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Cobalt-catalyzed synthesis of ε-caprolactam and nylon-6 from aminopentene and carbon monoxide

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Abstract

ε-Caprolactam and nylon-6 oligomers were synthesized from 4-pentene-1-amine and/or 3-pentene-1-amine and carbon monoxide using $Co_2(CO)_8$ as catalyst. The results show that the volatile fraction of the product mixture is composed of ε-caprolactam, 3-methyl-2-piperidinone and 3-ethyl-2-pyrrolidinone, while the solid residue mainly consists of nylon-6 oligomers. The addition of excess PEt_3 as ligand can significantly improve the regioselectivity to ε-caprolactam. Using 3-pentene-1-amine as starting material leads to the same results as 4-pentene-1-amine due to rapid C=C bond isomerization.

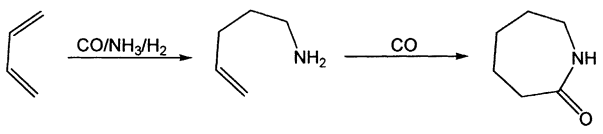
Keywords: Nylon-6; Caprolactam; Aminopentene; Carbon monoxide; Cobalt; Carbonylation; Catalysis

1. Introduction

Nylon-6 is one of the most important of the engineering thermoplastics being produced over 4 million tons annually. Nylon-6 has many desirable properties including its high thermal stability, good mechanical strength, toughness, along with enhanced processibility and excellent surface appearance [1,2]. Products based on nylon-6 find applications in the automotive, electrical, consumer, and other industrial sectors [1].

Nylon-6 is prepared from ε-caprolactam by ring-opening polymerization. The principal commercial processes for the manufacture of ε-caprolactam all consist of multiple steps and involves cyclohexanone and/or its oxime [1]. The cyclohexanone, in turn, is made by the oxidation of cyclohexanol. The cyclohexanol is manufactured either by cyclohexane oxidation or phenol hydrogenation. Apart from the relatively large number of steps involved, the required oxidations tend to have low selectivity at higher conversions. Moreover most conventional routes produces significant quantities of inorganic salts as byproducts, which is not always desired.

A possible alternative two-step synthesis of ε-caprolactam is shown in Eq. (1). The first step involves the hydroaminomethylation of butadiene by ammonia [3]. The second step involves the formation of the seven-membered lactam by intramolecular amidocarbonylation. Lactam formation via transition metal-catalyzed reaction of an unsaturated amine with carbon monoxide constitutes of an attractive synthetic route due to the simple procedure and relatively inexpensive feed stocks. Thus far, the only successful examples involve Falbe's synthesis of γ- and δ-lactams using a cobalt catalyst [4]. Additionally, Göbel and Imhof [5] and Murai and co-workers [6] have made lactams from α,β-unsaturated imines, carbon monoxide, and olefins using ruthenium catalysts. In this paper, we report the first catalytic synthesis of ε-caprolactam/nylon-6 oligomers from 4-pentene-1-amine and/or 3-pentene-1-amine and carbon monoxide.



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2. Experimental section

2.1. Characterization

NMR spectra were recorded at room temperature on a Bruker DPX-300 spectrometer using $CDCl_3$ as solvent (*1,1,1,3,3,3*-hexafluoro-2-propanol/$CDCl_3$ for $CDCl_3$ insoluble solid residue). The chemical shifts are referenced to the solvent resonance. GC analyses of reactant mixtures were carried out on a HP 5890 series II chromatograph operating from 100 to 200 °C with a heating rate of 5 °C/min.

2.2. Materials

Dicobalt octacarbonyl and phosphine ligands were obtained from Strem and used as received. Standard samples of ε-caprolactam and poly(ε-caprolactam) ($d = 1.084$) were purchased from Aldrich. Carbon monoxide was obtained from MG Industries and was used without further purification. All solvents were dried over calcium hydride and distilled under vacuum before use. 4-Pentene-1-amine [7] and 3-ethyl-2-pyrrolidinone [8] were synthesized by literature procedures. 3-Pentene-1-amine was donated by DSM company.

2.3. Synthesis of N-(trimethylsilyl)-2-piperidinone

The procedure similar to that reported for *N*-(trimethylsilyl)-2-pyrrolidinone was used [9]. The crude product was distilled under vacuum at 40 °C to give a colorless oil. ^{1}H NMR ($CDCl_3$, ppm): 3.19 (t, 2H, NC*H*$_2$), 2.37 (t, 2H, C*H*$_2$*C*=O), 1.73 (m, 4H, NCH$_2$C*H*$_2$C*H*$_2$), 0.26 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C NMR ($CDCl_3$, ppm): 176.7, 43.9, 32.4, 23.2, 20.7, −0.44.

