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γ-LACTAMS BY CATALYTIC CARBONYLATION OF CYCLOPROPYLAMINE

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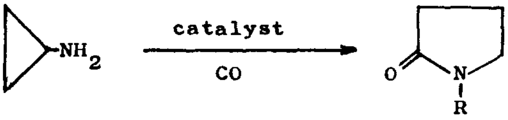
Diverse reports[1-6] of metal insertion into cyclopropanes to yield metal organic species prompted us to examine certain transition metal catalyzed reactions of compounds containing the cyclopropane ring. The present paper deals with the rhodium catalyzed carbonylation of cyclopropylamine (equation 1) to give γ-lactams (I-IV).



(I-IV) (1)

(I): R = cyclopropyl
(II): R = n-propyl
(III): R = allyl
(IV): R = H

A solution of cyclopropylamine in benzene was shaken in a stainless steel autoclave at various temperatures and pressures, using rhodium catalysts. The reaction mixture was distilled directly, and the fraction boiling between 95-110°/10 Torr collected. This contained the lactams (I-IV), which were separated by preparative gas chromatography and unambiguously identified by micro analyses and spectroscopic (IR,NMR) comparison with authentic samples.

Reaction conditions and results have been summarized in Table 1.
With $Rh_6(CO)_{16}$ as catalyst, the major product of carbonylation is N-cyclopropylpyrrolidone (I), while pyrrolidone (IV) and the two alkylpyrrolidones (II) and (III) constitute the byproducts. At lower temperatures, cyclopropylamine con-

versions are low, but more selective towards (I). With increasing reaction temperatures the total lactam yield improves, the optimum (ca. 60%, based on cyclopropylamine) being obtained at 130-140°C. Simultaneously, more of the lacatams (II) and (IV) are formed at the cost of (I).

Table 1: Catalytic carbonylation of cyclopropylamine[a]

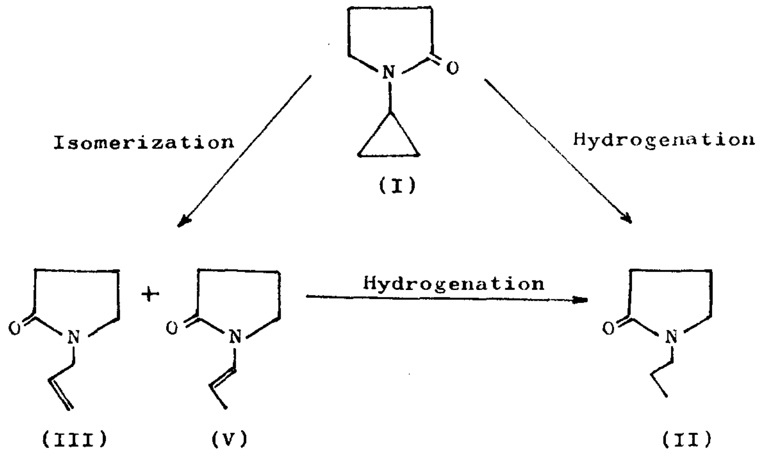
Catalyst	Temp. (°C)	CO-Pressure (atm)[b]	Total lacatam yield (%)[c]	Composition of lactam mixture(%)[d] I	II	III	IV
$Rh_6(CO)_{16}$	100	130	10	92	2	5	1
$Rh_6(CO)_{16}$	120	150	55	75	19	1	5
$Rh_6(CO)_{16}$	140	145	60	62	24	1	12
$Rh_6(CO)_{16}$[e]	130	145	22	89	7	2	2
$Rh_6(CO)_{16}$[f]	130	150	40	81	16	1	2
$ClRh(PPh_3)_3$	130	150	40	28	4	1	67

[a] Constant reaction conditions: 5 ml cyclopropylamine, 150 ml benzene,
5×10^{-5} mole catalyst, 5 hours,
0.5 l rocking autoclave;

[b] Initial pressure at room temperature; [c] Based on cyclopropylamine;
[d] Determined by gas chromatography; [e] In 300 ml benzene; [f] In 50 ml benzene.

N-Cyclopropylpyrrolidone (I) is presumably reduced at higher temperatures to N-propylpyrrolidone (II) by hydrogen, which is present as an impurity in commercial carbon monoxide. Such a reduction may well be preceeded by a rearrangement[7] of (I) to N-allyl- (III) and N-propen-1-ylpyrrolidone (V) (see equation 2).

Foregoing assumptions are corroborated by the fact that a benzene solution of cyclopropylamine, when treated with hexarhodiumhexadecacarbonyl under carbon monoxide pressure yields a mixture of the lactams (I)-(IV). The absence of (V) in the mixture may be attributed to the pronounced ease with which it is reduced to the saturated homolog (II)[8].



(2)

Surprisingly, with chlorotris(tripehnylphosphine)rhodium pyrrolidone (IV), and not (I), constitutes the main product of carbonylation.

Two paths may be considered for the formation of pyrrolidone (IV):

a) direct carbonylation of cyclopropylamine, and

b) hydrogenolytic cleavage[9] either of cyclopropane from (I), or of propene from (III) and (V), both of which, as already mentioned above, may result from in situ isomerization of (I).

It is likely that the reaction path b) is particularly promoted by the presence of chlorotris(triphenylphosphine)rhodium.

Both yield and distribution of products are influenced by the concentration of cyclopropylamine employed. In general, with highly dilute solutions conversions are low, while 10% and more concentrated solutions in benzene lead to extensive formation of non-volatile condensation products.

Investigation of other transition metal catalyzed reactions of cyclopropane derivatives, especially with carbon monoxide continues.

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