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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.

$$RNH_2 + R'SSR' + CO \longrightarrow RNH\text{-}CO\text{-}SR' + HSR' \qquad (1)$$

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 ($4x10^{-4}$ 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 tiethylamine ($5x10^{-3}$ 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 ($RNH\text{-}CO\text{-}Se^-$) 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 RNH-CO-Se$^-$ RNH$_3^+$ (R=iso-C$_3$H$_7$); on addition of diphenyldisulfide (0.01 mole) in an inert atmosphere selenium is precipitated and iso-propylthiocarbamic-acid-S-phenyl-ester formed:

$$\text{RNH-CO-Se}^- + C_6H_5SSC_6H_5 \longrightarrow \text{RNH-CO-SC}_6H_5 + HSC_6H_5 + Se \quad (70\%\ \text{yield}) \qquad (2)$$

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 =)	R'SSR' (R' =)	temp.(°C)	t$_{1/2}$(hours)(a)	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

(1) Methoden der Organische Chemie - Schwefel, Selen and Tellur Verbindungen, Band IX, E.Müller Ed., Stuttgart 1955, p.834.

(2) N.Sonoda, T.Yasuhara, K.Kondo, T.Ikeda and S.Tsutsumi, J.Am.Chem.Soc., 75, 3425 (1971).

(3) K.Kondo, N.Sonoda and S.Tsutsumi, Chem.Com., 307 (1972).

(4) The Chemistry of Organic Sulfur Compounds, Vol.1, N.Karasch and C.Y.Meyers Ed., Pergamon Press, Oxford 1961, p.83.

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