

Clarkson College of Technology, Department of Chemistry

N-Acyl Derivatives of ϵ -Caprolactam

L. Guy Donaruma, Richard P. Scelia, and Steven E. Schonfeld

The preparation and properties of a number of new N-acylcaprolactams are described. These compounds were found to be catalysts for the anionic polymerization of caprolactam.

In connection with work being carried out in our laboratories concerning the anionic polymerization of caprolactam (1), we had occasion to prepare a number of new N-acylcaprolactams. N-Acetylcaprolactam is known to be a catalyst for the fast polymerization of lactams (1). In order to study the effects of substitution in the catalyst molecule on the rate and degree of lactam polymerization, the following N-acylcaprolactams were prepared; N-acetylcaprolactam, N-benzoylcaprolactam, N-propionylcaprolactam, N-butyrylcaprolactam, N-decoylcaprolactam, N-stearylcaprolactam, N-4-methoxybenzoylcaprolactam, N-4-nitrobenzoylcaprolactam, N-4-aminobenzoylcaprolactam and N-4-cyanobenzoylcaprolactam. All the lactams except the N-acetyl (2) and N-benzoyl (3) derivatives are new compounds.

The lactams, with the exception of the aminobenzoyl- and cyanobenzoyl- derivatives were prepared by treating a pyridine solution of caprolactam with the ap-

propriate acyl chloride, or by reaction of the sodium salt of caprolactam with the requisite acyl chloride (see equations 1-2). The known N-acetyl- and N-benzoyl derivatives were prepared by the pyridine method. These two compounds have not previously been prepared in this fashion. The aminobenzoyl- lactam was prepared by catalytic reduction of 4-nitrobenzoylcaprolactam (see equation 3). The cyanobenzoyllactam was synthesized by diazotization of 4-aminobenzoylcaprolactam followed by treatment of the diazonium salt with cuprous cyanide (see equation 4). Surprisingly, fair yields of the cyanobenzoyl lactam were obtained even though it might be expected that the lactam ring would hydrolyze under the reaction conditions employed (4).

The N-acyl lactams prepared were screened as fast polymerization catalysts for caprolactam, and were found to be active. The compounds were also screened for anti-malarial activity, but were found to be inactive (5).

