CATALYTIC SYNTHESIS OF FLUOROAROMATIC URETHANES IN THE PRESENCE OF SELENIUM-CONTAINING COMPOUNDS

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Selenium and its compounds exhibit a high catalytic activity in the carbonylation of aromatic nitro compounds with the formation of urethanes [1, 2].

 $RC_6H_4NO_2 + 3CO + C_2H_5OH \rightarrow RC_6H_4NHCOOC_2H_5 + 2CO_2$

The reaction is promoted by addition of triethylamine, pyridine, aniline, quinoline, morpholine, or urotropine [3, 4].

In contrast to aromatic bromo- and chloronitro compounds, their fluoroaromatic analogs have been scarcely studied in this reaction, although the corresponding urethanes may be interesting in the synthesis of herbicides, pesticides, and medicinal preparations. We therefore studied the carbonylation of fluoroaromatic nitro compounds in absolute ethanol in the presence of selenourea $(NH_2)_2CSe$ as the catalyst and triethylamine Et₃N or pyridine (Py) as the promoter.

When the CO pressure is increased from 50 to 75 atm, the conversion of p-fluoronitrobenzene (FNB) increases from 40 to 85%. Further increase in the CO pressure to 100 atm leads to inappreciable decrease in the FNB conversion and in the yield of p-fluorophenylurethane (FPU) (Table 1). With a change in temperature, the conversion of the initial FNB reaches a maximum at 180°C, and then decreases (Fig. 1). The observed decrease in the selectivity of the FPU formation is apparently due to thermal decomposition of the urethane formed to isocyanate, which by reacting with traces of water present in the reaction medium transforms into the corresponding amine

 $p\text{-FC}_{6}\text{H}_{4}\text{NHCOOC}_{2}\text{H}_{5} \xrightarrow{-\text{C}_{c}\text{H}_{4}\text{OH}} \rightarrow p\text{-FC}_{6}\text{H}_{4}\text{NCO} \xrightarrow{\text{H}_{2}\text{O}} \rightarrow p\text{-FC}_{6}\text{H}_{4}\text{NH}_{2} + \text{CO}_{2}$

If the amount of the Se catalyst remains constant (0.002 mole), and the molar ratio $(NH_2)_2$ CSe: Et₃N changes from 1:0.25 to 1:0.5, the conversion of the initial FNB increases from 23 to 85%. Further change in the molar ratio to 1:2 decreases the conversion to 38%. Thus, the selectiv-



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TABLE 1. Influence of Initial CO Pressure on Conversion of p-Fluoronitrobenzene (FNB) and Yield of p-Fluorophenylurethane (FPU) in Carbonylation of FNB in Presence of $(NH_2)_2CSe$ (Ct) and Triethylamine (molar ratio FNB:alcohol:Ct:Et₃N = 20:280:2:1, 180°C, 2 h).

P _{CO} , atm	Conver- sion of FNB,%	Selectivity with res- pect to FPU, %	Yield of FPU,%	P ^{atm} CO' atm	Conver- sion of FNB,%	Selectivity with res- pect to FPU,%	Yield of FPU,%
50	40	100	40	85	80	99	79
70	60	100	60	95	80	98	79
75	85	97	83	100	80	100	80

TABLE 2. Influence of Molar Ratio $(NH_2)_2$ CSe (Ct): Triethylamine on Conversion of FNB and Selectivity of Formation of FPU (molar ratio FNB:alcohol = 1:14, initial CO pressure at 20°C 75 atm, 180°C, 2 h)

Molar ratio Ct:Et3N	Conversion of FNB, %	Selectivity with respect to FPU, %	Molar ratio Ct:Et ₃ N	Conversion of FNB, %	Selectivity with respect to FPU, %
1:0,25 1:0,33 1:0,55 1:1,00 1:2,00	23 68 85 68 38	100 100 97 100 100	0,84 : 1 2,10 : 1 2,60 : 1 4,20 : 1	54 85 81 82	100 99 100 100