2.4. Synthesis of 3-methyl-2-piperidinone

The procedure similar to that reported for 3-ethyl-2-pyrrolidinone was used [8]. A solution of *N*-(trimethylsilyl)-2-piperidinone (8.56 g, 50.0 mmol) in THF (10 ml) was added dropwise to a solution of lithium diisopropylamide (prepared from diisopropylamine (5.06 g, 50 mmol) and *n*-butyl lithium in hexanes (1.6 M, 33 ml, 50 mmol)) in THF (125 ml) at −78 °C. After 1 h, iodomethane (7.10 g, 50 mmol) was added and the solution was warmed to room temperature and stirred for overnight. Water (50 ml) was added, and the layers were separated. The organic layer was dried over $MgSO_4$. The solvent was removed and the crude yellow product was distilled in vacuum at 140 °C. The distillate was washed with cold hexanes to give white solid (1.5 g, 26.6%). ^{1}H NMR ($CDCl_3$, ppm): 6.22 (br, 1H, N*H*), 3.33 (m, 2H, NC*H*$_2$), 2.41 (m, 1H, C*HC*=O), 2.08–1.47 (m, 4H, NCH$_2$C*H*$_2$C*H*$_2$), 1.27 (d, 3H, CHC*H*$_3$). ^{13}C NMR ($CDCl_3$, ppm): 176.3, 42.5, 36.0, 29.3, 21.4, 17.6.

2.5. Synthesis of ε-caprolactam from 4-pentene-1-amine and carbon monoxide

In a typical experiment, to a 300 ml stainless steel autoclave equipped with a magnetic stir bar were charged $Co_2(CO)_8$ (0.06 g, 0.175 mmol), chlorobenzene (15 ml), triethylphosphine (1.0 g, 8.46 mmol), and 4-pentene-1-amine (0.6 g, 11.8 mmol) in a N_2-filled glove box. The autoclave was charged with 1,000 psi CO and then placed in a 200 °C oil bath (internal temperature 165 °C) for 18 h. The autoclave was cooled to room temperature and unreacted CO was vented. The solvent was removed and resultant mixture was distilled in vacuum at 200 °C to give lightly colored oil (0.35 g). Regioselectivity for ε-caprolactam (78%) was evaluated from the integration of carbonyl resonance in the ^{13}C NMR spectrum using an appropriate delay between pulses.

2.6. Purification of crude product by column chromatography

The distillate was purified by column chromatography using silica gel (0.040–0.063 mm) as solid phase and acetone as eluent. The solvent was removed in vacuum to afford a colorless oil. ^{13}C NMR spectrum of this product shows all the expected resonances for ε-caprolactam, 3-methyl-2-piperidinone, and 3-ethyl-2-pyrrolidinone.

2.7. Synthesis of ε-caprolactam from 4-pentene-1-amine and CO (determination of conversion and selectivity by GC)

The same procedure was used as above except 1,2-dichlorobenzene (0.5 g) was added to the reaction mixture as GC internal reference. The total conversion of 4-pentene-1-amine was determined by comparing GC intensity of 4-pentene-1-amine before and after reaction. The conversions for ε-caprolactam and isomers were determined from standard GC calibration curves.

3. Results and discussion

3.1. Catalytic reaction of 4-pentene-1-amine with carbon monoxide

Table 1 summarizes the results obtained. Using $Co_2(CO)_8$ alone, the formation of ε-caprolactam was observed above 132 °C. Fig. 1 shows the ^{13}C NMR spectrum of the purified distillate obtained from the reaction mixture. It essentially consists of resonances due to the three isomeric lactams: ε-caprolactam (179.8, 42.8, 36.9, 30.7, 29.8, 23.4 ppm), 3-methyl-2-piperidinone (176.4, 42.6, 36.2, 29.5, 21.5, 17.8 ppm), and 3-ethyl-2-pyrrolidinone (181.3, 42.7, 40.7, 26.9, 23.8, 11.6 ppm). As the spectrum indicates, the regioselectivity for intramolecular carbonylation to ε-caprolactam was low and became lower as the reaction temperature was

Table 1
Reaction of 4-pentene-1-amine with CO in the presence of $Co_2(CO)_8$[a]

Run	Ligand (molar ratio)	Temperature (°C)	Time (h)	Crude (g)	Distillate (g)	Regioselectivity for ε-caprolactam[c], % (conversion, %)
1	0	180	22	0.6	0.3	24.1 (9.1)
2[b]	0	155	16	0.8	0.4	32.2 (16.1)
3	0	132	16	0	0	0 (0)
4	PPh_3 (3/1)	185	12	0.9	0.6	19.5 (14.7)
5	$Ph_2PC_2H_4PPh_2$ (1/1)	175	18	0.8	0.5	15.6 (9.8)
6	$Me_2PC_2H_4PMe_2$ (5/1)	165	18	0	0	0 (0)
7	P(*t*-Bu)$_3$ (50/1)	165	18	0.8	0.5	22 (13.8)
8	P(*i*-Pr)$_3$ (50/1)	165	18	0.8	0.5	31.6 (19.8)
9	PMe_3 (50/1)	165	18	0.8	0.5	69.0 (43.3)
10	PEt_3 (3/1)	165	18	0.6	0.4	61.7 (30.9)
11	PEt_3 (10/1)	165	18	–	0.4	70.4 (35.3)
12	PEt_3 (25/1)	165	18	0.6	0.4	78.7 (39.5)
13	PEt_3 (50/1)	165	18	0.7	0.5	78.2 (49.0)
14	PEt_3 (100/1)	165	18	0.8	0.4	80.6 (40.4)

