

1,1'-Thiocarbonylbis(π -excessive *N*-Heteroaromatics)

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Several symmetrical thioureas, in which the two amido nitrogens are incorporated into separate aromatic rings, are prepared by the action of thiophosgene on π -excessive nitrogen-heteroaromatic bases and/or their metallic salts.

A SERIES of *N,N'*-thiocarbonylbis(cyclic *N*-hetero-paraffins) (1), *N,N'*-thiocarbonylbis(3,5-dimethylpyrazole), and *N,N'*-thiocarbonyldiimidazole (2) were previously synthesized by the action of thiophosgene on *N*-heterocycles. The adaptability of this *N,N'*-acylation is demonstrated by modifying the original method, using the sodium salt of the base. Recognizing that the π -excessive *N*-heterocycles may not be basic and that the attack by thiophosgene is electrophilic, these salts are prepared, improving the yield in some cases and allowing formation of the desired product in others.

Pyrrrole, pyrazole, tetraiodopyrrole, indole, 2,5-dimethylpyrrole, and carbazole fail to yield the desired symmetrical thiocarbonyl products. The latter polycyclic base does not react with thiophosgene and does not form the sodium salt with either sodium metal or sodium hydride. Pyrazole forms a golden oil with thiophosgene which gives a positive test for C=S. The others immediately form polymeric dyes upon the addition of thiophosgene despite the use of the salt form of the base or proton acceptors.

The 1,1-thiocarbonylbis(π -excessive *N*-heteroaromatics) are all yellow crystalline products, insoluble in water and soluble in chloroform. The products all give positive $\text{NaN}_3\text{-I}_2$ tests for C=S (3), and no SH absorption in the infrared region.

EXPERIMENTAL

1,1'-Thiocarbonyldibenzimidazole.—*Sodium Salt Method.*—Sodium, 1.2 Gm. (0.05 mole), is mixed with 25 ml. of toluene and stirred vigorously while heating to obtain a fine suspension. Then 23.4 Gm. of benzimidazole (0.2 mole) is suspended in 200 ml. of toluene and added. The mixture is refluxed for 2 hr. with vigorous stirring. It is cooled in an ice bath and 6 Gm. of thiophosgene (0.05 mole) in 15 ml. of toluene is added dropwise, followed by refluxing for 2.5 hr. Acetone is added to remove the excess sodium (the reaction mixture is deep yellow at this stage). While still hot, the mixture is filtered through a Buchner funnel and the solid is washed several times with cold toluene. The orange-red filtrate is cooled slowly in a cold water bath. Yellow needle-like crystals are separated. Yield, 12.8 Gm. (90%), m.p. 149–150°.

*Anal.*¹—Calcd. for $\text{C}_{15}\text{H}_{10}\text{N}_4\text{S}$: C, 64.7; H,

3.60; N, 20.1; S, 11.5. Found: C, 64.2; H, 3.66; N, 19.4; S, 11.2.

1,1'-Thiocarbonyldibenzimidazole.—*Free Base Method.*—Six grams of benzimidazole (0.051 mole) is mixed with 75 ml. toluene. The mixture is heated at reflux temperature for 0.5 hr.; the solid does not dissolve. The reaction mixture is then cooled to 5° and 1.5 Gm. of thiophosgene (0.013 mole) in 15 ml. of toluene is added dropwise with stirring. The density of the suspension immediately increases. Reflux 1 hr. to produce a coarse precipitate. The mixture is filtered and the white residue washed several times with toluene. The bright yellow filtrate is cooled in an ice bath and a yellow solid separates, m.p. 149–150°.

1,1'-Thiocarbonyldiindazole.—*Free Base Method.*—Three grams of indazole (0.026 mole) is dissolved in 50 ml. of acetone, giving a colorless solution. Twenty milliliters of acetone is then added, followed by the addition of 1 Gm. of thiophosgene (0.009 mole) in 15 ml. of acetone. The reaction mixture is stirred at room temperature for 1 hr., then refluxed for 1 hr. The color changes gradually from light brown to green. On cooling to room temperature, a white precipitate separates. It is filtered off and the filtrate cooled in an ice bath for 1 hr. More white precipitate separates. This is filtered off and the filtrate evaporated to near dryness. It does not solidify on cooling. To this semisolid mass, cold cyclohexane is added. On scratching, a solid immediately forms. It is separated and dried in air. Yield, 3 Gm. (62%), m.p. 225–226°.

*Anal.*¹—Calcd. for $\text{C}_{15}\text{H}_{10}\text{N}_4\text{S}$: N, 20.2. Found: N, 20.2.

1,1'-Thiocarbonyldibenzotriazole.—*Sodium Salt Method.*—Six grams of benzotriazole (0.05 mole) is suspended in 70 ml. of Na-dried benzene. To this suspension, 2.4 Gm. of 50% NaH suspended in oil is added in portions. A vigorous reaction takes place. Hydrogen evolves and a curdy precipitate is readily formed. The reaction mixture is then refluxed for 1 hr. To this hot mixture, 2.9 Gm. of thiophosgene (0.025 mole) is added dropwise. The precipitate turns to a fine white-yellow powder. The mixture is stirred at room temperature for 1 hr., then filtered through a Buchner funnel. The dark yellow filtrate is evaporated, then cooled in an ice bath. No crystals separate. The solid residue left on the funnel is extracted with hot acetone, from which yellow crystals are obtained, m.p. 176–178°.

*Anal.*¹—Calcd. for $\text{C}_{15}\text{H}_8\text{N}_6\text{S}$: C, 55.6; H, 2.86; N, 30.0; S, 11.4. Found: C, 54.4; H, 3.05; N, 30.4; S, 12.0.

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