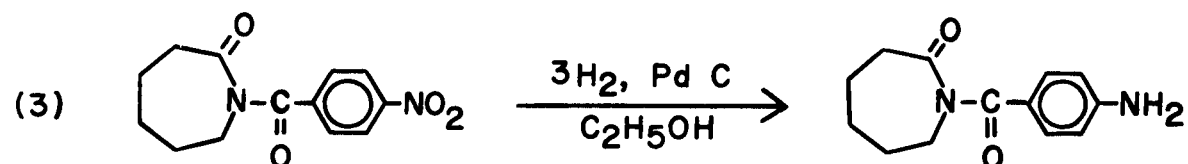
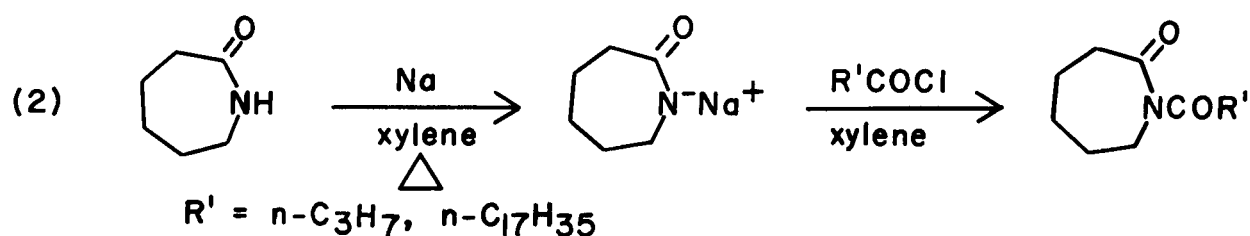
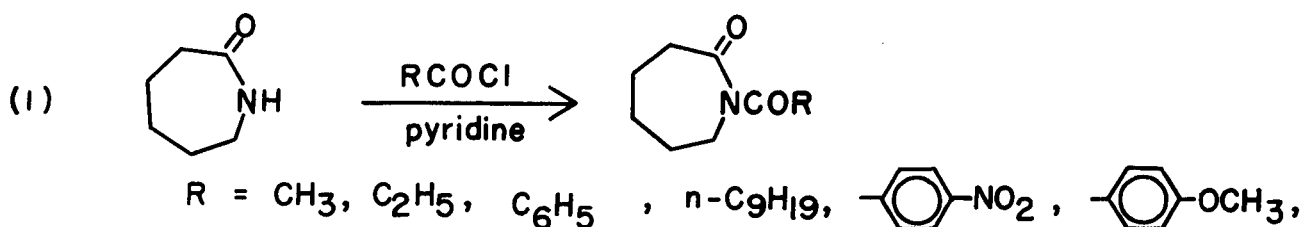
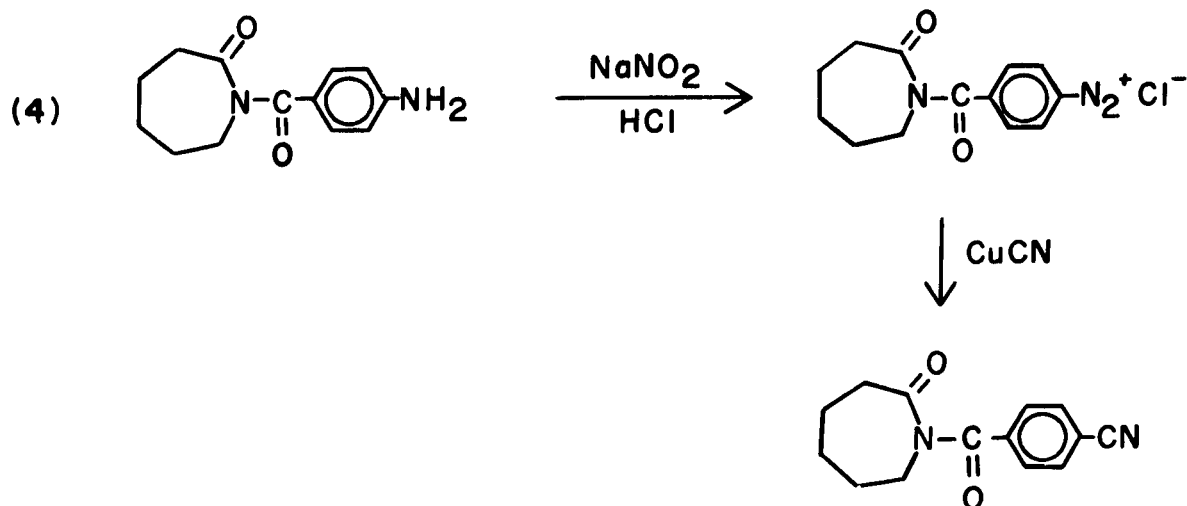


Table I
Properties of Some N-Acylcaprolactams

N-Acyl Group (% Yield)	Physical Constants	Analyses				Infrared Data (a) (cm^{-1})
		%C calcd.	%C found	%H calcd.	%H found	
Acetyl (30%)	b.p. (0.14 mm) 126° $n_D^{25} = 1.4868$ $d_4^{25} = 1.1335$	61.90	61.73	8.38	8.26	740s, 855w, 885s, 970m, 1090w, 1130w, 1165w, 1190m, 1265m, 1335m, 1360w, 1375m, 1390w, 1465w, 1595s, 2850w, 2935w, 3010w.
Propionyl (59%)	b.p. (0.1 mm) 85° $n_D^{25} = 1.4870$	63.80	63.79	8.88	9.24	715m, 850w, 875w, 930w, 975s, 945m, 1100m, 1155s, 1180s, 1265m, 1340m, 1365s, 1385s, 1465s, 1685s, 2840m, 2910s, 2980m.
Butyryl (20%)	b.p. (0.1 mm) 100° $n_D^{25} = 1.4818$ $d_4^{25} = 1.0845$	65.50	65.29	9.35	9.33	845w, 880w, 915w, 965s, 1155s, 1185s, 1205s, 1245w, 1260m, 1290w, 1315w, 1330m, 1350m, 1370m, 1390s, 1440m, 1460m, 1700s, 1870m, 2890m, 2940s, 2970s.
Decoyl (37%)	b.p. (0.1 mm) 175° $n_D^{25} = 1.4740$	71.91	71.51	10.86	11.22	845w, 870w, 920w, 970s, 1030w, 1070m, 1085m, 1140s, 1165s, 1240s, 1320s, 1340m, 1375s, 1410m, 1440s, 1660s, 1780w, 2780s, 2800s.
Stearyl (20%)	m.p. 37-39° b.p. (0.1 mm) 156°	74.80	74.63	11.87	11.94	865w, 970w, 1070w, 1090w, 1140s, 1170m, 1245m, 1320m, 1335w, 1370m, 1455m, 1680s, 2860s, 2925s.
Benzoyl (25%)	m.p. 69°	71.80	71.77	6.92	6.98	695s, 850w, 875w, 920m, 975s, 1080m, 1150s, 1175s, 1275s, 1330s, 1350s, 1380s, 1450s, 1675s, 2860m, 2940s, 3000m.
4-Methoxy- benzoyl (68%)	m.p. 76°	67.90	68.00	6.86	6.46	970s, 1020s, 1160s, 1240s, 1500s, 1590s, 1660s, 1760s, 2930s,
4-Nitrobenzoyl (90%)	m.p. 105°	59.40	60.00	5.34	5.42	855m, 975m, 1145m, 1185m, 1285s, 1360s, 1525s, 1690s, 2940m.
4-Amino- benzoyl (90%)	m.p. 152-3°	67.20	67.12	6.88	7.26	835w, 875w, 915w, 925w, 960w, 970s, 1040w, 1080w, 1140m, 1170s, 1265s, 1295m, 1330m, 1350w, 1380w, 1440w, 1500w, 1620s, 1630s, 1670s, 2880w, 2910w, 2990w.
4-Cyano- benzoyl (37%)	m.p. 114-115°	69.40	69.32	5.78	6.09	845w, 873w, 918w, 970m, 1020w, 1045w, 1080w, 1140m, 1175m, 1260s, 1300m, 1340m, 1345m, 1360m, 1380m, 1435w, 1500w, 1690s, 2220w, 2800w, 2900m, 1980m.