[a] Conditions: $Co_2(CO)_8$, 0.06 g; 4-pentene-1-amine, 0.6 g; benzene, 12 ml; CO, 1000 psi. Crude product was obtained by solvent removal. It was then distilled at 200 °C under vacuum.
[b] 200 psi H_2, 800 psi CO.
[c] Based on the integration of the carbonyl resonance in the ^{13}C NMR spectra of the mixture.

raised. In an effort to increase the ε-caprolactam regioselectivity, the effect of adding mono and bidentate phosphines was studied next. Of all the phosphines examined, the small, highly basic, PMe_3 and PEt_3 appeared to be most promising. For example, the addition of 3 eq. of PEt_3 doubled the regioselectivity for ε-caprolactam. Further increase in regioselectivity of up to 80% was obtained when PEt_3/Co ratio was increased to 25:1. Beyond this, no further increase in regioselectivity was observed. The effect of added PEt_3 is most evident from the ^{13}C NMR spectra (Fig. 2) of the crude distillates obtained from reactions in the presence (lower) and absence (upper) of PEt_3. As is evident, in the absence of the added ligand the more stable six-membered ring product, 3-methyl-2-piperidinone, predominates. However, the addition of excess PEt_3 results in the seven-membered ring product, ε-caprolactam, being the favored product.

The possible mechanisms for the formation of ε-caprolactam and its two isomersare illustrated in Scheme 1.

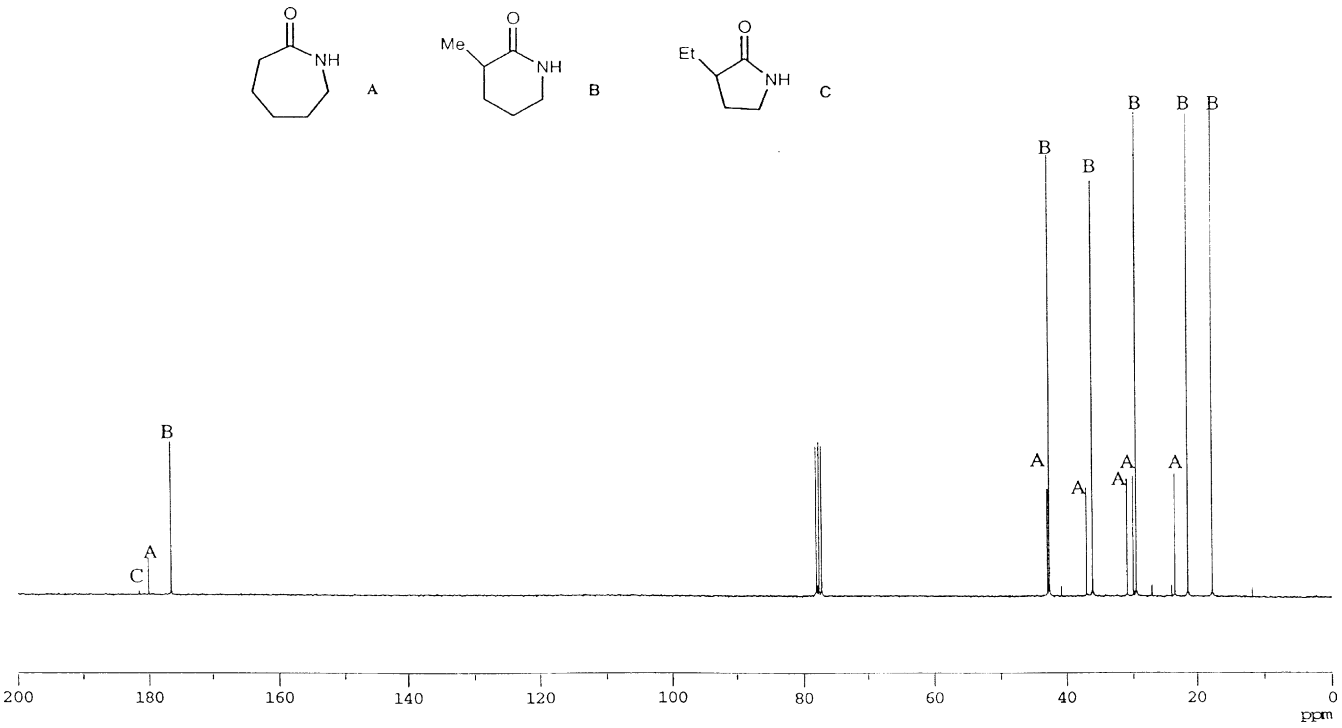


Fig. 1. ^{13}C NMR ($CDCl_3$) spectrum of a purified distillate.

