=}S}\ (\text{traces}) + \underset{\mathbf{8}}{(\mathrm{PhCH_2})_2\mathrm{N}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}S{-}S{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{N(CH_2Ph)_2}}\ (67\%)$$

Scheme 1.



Scheme 2.



Scheme 3.

was crystallized from chloroform–ligroin mixture to yield 10.6 g (53%) of **1**, mp 43—45 °C, lit,[6] mp 49 °C.

*Reactions of **1** with Sodium Nitrite.* A mixture of dibenzylthiocarbamoyl chloride (3.2 g, 12 mmol) and sodium nitrite (1.0 g, 14.5 mmol) in dry acetonitrile (40 ml) was stirred overnight in a flask covered with aluminum foil and connected to a gas bubbler. The insoluble inorganic material was filtered, and the acetonitrile solution was evaporated *in vacuo* to leave a residue, which was deposited on a preparative column chromatography (silica gel mesh 60—200, g). Elution with a mixture of benzene and hexanes (1:2 v/v, 150 ml) gave benzyl isothiocyanate (20 mg) whose IR and NMR spectra were superimposable upon those of an authentic sample.[4,7] Further elution (200 ml) afforded dibenzylcarbamoyl chloride (566 mg, 2.2 mmol, 19%), identical to an authentic sample.[1] Continued elution with the same mixture (100 ml) and with a mixture of benzene and hexanes (1:1 v/v, 100 ml) yielded *N*-nitrosodibenzylamine (**4**, 425 mg, 1.9 mmol, 16%) and trace amounts of benzaldehyde; their structures were established by their spectra data and by addition of authentic samples to the NMR samples. Elution with benzene–hexane (1:1 v/v, 100 ml) and with benzene (200 ml) gave crude bis(dibenzylcarbamoyl) disulfide (797 mg, 1.6 mmol, 31%) mp 130—131.5 °C. The crude disulfide was recrystallized from dichloromethane–hexane mixture to afford colorless crystals, mp 132.5—133 °C. IR (KBr): 1675 cm^{-1} ($\rangle$C=O); NMR ($CDCl_3$): δ 7.30 (s, Ar$\underline{H}$, 20H), δ 4.60 (s, Ph$C\underline{H}_2$ 8H); mass spectrum [*m/e*, (relative intensity)]: 512 (very weak),[3] 256 (0.05), 224 (6), 196 (0.3), 91 (100). Found: C, 70.38; H, 5.75; N, 5.33 S, 12.46. Calcd for $C_{30}H_{28}N_2O_2S_2$: C, 70.28; H, 5.50; N, 5.47; S, 12.51.

The reaction was repeated using 11.7 mmol of **1** and 11.7 mmol of sodium nitrite. After overnight stirring, the acetonitrile was evaporated *in vacuo* to leave a solid residue which was stirred with a mixture (20 ml) of ether and petroleum ether (1:3 v/v). The insoluble solid left after the first extraction was stirred with dichloromethane (25 ml×2). Evaporation of dichloromethane from the second extract gave bis(dibenzylcarbamoyl) disulfide (1.97 g, 3.8 mmol, 65%). Evaporation of the solvents from the first extract gave a residue (0.7 g), which was chromatographed on silica gel (mesh 60—200, 20 g). Elution with benzene–hexane mixture (1:1 v/v, 150 ml) gave a mixture of dibenzylcarbamoyl chloride (1.2 mmol, 10%) and *N*-nitrosodibenzylamine (0.1 mmol, 0.8%) whose molar ratio was estimated by the NMR integration under benzyl protons. Continued elution with the same mixture (150 ml) yielded *N*-nitrosodibenzylamine (0.9 mmol, 7.7%). Elution with benzene (200 ml) afforded bis(dibenzylcarbamoyl) disulfide (38 mg, 0.07 mmol, 1.2%).

The same reaction was carried out using 6.2 mmol of dibenzylthiocarbamoyl chloride and 8.7 mmol of sodium nitrite for 4 d. The acetonitrile was evaporated under reduced pressure to give a solid residue. The solid was stirred with ether (25 ml), and the solid left after the first extraction was stirred with dichloromethane (25 ml×2). Evaporation of dichloromethane from the second extract afforded bis(dibenzylcarbamoyl) disulfide (411 mg, 0.8 mmol, 26%). Evaporation of ether from the first extract gave a residue (1.06 g) which was stirred with a mixture (25 ml) of petroleum ether and ether (2:1 v/v) to leave a mixture (322 mg) of the disulfide (0.48 mmol, 15.5%) and *N*-nitrosodibenzylamine (0.34 mmol, 5.5%). The extract was concentrated under reduced pressure to yield a mixture of dibenzylcarbamoyl chloride (0.6 mmol, 10%) and *N*-nitrosodibenzylamine (2.1 mmol, 33%) whose molar ratio was estimated by the NMR integration under benzyl protons.

Control Experiments. *Reaction of Bis(dibenzylcarbamoyl) Disulfide with Sodium Chloride*: A mixture of the disulfide (200 mg) and sodium chloride (1.0 g) in a mixture of acetonitrile (20 ml) and dichloromethane (5 ml) was stirred at room temperature overnight. Inorganic material was filtered, and filtrate was concentrated on a rotary evaporator to give a quantitative recovery of the disulfide.

Reaction of Bis(dibenzylcarbamoyl) Disulfide with Sodium Nitrite: A mixture of the disulfide (76 mg) and sodium nitrite (1.0 g) in acetonitrile (30 ml) was stirred at room temperature for 3 d. The mixture was filtered, and washed with dichloromethane (50 ml). The acetonitrile filtrate and the dichloromethane solution were combined and concentrated under reduced pressure to afford the unreacted disulfide (66 mg) in 86% recovery.

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