(a) w = weak intensity, m = medium intensity, s = strong intensity.



EXPERIMENTAL

Preparation of N-Acyl Lactams.

Pyridine method.

Benzene (200 ml.), pyridine (90 ml.), caprolactam (11.3 g.; 0.1 mole), and 0.1 M of the acyl chloride were mixed and heated at 90–100° for 30 min. The mixture was then poured into 500 ml. of water and the benzene layer washed with 5% sodium carbonate solution. The benzene solution was dried and the solvent removed. The crude product was recrystallized from ligroin or distilled at reduced pressure.

Sodium salt method.

A suspension of 2.3 g. (0.1 M) of sodium chunks in xylene (200 ml.) was heated to reflux with fast stirring. When the sodium was powdered, the slurry was cooled rapidly to room temperature while the initial stirring rate was maintained. To the suspension of sodium powder was added (11.3 g.; 0.1 mole) of caprolactam. This mixture was stirred at 100° until the sodium had disappeared. The acyl chloride was then added and the mixture stirred until the voluminous lactam salt was replaced in suspension, by a sodium chloride precipitate. The mixture was cooled, filtered, and the solvent allowed to evaporate at room temperature. The residue was recrystallized from ligroin or distilled at reduced pressure.

4-Aminobenzoylcaprolactam.

An ethanol solution of 4-nitrobenzoylcaprolactam (26.2 g.; 0.1 mole of the lactam in 50 ml. of ethanol) was shaken with hydrogen at 50 p.s.i. ga. in the presence of 0.3 g. of 5% Pd-C until the theoretical quantity of hydrogen was absorbed. When the reduction was complete, the solution was filtered and the solvent removed from the filtrate by distillation. The residue was recrystallized from ethyl acetate to yield 21 g. (90%) of 4-aminobenzoylcaprolactam, m.p. 152–153°.

4-Cyanobenzoylcaprolactam.

A mixture of 46.4 g. (0.2 mole) 4-aminobenzoylcaprolactam, 50 ml. of conc. hydrochloric acid and 200 g. of cracked ice was prepared and treated at 0–5° during 15 min. with a solution of 15 g. (0.22 mole) of sodium nitrite dissolved in 50 ml. of water. The mixture was then neutralized to pH 7 with solid sodium carbonate. Enough ice was added to bring the temperature to 0–5°, 100 ml. of benzene was added, and a previously prepared solution of cuprous cyanide (6) was added over a 30 min. period at 0–5° with strong agitation. When the addition was complete, the mixture was allowed to warm to room temperature and then stirred for 2 hrs. The benzene layer was separated and dried. The solvent was removed under vacuum and the residue recrystallized from ethanol. The yield of product melting at 114–115° was 18 g. (37%).

Infrared spectra of all products were taken in chloroform.

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