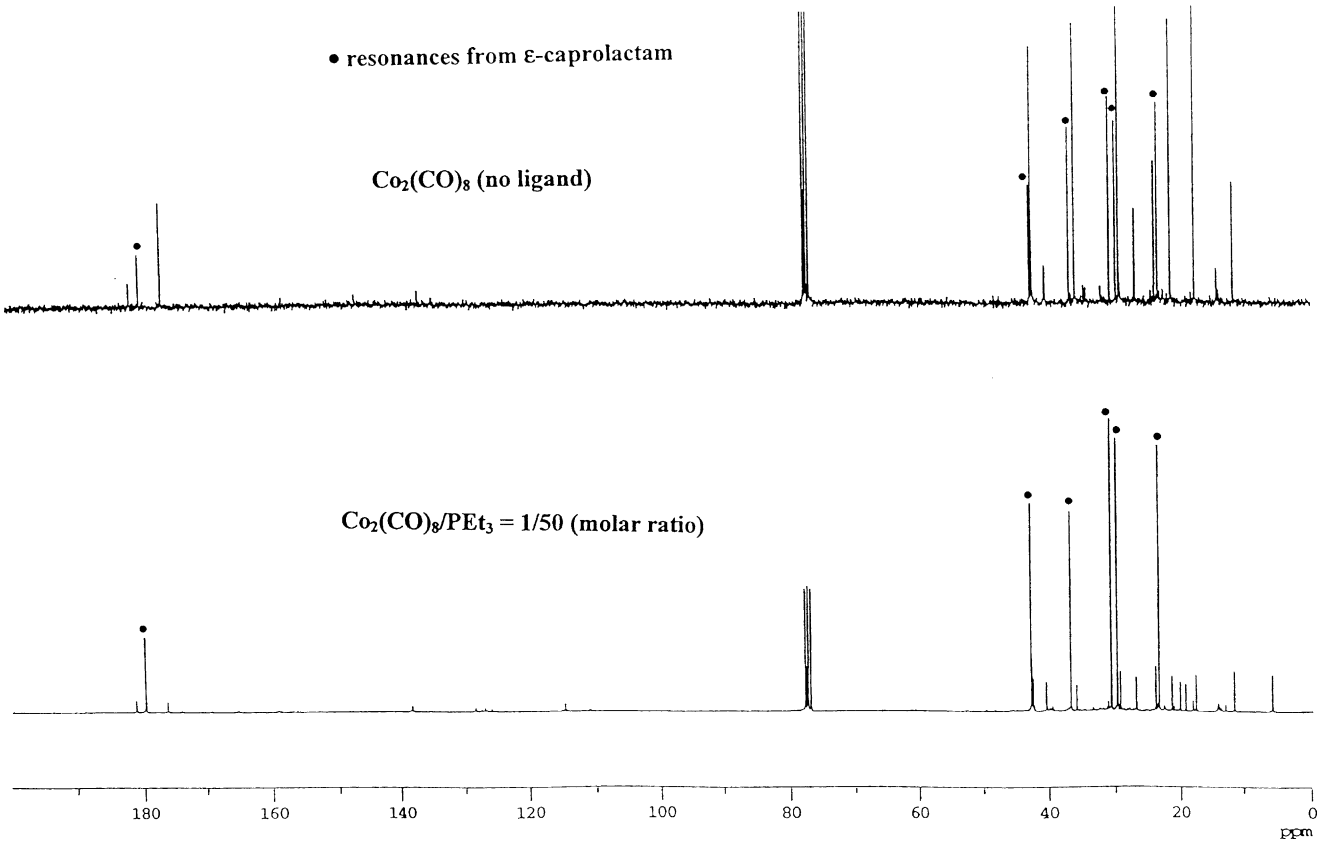


Fig. 2. ^{13}C NMR ($CDCl_3$) spectra of lactams prepared from 4-pentene-1-amine and CO using $Co_2(CO)_8$ (upper) and $Co_2(CO)_8/PEt_3$ (lower, $Co_2(CO)_8/PEt_3$ = 1/50) catalyst.

They all involve the insertion of the olefinic C=C bond into a Co–H bond, followed by CO insertion and intramolecular nucleophilic attack by the amine functionality on the resultant Co-acyl species. ε-Caprolactam results from a 1,2 insertion of the olefin while 3-methyl-2-piperidinone is formed from the opposite 2,1-insertion or from a 1,2-insertion after isomerization of the vinylic C=C bond. Presumably the addition of an excess of the strongly coordinating PEt_3 (and PMe_3) results in a crowded Co-hydride species which favors 1,2 insertion. An interesting question is why P(*t*-Bu)$_3$ and P(*i*-Pr)$_3$ are not equally effective. One possible explanation is that because of their bulkiness, fewer phosphine molecules can coordinate to the cobalt center, such that the *net* crowding around cobalt is actually lower than that obtained in the presence of PEt_3 and PMe_3. The formation of 3-ethyl-2-pyrrolidinone requires an initial C=C bond isomerization prior to olefin insertion. Carbonylation of the resulting internal olefin will also be disfavored when the cobalt species is sterically crowded.

The possibility of C=C bond isomerization under the reaction conditions was tested by heating a mixture of 4-pentene-1-amine and $Co_2(CO)_8$ in chlorobenzene to 170 °C for 4 h in the presence of 200 psi of CO (a lower pressure CO compared to the reactions in Table 1 was used to avoid high conversion of the monomer). At the end of this period, a ^1H NMR spectrum of the reaction mixture exhibited resonances at 5.66–5.20 ppm due to the presence of internal C=C bonds, suggesting partial isomerization.

The effect of solvent on the reaction was briefly examined (Table 2). Similar regioselectivity for ε-caprolactam was observed with all the aromatic solvents tested, whereas use of hexane gave lower regioselectivity.

