Tetrahedron Letters No. 34, pp 2899 - 2900, 1974. Pergamon Press. Printed in Great Britain.

SYNTHESIS OF HETEROCYCLES BY SELENIUM CATALYZED CARBONYLATION OF BIFUNCTIONAL COMPOUNDS.

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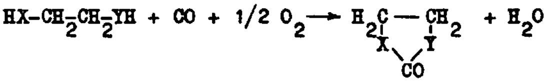
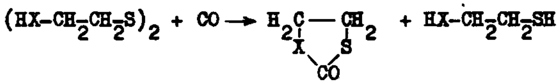
(Received in UK 25 June 1974; accepted for publication 3 July 1974)

Recent investigations have suggested that carbonyl selenide (SeCO), formed in situ by reaction of selenium with carbon monoxide in the presence of a base catalyst, is an active intermediate in the carbonylation reactions of aliphatic and aromatic amines to ureas$^{(1,2)}$, and of aliphatic sodium alkolates to carbonates$^{(3)}$.

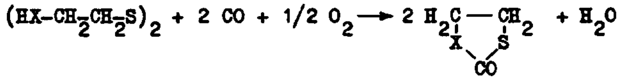
We have extended this reaction to other substrates, and here report some selenium catalyzed carbonylations in which five membered heterocycles are obtained from alpha,beta-bifunctional compounds:


(X = NH, S; Y = O, S) (1)

Sulphur containing heterocycles are also obtained by reaction of a 2,2'-bifunctional disulphide with carbon monoxide using selenium as catalyst:


(X = NH, O) (2)

When reaction (2) is carried out in the presence of oxygen, which reoxidizes the thiol to disulphide, the heterocyclic compound is obtained as the only organic product:

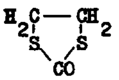
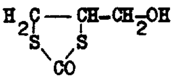
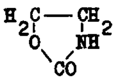
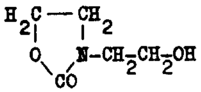
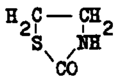
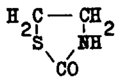
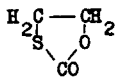

(X = NH, O) (3)

When the substrate undergoing carbonylation does not contain an amino group, triethylamine must be used as cocatalyst$^{(2)}$. The reactions are carried out in mild conditions and high yields are obtained.

In a typical reaction, 2-aminoethanol (0.02 mole) and amorphous selenium (0.001 g-atom) were charged in the autoclave together with 25 ml of tetrahydrofuran. A mixture of carbon monoxide and oxygen (4:1 volume:volume) was compressed at 3 atm and the content of the autoclave stirred and heated at 60°C. When no more absortion was observed, the gas was discharged and selenium recovered. After distillation of the solvent, 2-oxazolidone was collected in 95% yield. It was identified by comparison of the infrared and mass spectra and g.l.c. retention time with those of an autentic speciemen. The substrates reported in the table were carbonylated with an almost identical procedure.

These reactions may provide a convenient and easy route to heterocycles. Work is in progress for further applications to other bifunctional compounds, with particular regards to reaction (2) wich provides a new selective tool for the reductive cleavage of sulphur-sulphur bonds.

TABLE

Substrate	Reaction time (h)	Temp. °C	Product	Yield %
$HS-CH_2-CH_2-SH$[b,c]	10	25		90
$HS-CH_2-CH(SH)-CH_2-OH$[b,c]	10	25		85
$HO-CH_2-CH_2-NH_2$[a]	2	60		95
$(HO-CH_2-CH_2)_2NH$[a]	4	60		83
$(NH_2-CH_2-CH_2-S)_2$[a]	2	60		90
$HS-CH_2-CH_2-NH_2$[a]	2	60		95
$(HO-CH_2-CH_2-S)_2$[b,c,d]	20	60		60

Substrate (0.02 mole) and amorphous selenium (0.001 g-atom) were treated in 25 ml of THF with a mixture of CO/O$_2$ ([a]4:1, [b]10:1 vol:vol) at 3 atm. [c]Triethylamine (0.005 mole) was added as cocatalyst. [d]Selenium was not recovered and CO$_2$ was formed during the reaction.

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Acknowledgment - We thank Mr. B.Anfossi for the assistence during the course of this work.