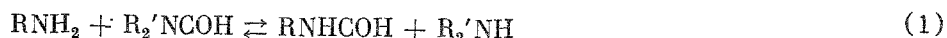


CATALYSIS BY TRANSITION-METAL SALTS OF TRANSAMIDATION
BETWEEN ALLYL- AND n-BUTYLAMINES AND DMFA

A. A. Belyi, O. N. Andryushin,
and V. F. Kuznetsov

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Transamidation reactions (1) are catalyzed by acids [1], bases [2], and CO₂ [3]:



Recently, it was determined that low-valence Ni complexes catalyze a similar reaction of secondary amines with DMFA [4].

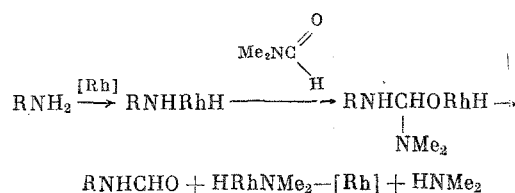
We have observed that the salts of some transition metals can also catalyze reaction (1) with the participation of DMFA. After 4 h of heating of allylamine (AA) with DMFA in the presence of RhCl₃·3H₂O at 80°C, small amounts of N-allylformamide (AFA) appeared in the reaction mixture. With an increase in the temperature and the reaction time, its yield increased, and at 100°C in 8 h it reached 40% on the basis of the starting AA. A further increase in the temperature did not affect the yield of AFA, and at 140°C the system lost homogeneity because of the deposition of metallic Rh.

Blank runs showed that with heating (8 h) of AA with DMFA in an Ar atmosphere without a catalyst the formation of AFA did not occur, and when Ar was replaced by air ~3% AFA was formed during the same time. Therefore, all the catalytic experiments were carried out in sealed evacuated glass ampuls.

As is evident from Table 1, not only Rh salts, but also chlorides of other transition metals can catalyze the conversion of AA to AFA, but the greatest activity is observed in the case of RhCl₃·3H₂O. Unlike DMFA, other amides, e.g., acetamide or N,N-dimethylacetamide, do not react with AA under these conditions.

It seemed of interest to extend this reaction to aliphatic amines, which undergo transamidation with greatest difficulty in the presence of DMFA [5]. We found that n-butylamine reacts with DMFA in the presence of RhCl₃·3H₂O (0.25 mmole, RhCl₃·BuNH₂ ratio of 1:50, 100°C, 8 h), giving N-butylformamide in 30% yield on the basis of the starting amine. Under acid-catalysis conditions, such a reaction requires many hours of heating at 200°C [5].

It seems probable that the found reaction is similar in mechanism to the acylation of amines by carboxylic acid esters in the presence of RhCl₃ as a catalyst [6] and occurs according to the scheme



R = CH₂CH=CH₂, Bu

EXPERIMENTAL

GLC analysis of the reaction products was carried out at 175°C, on a Tsvet-100 chromatograph with a 1000 × 3 mm steel column packed with Polysorb-1 (0.25-0.31), a He carrier gas flow rate of 25 ml/min, and a flame-ionization detector.

The DMFA [7] and AA [7], purified by standard procedures, were distilled and stored under Ar.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 4, pp. 854-855, April, 1986. Original article submitted February 7, 1985.

TABLE 1. Reaction of Allylamine with DMFA in the Presence of Transition-Metal Salts (100°C, 8 h)

Salt	Yield of AFA on basis of starting amine, %	Yield of AFA, moles per mole of metal salt	Salt	Yield of AFA on basis of starting amine, %	Yield of AFA, moles per mole of metal salt
—	0	—	PdCl ₂	24	31
RhCl ₃ ·3H ₂ O	40	49	CuCl ₂	24	29
FeCl ₂	34	40	NiCl ₂	5	1,6
CoCl ₂	32	37			

Reaction between the Amines and DMFA. Into a glass ampul in an Ar stream were placed 0.05 g (0.25 mmole) of RhCl₃·3H₂O, 2 ml (27 mmoles) of AA, and 5 ml (65 mmoles) of DMFA. The ampul was evacuated, sealed, and kept in an oil bath for 8 h at 100°C. Then a fraction with bp 71-73°C (10 mm) was withdrawn from the reaction mixture. The PMR, IR, and mass spectra of the obtained substance agreed with the spectra of the standard sample of AFA.

Runs were carried out by a similar procedure with n-butylamine and chlorides of other transition metals. The yield of AFA was determined by GLC.

CONCLUSIONS

Chlorides of Rh, Pd, Fe, Co, Ni, and Cu catalyze the transamidation between DMFA and allylamide, and RhCl₃ also catalyzes the reactions of DMFA with n-butylamine.

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