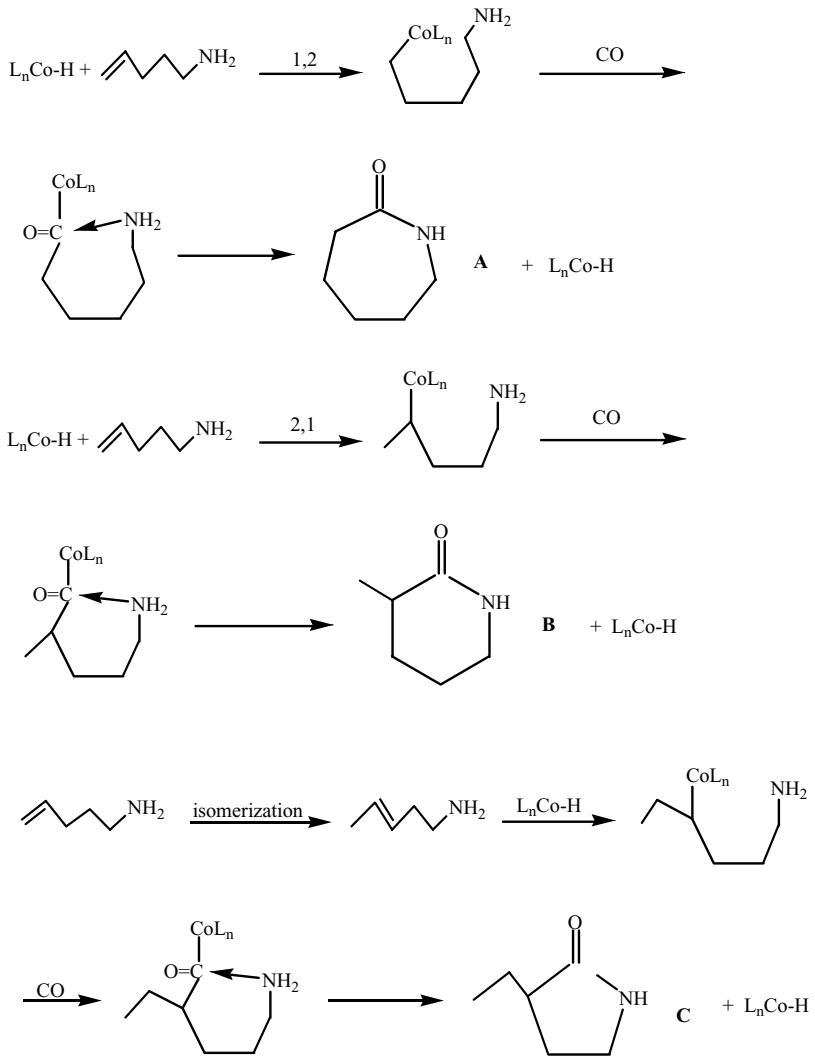
3.2. Catalytic reaction of 3-pentene-1-amine with carbon monoxide

The hydroaminomethylation of butadiene shown in Eq. (1), if successful, is likely to yield a mixture of 4- and

Table 2
Effect of solvent[a]

Run	Solvent	Crude (g)	Distillate (g)	Regioselectivity for ε-caprolactam[c], % (conversion, %)
1[b]	Benzene	0.8	0.5	75.8 (47.5)
2	Toluene	0.6	0.4	75.8 (38.0)
3	Chlorobenzene	0.5	0.4	78.7 (39.5)
4	Hexane	0.5	0.3	59.2 (22.3)

[a] Conditions: $Co_2(CO)_8$, 0.06 g; 4-pentene-1-amine, 0.6 g; Et_3P/Co = 50/1; solvent, 12 ml; CO, 1000 psi, 5 h, 165 °C.
[b] 18 h.
[c] Based on the integration of the carbonyl resonance in the ^{13}C NMR spectra of the mixture.



Scheme 1. Possible mechanisms for the formation of lactam isomers.

3-pentene-1-amine because of facile metal-catalyzed C=C bond isomerization. Consequently, we examined the reactivity of the latter substrate for the formation of ε-caprolactam and our results are summarized in Table 3. The reaction of 3-pentene-1-amine and CO in the presence of $Co_2(CO)_8$, but without added PEt_3, leads to much lower regioselectivity than that observed starting with 4-pentene-1-amine. However, the addition of an excess of PEt_3 results in a dramatic improvement in regioselectivity for ε-caprolactam, eventually becoming comparable with that observed with 4-pentene-1-amine under identical reaction conditions.

Table 3
Reaction of 3-pentene-1-amine with CO in the presence of $Co_2(CO)_8$[a]

Run	$PEt_3/Co_2(CO)_8$ molar ratio	Time (h)	Distillate (g)	Regioselectivity for ε-caprolactam[c], % (conversion, %)
1	0	18	0.5	7.8 (4.9)
2[b]	10	18	0.2	67.5 (16.9)
3[b]	20	18	0.3	63.5 (23.9)
4	50	17	0.4	70.0 (35.1)
5	100	7	0.3	78.1 (29.4)

[a] Conditions: $Co_2(CO)_8$, 0.06 g; 3-pentene1-1-amine, 0.6 g; chlorobenzene, 12 ml; CO, 1000 psi, 165 °C. Crude product was obtained by solvent removal. It was then distilled at 200 °C under vacuum.

