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CARBONYLATION OF m-FLUORONITROBENZENE IN THE

PRESENCE OF SELENIUM-CONTAINING CATALYSTS

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Selenium and its compounds exhibit a high catalytic activity and selectivity in the carbonylation of aromatic nitro compounds to give carbamates [1, 2]. p-Fluoronitrobenzene (FNB) in the presence of the  $(NH_2)_2$ CSe catalyst and either Et<sub>3</sub>N or pyridine (Py) as the promoter is converted in high yield to the corresponding carbamate [3].

 $RC_6H_4NO_2 + 3CO + C_2H_5OH \rightarrow RC_6H_4NHCO_2C_2H_5 + 2CO_2$ 

The present paper is devoted to a further study of this reaction in order to elucidate the effect of the catalyst composition, temperature, and CO pressure on the synthesis of m-fluorophenyl carbamate (FPC).

Various organic bases are used as activating additives to Se-containing catalysts for the carbonylation of nitro compounds with carbon monoxide [4].

We studied the effect of organic amines on the yield of FPC when m-FNB is carbonylated in the presence of  $(NH_2)_2CSe$  (Table 1). All of the employed additives exhibit an activating effect. Et<sub>3</sub>N is characterized by the greatest promoting effect, and the yield in its presence was 48%. This is apparently related to the greater basicity of Et<sub>3</sub>N when compared with the other promoters. The promoting activity of the amine increases with increase in its basicity. Taking into account the obtained results, Et<sub>3</sub>N was selected as the promoter when FNB was carbonylated under various conditions.

With increase in the CO pressure from 40 to 60 atm the FNB conversion increases from 79 to 100%. A further increase in the pressure up to 120 atm leads to a decrease in the FNB conversion to 80% (Table 2). The selectivity of forming the corresponding FPC was 98-100%.

When the synthesis temperature is increased the FNB conversion reaches a maximum at 170°C and then it decreases (Fig. 1). Here the selectivity of forming the corresponding FPC does not change, which is apparently related to the heat stability of the latter.

TABLE 1. Effect of Promoting Additives on Carbonylation of m-FNB (FNB:Cat:promoter mole ratio = 20:2:1, initial CO pressure at 20°C, 60 atm, 180°C, 40 min)

TABLE 2. Effect of CO Pressure on Carbonylation of m-FNB (FNB:Cat:Et<sub>3</sub>N mole ratio = 20:2:1, 180°C, 2 h)

FNB con-

version %

79 100 79

81

75

Selectivity

based on FPC.

99

100

99 100

100

UDC 542.97:547.548

Promoter	р <i>К</i> В	Yield of FPC,%	P <sub>CO</sub> , atn
Triethylamine Imidazole Tris(methoxy)- aminomethane	2,99 6,97 5,70 6,80	25 48 40 41	40 60 80 100 120
α-Aminopyridine Pyridine	8,82	38	

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At a constant amount of  $Et_3N$  (0.0004 mole), increasing the  $(NH_2)_2CSe:Et_3N$  mole ratio from 0.5.1 to 2.0.1 leads to an increase in the FNB conversion from 34 to 100%, but here the selectivity of forming the FPC decreases (Table 3).

At a constant amount of Se catalyst in the reaction medium (0.0004 mole) a change in the  $(NH_2)_2CSe:Et_3N$  mole ratio from 1.0:1.0 to 1.0:4.0 leads to an increase in the FNB conversion from 81 to 100%. Here the selectivity based on FPC decreases from 100 to 85% due to the formation of the corresponding amine.

## EXPERIMENTAL

Pure FNB with mp 41°C was used. The carbonylation was run in an 0.08-liter stainless steel autoclave, using in each experiment 1.07 g of FNB, 0.045 g of  $(NH_2)_2CSe$ , 6 ml of abs. EtOH, and the organic bases in a mole ratio to the catalyst ranging from 1:0.5 to 5:1. The reaction mixture was agitated by a back-and-forth motion of the autoclave in a horizontal plane. The autoclave was previously purged twice with CO, after which the CO pressure was raised and the autoclave was heated at a given temperature for a definite time.

The analysis was done by the GLC method  $(1.5 \times 33 \text{ mm column packed with } 5\% \text{ XE-60 deposited on Chromaton N-AM-DMCS, 190°C, LCM-8MD chromatograph, and flame-ionization detector). The quantitative calculation was made by the absolute calibration method. The obtained carbamate was isolated by filtering the chilled reaction mixture and subsequent recrystal-lization from hexane solution.$ 

m-Fluorophenyl carbamate, mp 36°C, IR spectrum (v, cm<sup>-1</sup>): 1700 (C=0), 3310 (N-H). Found: C 58.6; H 5.6; N 7.8; F 9.8%. C<sub>9</sub>H<sub>10</sub>NO<sub>2</sub>F. Calculated: C 59.0; H 5.4; N 7.7; F 10.4%.

## CONCLUSIONS

The additives triethylamine, pyridine, imidazole,  $\alpha$ -aminopyridine, and tris(hydroxymethyl)aminomethane exert a promoting effect on the carbonylation of m-fluoronitrobenzene in the presence of selenourea.

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TABLE 3. Effect of  $(NH_2)_2CSe:Et_3N$  Mole Ratio on Carbonylation of m-FNB (FNB:alcohol mole ratio = 1:14, initial CO pressure at 20°C = 60 atm, 170°C, 2 h)

Mole ratio (NH <sub>2</sub> ) <sub>2</sub> CSe : Et <sub>3</sub> N	FNB con- version, %	Selectivity based on FPC, %	Mole ratio (NH <sub>2</sub> ) <sub>2</sub> CSe : Et <sub>8</sub> N	FNB con- version, %	Selectivity based on FPC,%
0,5 : 1,0 1,0 : 1,0 2,0 : 4,0 3,0 : 1,0	34 81 100 100	100 100 91 92	1,0 : 2,0 1,0 : 3,0 1,0 : 4,0	82 94 100	100 96 85