TABLE II

PROPERTIES OF 1,3,5-TRINITROBENZENE ADDUCTS OF INDOLE-3-ACETIC ACID AND OF SEVERAL ESTERS OF INDOLE-3-ACETIC ACID

| Trinitrobenzene derivative of | M.p., °C. | Color | Formula | Analyses, % Calcd. C | H | N | Found C | H | N |
|---|---|---|---|---|---|---|---|---|---|
| Indole-3-acetic acid | 199 dec. | Orange | $C_{16}H_{12}N_4O_8$ | 49.5 | 3.1 | 14.4 | 49.7 | 2.9 | 14.4 |
| Methyl ester | 135 | Yellow | $C_{17}H_{14}N_4O_8$ | 50.8 | 3.6 | 13.9 | 50.8 | 3.6 | 13.6 |
| Ethyl ester | 88 | Yellow | $C_{18}H_{16}N_4O_8$ | 51.9 | 3.9 | 13.5 | 51.9 | 3.8 | 13.4 |
| *n*-Propyl ester | 111 | Yellow | $C_{19}H_{18}N_4O_8$ | 53.0 | 4.2 | 13.0 | 53.2 | 4.4 | 13.2 |
| *n*-Butyl ester | 101 | Yellow | $C_{26}H_{20}N_4O_8$ | 54.1 | 4.5 | 12.6 | 54.4 | 4.4 | 12.8 |
| *n*-Amyl ester | 96 | Yellow | $C_{21}H_{22}N_4O_8$ | 55.0 | 4.8 | 12.2 | 54.9 | 5.0 | 12.1 |

**Preparation of the Addition Products.**[5]—One millimole of the indole-3-acetic acid derivative and one millimole of 1,3,5-trinitrobenzene were dissolved in 10 ml. of hot absolute ethanol and placed in the refrigerator to cool. The crystals which formed were recrystallized once from absolute ethanol and dried at room temperature *in vacuo* over phosphorus pentoxide prior to analysis. The properties of these derivatives are shown in Table II.

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[5] J. J. Sudborough, *J. Chem. Soc.*, **109**, 1339 (1916).

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## A Preparative Method for Thiosemicarbazones of Aromatic Aldehydes[1]

BY BRUNO PUETZER, WILLIAM E. HAMLIN[2] AND LEON KATZ

In the course of experiments designed to prepare chemotherapeutically active thiosemicarbazones a new method was sought which would eliminate the use of thiosemicarbazide. It has been found that an aqueous solution of hydrazinium thiocyanate will react with aromatic aldehydes in the presence of acetic acid to give the respective thiosemicarbazones directly. The products listed in Table I were prepared this way and compared with products made from the aromatic aldehyde and thiosemicarbazide.

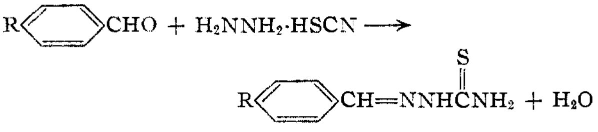

TABLE I

BENZALDEHYDE THIOSEMICARBAZONES

| Benzaldehyde | Yield, % | M. p., °C., dec. [a] | [b] |
|---|---|---|---|
| 4-$CH_3CONH$ | 86 | 234–236 | 235–236 |
| 4-$(CH_3)_2N$ | 97 | 211–214 | 214–215 |
| 4-OH | 88 | 229–231 | 231–232 |
| 2-OH | 81 | 220–223 | 228–229 |
| 4-$NO_2$ | 86 | 247–249 | 257–259 |

[a] Material isolated directly from reaction mixture, not recrystallized. [b] Recrystallized material prepared by condensation of thiosemicarbazide and the respective benzaldehyde. All melting points were uncorrected.