[b] $Co_2(CO)_8$, 0.03 g.

[c] Based on the integration of the carbonyl resonance in the ^{13}C NMR spectra of the mixture.

As illustrated in Scheme 1, the only way ε-caprolactam can be formed from 3-pentene-1-amine is by the initial isomerization of the substrate to 4-pentene-1-amine. Indeed, the formation of 4-pentene-1-amine from 3-pentene-1-amine was observed by ^1H NMR spectroscopy when the latter was heated in chlorobenzene at 165 °C for 20 h in the presence of $Co_2(CO)_8/PEt_3$ (ratio, 1:10). The amount of 4-pentene-1-amine in the isomeric mixture under these conditions was only 6.25%. This is not surprising since terminal olefins have significantly lower thermodynamic stability compared to the corresponding internal isomers. However, the isomerization process itself is obviously facile given that the regioselectivity for ε-caprolactam starting

Table 4
Reaction of isomeric pentene-1-amine mixture with CO in the presence of $Co_2(CO)_8$[a]

Run	4-pentene-1-amine (g)	3-pentene-1-amine (g)	PEt_3/Co molar ratio	Yield (g)	Regioselectivity for ε-caprolactam[b], % (conversion, %)
1	0	0.6	0	0.48	7.8 (4.7)
2	0	0.6	50	0.42	70.0 (36.9)
3	0.2	0.4	25	0.30	74.6 (28.1)
4	0.3	0.3	25	0.39	72.5 (35.5)
5	0.4	0.2	25	0.32	69.4 (27.8)
6	0.5	0.1	25	0.41	67.6 (34.7)

[a] Conditions: $Co_2(CO)_8$, 0.06 g; chlorobenzene, 10 ml; CO, 1000 psi, 165 °C, 18 h. Crude product was obtained by solvent removal. It was then distilled at 200 °C under vacuum.
[b] Based on the integration of the carbonyl resonance in the ^{13}C NMR spectra of the mixture.

from 3-pentene-1-amine exceeds 70%. Overall, our observations suggest a rapid equilibration between 3- and 4-pentene-1-amine with the latter reacting faster to form ε-caprolactam through the sterically easier 1,2-insertion of the terminal C=C bond into a Co–H bond.

The similar reactivity and selectivity observed with 3- and 4-pentene-1-amine was further underscored by running reactions with mixtures of the two. As shown in Table 4, the product yield and selectivity remained unchanged through a wide range of 3-pentene-1-amine fraction in the reaction mixture (16.7–100%).

3.3. Conversion and selectivity for lactam isomers using gas chromatographic analysis

Gas chromatographic (GC) analysis of the product mixtures were carried out to complement the ^{13}C NMR studies described above. The three lactam isomers were

Table 5
Reaction of 4-pentene-1-amine with CO in the presence of $Co_2(CO)_8/PEt_3$[a]

Run	Temperature (°C)	PEt_3/Co molar ratio	Time (h)	Conversion (%)	ε-Caprolactam (%)	Methyl isomer (%)	Ethyl isomer (%)	Oligomer+[e] (%)
1[b]	210	0	2	100	6.5	35.3	9.4	48.8
2[b]	190	0	2	100	9.1	44.6	8.4	37.9
3[b]	165	0	2	100	11.6	37.5	6.1	44.8
4[b]	135	0	2	0	0	0	0	0
5	165	0	2	100	16.9	29.9	3.9	49.3
6	165	2	16	100	23.9	23.5	4.2	48.4
7	165	5	16	69.5	20.7	5.7	6.1	37.0
8	165	10	48	92.3	31.2	7.0	8.0	46.1
9	165	25	2	31.5	4.7	0.8	0.6	25.4
10	190	25	16	88.5	23.6	7.6	7.7	49.6
11[c]	165	25	22	95.9	35.2	5.6	6.5	48.6
12[d]	165	25	21	89.7	41.9	7.2	7.1	33.5

[a] Conditions: $Co_2(CO)_8$, 0.02 g; 4-pentene-1-amine, 0.1 g; chlorobenzene, 15 ml; CO, 1500 psi.
[b] CO, 500 psi; 4-pentene-1-amine, 0.2 g.
[c] $Co_2(CO)_8$, 0.15 g; 4-pentene-1-amine, 4 g.
[d] $Co_2(CO)_8$, 0.15 g; 4-pentene-1-amine, 2 g.
[e] Predominantly nylon-6 oligomers (see text).

Table 6
Reaction of 3-pentene-1-amine with CO in the presence of $Co_2(CO)_8/PEt_3$[a]

Run	PEt_3/Co molar ratio	Conversion (%)	ε-Caprolactam (%)	Methyl isomer (%)	Ethyl isomer (%)	Oligomer+[c] (%)
1[b]	0	100	3.5	32.4	12.3	51.8
2	3	100	10.3	15.7	9.8	64.2
3	10	78.4	23.9	4.4	5.2	44.9
4	25	75.0	21.3	3.2	3.9	46.6

[a] Conditions: $Co_2(CO)_8$, 0.02 g; 3-pentene-1-amine, 0.1 g; chlorobenzene, 15 ml; CO, 1500 psi; 165 °C, 18 h.
[b] 5.5 h.
[c] Predominantly nylon-6 oligomers (see text).

