

SELENIUM CATALYZED CARBONYLATION OF AMINES AND DISULFIDES.
A NEW SYNTHESIS OF THIOCARBAMATES.

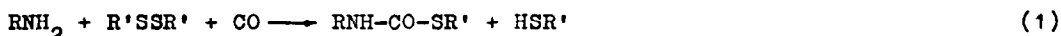
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Despite the availability of several methods for the preparation of thiocarbamic-acid-S-esters, the most widely used routes to these compounds are the reactions of isocyanates with thiols and of chlorothiocarbonates with amines⁽¹⁾.

It has now been found that a more direct preparation of thiocarbamates is effected by combining primary aliphatic amines and disulfides in equimolecular ratio with carbon monoxide in the presence of selenium as a catalyst.

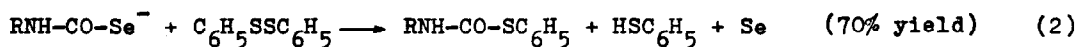


The conditions required are mild and aromatic amines can be used provided that triethylamine is added as a co-catalyst.

In a typical reaction iso-propylamine (0.01 mole), diphenyldisulfide (0.01 mole) and selenium (4×10^{-4} g-atom) were charged in the autoclave together with 20 ml of acetonitrile. Carbon monoxide was compressed at 4 atm and the contents of the autoclave were stirred and heated at 20°C. After distillation of the solvent the crude solid was dissolved in light petroleum, the solution was filtered in order to recover selenium and the by-product N,N'-di-iso-propylurea (0.1 g). Cooling the solution gave 1.65 g of iso-propylthiocarbamic-acid-S-phenyl-ester identical to an authentic specimen (85% yield). The aromatic amines reported in the table were carbonylated at 60°C by an almost identical procedure in the presence of triethylamine (5×10^{-3} mole) as a co-catalyst. The crude solid was dissolved in benzene, and light petroleum added. On cooling thiocarbanilic-acid-S-ester separated.

These selenium-catalyzed systems are similar to those previously reported for the carbonylation of aliphatic⁽²⁾ and aromatic amines⁽³⁾ to ureas. Therefore a selenocarbamate intermediate (RNH-CO-Se^-) may be similarly involved. In support to this hypothesis the reaction of a mixture of iso-propylamine (0.02 mole) and selenium (0.01 g-atom) in acetonitrile (40 ml)

with carbon monoxide (4 atm) gives the salt $\text{RNH-CO-Se}^- \text{RNH}_3^+$ ($\text{R}=\text{iso-C}_3\text{H}_7$); on addition of diphenyldisulfide (0.01 mole) in an inert atmosphere selenium is precipitated and iso-propylthiocarbamic-acid-S-phenyl-ester formed:



While detailed information concerning this reaction of selenocarbamate anion with the disulfide is lacking to date, an ionic cleavage of sulfur-sulfur bond⁽⁴⁾ by attack of the nucleophilic selenocarbamate may be suggested.

TABLE

| RNH_2 (R =) | $\text{R}'\text{SSR}'$ ($\text{R}' =$) | temp. (°C) | $t_{\frac{1}{2}}$ (hours) ^(a) | $\text{RNH-CO-SR}'$ (yield%) ^(b) |
|---|--|--------------------|--|---|
| iso-C ₃ H ₇ | C ₆ H ₅ | 20 | very fast | 85 |
| tert-C ₄ H ₉ | C ₆ H ₅ | 20 | very fast | 84 |
| C ₆ H ₁₁ | C ₆ H ₅ | 20 | very fast | 87 |
| n-C ₄ H ₉ | CH ₃ | -5 ^(c) | 3 | 73 |
| iso-C ₃ H ₇ | CH ₃ | -5 ^(c') | 3 | 77 |
| p-CH ₃ C ₆ H ₄ | iso-C ₄ H ₉ | 60 | 0.5 | 92 |
| o-CH ₃ C ₆ H ₄ | iso-C ₄ H ₉ | 60 | 3.5 | 92 |
| C ₆ H ₅ | iso-C ₄ H ₉ | 60 | 1 | 87 |
| C ₆ H ₅ | sec-C ₄ H ₉ | 60 | 2.5 | 83 |
| C ₆ H ₅ | tert-C ₄ H ₉ | 60 | -(d) | 0 |
| C ₆ H ₅ | C ₆ H ₅ | 60 | 1.2 | 50 |
| p-ClC ₆ H ₄ | iso-C ₄ H ₉ | 60 | 1.5 | 90 |
| p-NO ₂ C ₆ H ₄ | iso-C ₄ H ₉ | 60 | -(d) | 0 |

(a) Half reaction time. (b) Yield at the complete reaction. (c) If the reaction is carried out at 20°C N,N'-di-n-butylurea, and (c') N,N'-di-iso-propylurea are the main products. (d) Aromatic amine and disulfide were recovered unchanged after ten hours.

REFERENCES

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