### Experimental

**Preparation of Hydrazinium Thiocyanate Solution.**—Into a 4-l. beaker were charged 485 g. (5.0 moles) potassium thiocyanate, 425 g. (95% real, 2.50 moles real) dihydrazine sulfate, and 1 l. of water. The mixture was stirred and heated to 95° in 20 minutes, held at 95° five minutes, and cooled to 10° in three-quarter hour. The white slurry of potassium sulfate was collected on a Büchner funnel containing a thin bed of filter-cel, sucked well and the cake washed with 50 ml. of water. The volume of the filtrate was 1335 ml., equivalent to 0.00375 mole of hydrazinium thiocyanate per ml. This solution was used without further analysis.

**4-Dimethylaminobenzaldehyde Thiosemicarbazone.**—Into a 500-ml. three-necked flask equipped with a glas-col mantle, sealed stirrer, reflux condenser and thermometer were charged 28.5 g. (0.191 mole) of dimethylaminobenzaldehyde and 150 ml. of glacial acetic acid. This mixture was stirred and heated to 100°. Ninety-five ml. of the hydrazinium thiocyanate solution described above (0.356 mole) was heated to 100° and added to the acetic acid solution. After five minutes a red precipitate began to appear. The slurry was held at 95–100° for one hour longer, cooled to 10°, and filtered through a Büchner funnel. The cake was washed with 500 ml. of water and dried *in vacuo* at 65° for 15 hours. The weight of solid, m.p. 211–214° dec., was 40.7 g. An additional 0.5 g. of material was obtained from the filtrate.

As a solvent for the aromatic aldehydes ethanolic acetic acid of varying composition can be employed. A series of experiments were run with 4-acetylaminobenzaldehyde to determine the optimum usage of hydrazinium thiocyanate. An excess of 25–50% appeared to give the optimum yields.

Fractional crystallization from glacial acetic acid of the thiosemicarbazone formed from 4-nitrobenzaldehyde led to the isolation of a small quantity of azine; m.p. 307–309°. *Anal.* Calcd. for $C_{14}H_{10}O_4N_4$: C, 56.38; H, 3.36; N, 18.78. Found: C, 56.50; H, 3.30; N, 18.97.

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[1] After the completion of this work a report by Stig Sunner (*C. A.*, **45**, 548b (1951)) appeared which described the reaction of hydrazinium thiocyanate with acetone to yield acetone thiosemicarbazone. At least two products were formed in this reaction whereas we obtained only the respective thiosemicarbazone under the conditions described in the experimental section with the exception of 4-nitrobenzaldehyde. In this case less than 5% of azine was isolated.

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## The Double Sulfates of Zirconium and the Bivalent Metals

BY S. R. PATEL

A series of compounds of the type $RSO_4 \cdot Zr(SO_4)_2$ (where R = a bivalent metal) has been prepared (Table I). The compound $MgSO_4 \cdot Zr(SO_4)_2$ a typical example, was obtained by heating together 0.1 g. of zirconium nitrate (=0.04 g. zirconia) and 0.025 g. to 0.4 g. of $MgSO_4 \cdot 7H_2O$ in 40 cc. of sulfuric acid (sp. gr. 1.79). A clear solution was first obtained from which on further concentration a precipitate separated which after washing free from adhering sulfuric acid with absolute alcohol and then drying at 230° agreed with the formula $MgSO_4 \cdot Zr(SO_4)_2$.

TABLE I

| R | Calcd., % R | Zr | $SO_4$ | Found, % R | Zr | $SO_4$ |
|---|---|---|---|---|---|---|
| Mg | 6.024 | 22.59 | 71.39 | 5.58 | 22.73 | 71.60 |
| Zn | 14.70 | 20.50 | 64.79 | 15.11 | 20.18 | 65.05 |
| Cd | 22.85 | 18.55 | 58.60 | 22.63 | 18.51 | 58.54 |
| Co | 13.45 | 20.81 | 65.75 | 13.82 | 20.71 | 66.05 |
| Mn | 12.65 | 21.00 | 66.36 | 12.48 | 21.19 | 66.52 |