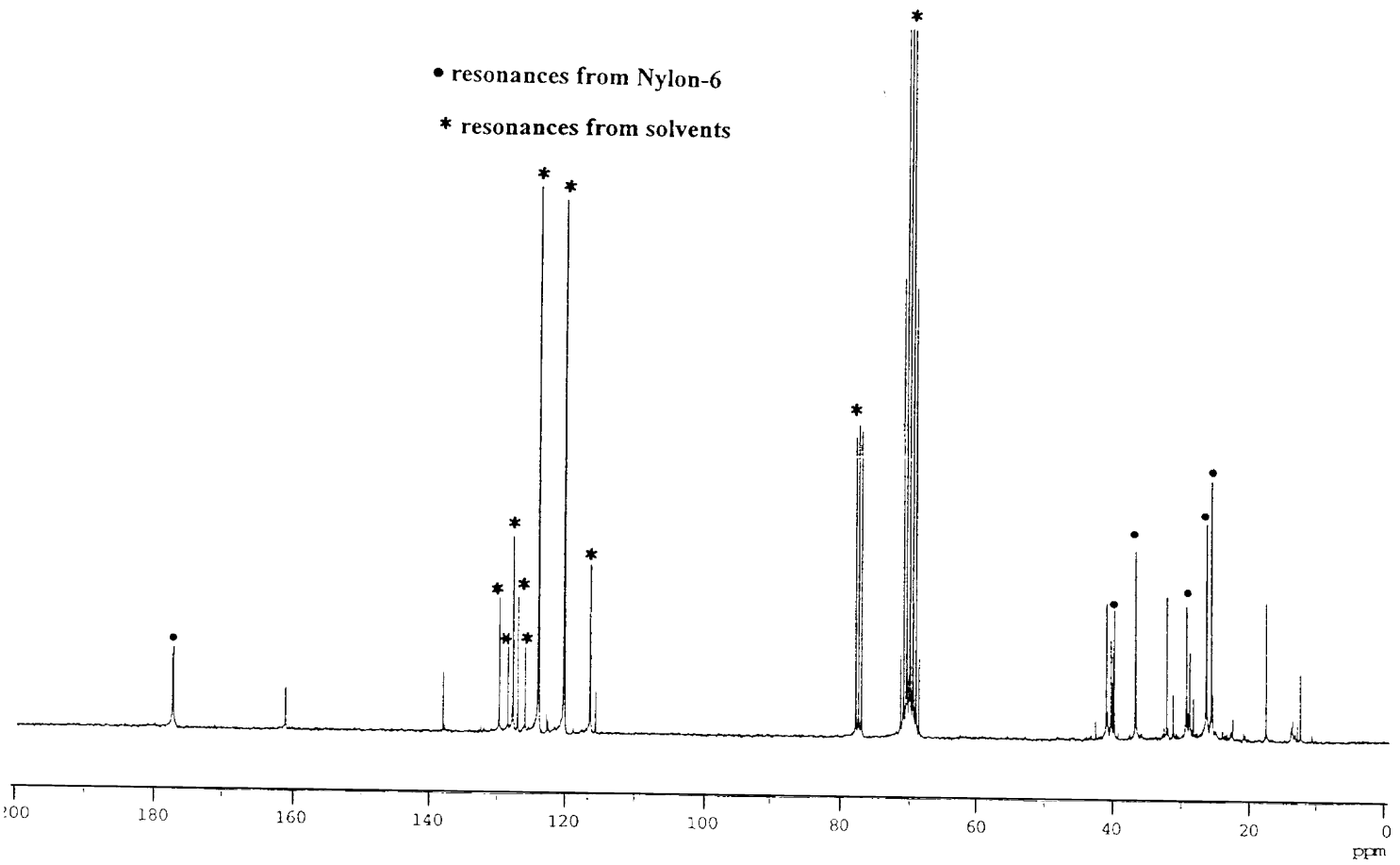


Fig. 3. ^{13}C NMR (*1,1,1,3,3,3*-hexafluoro-2-propanol/$CDCl_3$) spectrum of solid fraction prepared from 4-pentene-1-amine and CO using $Co_2(CO)_8/PEt_3$ (molar ratio, 1:25) catalyst.

found to have the same FID sensitivity and were readily separable by GC. Starting at 100 °C and heating rate of 5 °C/min, the retention times for 3-ethyl-2-piperidinone, 3-methyl-2-pyrrolidinone and ε-caprolactam were found to be 7.91, 8.21, 9.27 min, respectively. In order to quantify the isomeric lactams, a standard linear GC calibration curve was constructed using commercial ε-caprolactam and 1,2-dichlorobenzene as internal reference.