TABLE 3. Influence of Molar Ratio $(NH_2)_2CSe$ (Ct):Pyridine on FNB Conversion and Selectivity of FPU Formation (molar ratio FNB:alcohol:Ct = 10:140: 1, initial CO pressure at 20°C 75 atm, 180°C, 2 h)

Molar ratio Ct:Py	Conversion of FNB, %	Selectivity with respect to FPU %		
1:1,0	43	100		
1:2,5	76	100		
1:3,5	85	98		
1:5,0	92	98		
1:6,3	87	100		

ity of formation of the corresponding FPU is close to 100% (Table 2). At a constant amount of Et_3N (0.1 mole), the increase in the $(NH_2)_2CSe:Et_3N$ molar ratio from 0.84:1 to 2.1:1 leads to increase in the conversion from 54 to 85%. However, with further increase in this ratio to 4.2:1, the conversion of FNB somewhat decreases. At the same time, an increase in the catalyst:Et_3N molar ratio does not decrease the selectivity of the process (see Table 2).

When Py is used as a promoter during the carbonylation of FNB, the change in the catalyst: Py molar ratio from 1:1 to 1:5 leads to an increase in the FNB conversion from 43 to 92%. Further change in this ratio to 1:6.3 does not appreciably influence the conversion of FNB. The selectivity of the FPU formation in the presence of Py is close to 100% (Table 3).

2,4-Dinitrofluorobenzene (DNFB) at 140°C and at initial CO pressure of 10 atm converts into the corresponding monourethane to the extent of 99% (according to the data of elemental analysis). Increase in the initial CO pressure to 75 atm did not lead to the formation of the corresponding diurethane, although during carbonylation of 2,4-dinitrotoluene on Pd catalysts, the yields of diurethane increased with the increase in the initial CO pressure [5].

EXPERIMENTAL

p-Fluoronitrobenzene (FNB) was obtained by nitration of grade "pure" fluorobenzene by a mixture of nitric (d 1.5) and sulfuric (d 1.84) acids at -3 to 0°C, and was isolated by fractional distillation followed by freezing, mp 27°C, purity 99.6%. 2,4-Dinitrofluorobenzene (DFNB) — a preparation from firm "Chemapol," was used, mp 24.3°C, purity 99.8%.

The carbonylation was carried out in a rotating stainless steel autoclave with a capacity of 0.15 liter, in each experiment using 2.86 g of FNB, or 3.84 g of DFNB, 16 ml of ethanol, 0.25 g of $(NH_2)_2CSe$, with the ratio of the organic bases to the catalyst of 0.25:1 to 6.3:1. The autoclave was purged twice with CO, the CO pressure was increased, and the mixture was left to stand at the given temperature for 2 h.

The analysis was carried out by the GLC method (3 m \times 33 mm column with XE-60 on Chromatone N-AM-DMCS, 190°C, flame ionization detector). The quantitative analysis was carried out by the absolute calibration method. The urethanes obtained were isolated by filtration, with cooling of the reaction mixture, followed by recrystallization from hexane.

p-Fluorophenylurethane (FPU), mp 59-60°C, IR spectrum (ν , cm⁻¹): 1690 (C = 0, 3300 (NH). Found: C 58.7; H 5.5; N 7.9; F 9.9%. C₉H₁₀NO₂F. Calculated: C 59.0; H 5.4; N 7.7; F 10.4%. Monourethane from DFNB, mp 80°C. IR spectrum (ν , cm⁻¹): 1610 (C = 0), 2980 (NH). Found: C 46.2; H 4.1; N 12.8; F 8.0%. C₉H₉N₂O₄F. Calculated: C 47.4; H 4.0; N 12.3; F 8.3%.

CONCLUSIONS

Urethanes of a fluoroaromatic series were synthesized by carbonylation of the corresponding fluoro-nitro compounds in alcohol, using selenourea as the catalyst with the addition of organic bases.

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