The results obtained for the $Co_2(CO)_8$-catalyzed reaction of 4-pentene-1-amine with CO is summarized in Table 5. In the absence of an added ligand, the conversion of 4-pentene-1-amine was complete within 2 h. However, consistent with the ^{13}C NMR analysis data, the regioselectivity to ε-caprolactam decreased with increasing reaction temperature (runs 1–3). Furthermore, 3-methyl-2-piperidinone was the predominant product under these conditions. When PEt_3 was added as a ligand to the reaction mixture, the reaction proceeded much more slowly. On the other hand, the GC data further confirmed that the conversion to ε-caprolactam is markedly improved by the addition of PEt_3 (5–25 eq.). The relative selectivities to ε-caprolactam, ranging from 64 to 75% of the total volatiles (runs 6–12), are very similar to the selectivities based on ^{13}C NMR data as shown in Table 1. Table 6 summarizes the GC results for the reaction of 3-pentene-1-amine with CO. The selectivities relative to total volatiles for ε-caprolactam were 70% (10 eq. PEt_3) and 75% (25 eq. PEt_3), which are comparable with the ^{13}C NMR-based values of 68% (10 equivalent PEt_3) and 70% (50 eq. PEt_3) as shown in Table 3.

3.4. Analysis of solid residue

As indicated in Tables 1 and 2, the distillation of the crude product mixtures to remove the isomeric lactams invariably leaves behind a considerable amount of solid residue (30–50%). This is also suggested by the GC data where the products other than the three lactams are grouped under "oligomer+" (Tables 5 and 6). Fig. 3 shows a ^{13}C NMR spectrum (solvent: *1,1,1,3,3,3*-hexafluoro-2-propanol + $CDCl_3$) of the solid residue, following the removal of the volatiles, from the reaction of 4-pentene-1-amine with CO using $Co_2(CO)_8/PEt_3$ catalyst (molar ratio, 1:25). The principal resonances, at 177.6, 40.2, 37.1, 29.6, 26.7, 26.0 ppm, correspond to those of nylon-6. The IR spectrum also shows the characteristic amide group absorbance at 1642 cm^{-1}. These observations, combined with the fact that ε-caprolactam is the predominant volatile product, imply that the main component of solid residue is nylon-6 oligomers.

Table 7
Reaction of 4-pentene-1-amine with CO in the presence of $Co_2(CO)_8$ without solvent[a]

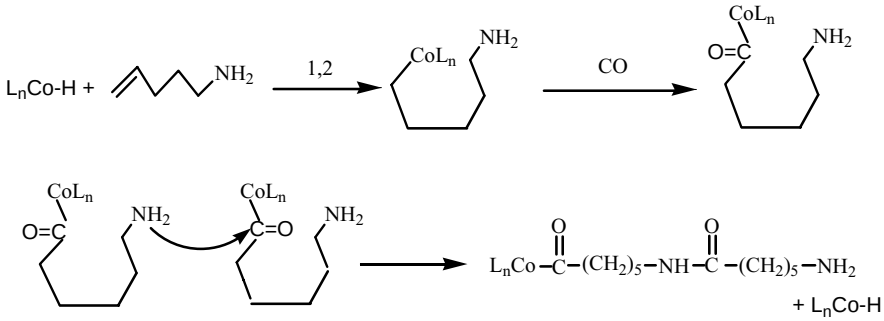
Ligand (molar ratio)	PEt_3 (25/1)
Temperature (°C)	165
Time (h)	10
Solid (g)	3.7
Distillate (g)	1.1
Regioselectivity for ε-caprolactam[b], % (conversion, %)	45.0 (6.2)

[a] Conditions: $Co_2(CO)_8$, 0.12 g; 4-pentene-1-amine, 6.0 g; CO, 1000 psi. Crude product was obtained by monomer removal. It was then distilled at 200 °C under vacuum.

[b] Based on the integration of the carbonyl resonance in the ^{13}C NMR spectra of the mixture.

In order to find out whether the nylon-6 oligomers were formed through ring opening of the isomeric lactams or by an independent pathway, ε-caprolactam and its two isomer were heated to 165 °C for 18 h in chlorobenzene with CO (1000 psi) and $Co_2(CO)_8/PEt_3$ (molar ratio, 1:10). There was no formation of ring opened products. Thus, it appears that the nylon-6 is formed through an independent pathway, presumably an intermolecular version of the lactam forming reaction (see Scheme 2).

Table 7 summarizes the results of a reaction of 4-pentene-1-amine with CO in the absence of a solvent. Two features of the reaction are noteworthy: (a) the amount of solid residue remaining after distillation is much higher (77% of total weight) and (b) the relative amount of ε-caprolactam (45%) in the distillate is much lower than that observed in comparable reactions using a solvent (e.g., entry 12, Table 1). Both of these observations can be rationalized on the basis of the intermolecular reaction being favored over the intramolecular version when the reactant concentration is increased.



Scheme 2. Possible mechanism for the formation of nylon-6 oligomers.

4. Conclusion

We have described the first synthesis of ε-caprolactam and nylon-6 oligomers from 4-pentene-1-amine and/or 3-pentene-1-amine and carbon monoxide using $Co_2(CO)_8$ as catalyst. The results show that the volatile fraction of the product mixture is composed of ε-caprolactam, 3-methyl-2-piperidinone and 3-ethyl-2-pyrrolidinone, while the solid residue mainly consists of nylon-6 oligomers. The addition of excess PEt_3 as ligand can significantly improve the regioselectivity for ε-caprolactam. Using 3-pentene-1-amine as starting material leads to the same results as 4-pentene-1-amine due to rapid C=C bond isomerization.

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