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## Cocatalysts for the Polymerization of $\epsilon$ -Caprolactam

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**The preparation, characterization, and properties of several new caprolactam anionic polymerization cocatalysts are described. An improved method for the preparation of some of the compounds is discussed. The specific compounds reported are: *N-n*-valeryl-, *N-n*-hexanoyl-, *N-n*-heptanoyl-, *N-n*-octanoyl-, *N-n*-nonanoyl-, *N-n*-decanoyl-, *N-n*-undecanoyl-, *N*-lauryl-, *N-n*-tridecanoyl-, *N*-myristoyl-, *N*-4-methoxybenzoyl-, *N*-4-chlorobenzoyl-, *N*-4-bromobenzoyl-, and *N*-4-iodobenzoylcaprolactams.**

IN A previous publication (3), the preparation of several new *N*-acyl caprolactam derivatives was reported. These compounds were prepared in order to study steric and electronic effects in the catalysis of the fast anionic polymerization of caprolactam (2). To round out the kinetic studies, a larger number of homologous and analogous catalysts were prepared (see Table I). In addition, a more reliable method for the preparation of *N*-4-methoxybenzoylcaprolactam was desired.

In previous work (3) two general types of reaction systems for acylating caprolactam were employed. In one, the lactam was dissolved in dry pyridine and the appropriate acyl chloride was added to the solution. The other method involved treating the sodium salt of caprolactam with the requisite acid chloride. Of the two procedures reported (3), the pyridine method was superior. However, when it was employed to prepare para-substituted *N*-benzoylcaprolactams, the yields of the desired products were low when the substituent was electropositive with respect to the benzene nucleus, and where the substituent was methoxy, the reaction was very erratic; often, none of the desired product was obtained. Indeed, the authors have found that the product reported previously was not pure *N*-4-methoxybenzoyl caprolactam, but a mixture of the acyl lactam and 4-methoxybenzoic acid anhydride (3). Thompson (6) reported similar results upon attempting to acylate amides. Furthermore, the addition of solutions of acyl halides in pyridine to water yields anhydrides (4). Adkins and Thompson (1) have isolated pyridine-acyl halide adducts. Since our product isolation procedure involved addition of

the reaction mixture to water (3), it is not surprising that the major products were anhydrides, if the assumption is made that the pyridine-acyl halide adduct is stable enough so that its rate of reaction with caprolactam is slow. On the other hand, when 4-nitrobenzoyl chloride was employed in an otherwise identical reaction system (3), no anhydride was isolated, and the yield of *N*-4-nitrobenzoylcaprolactam was 90%. Thus, it is possible, by comparing resonance structures of the pyridinium adducts, to assume that the electron-withdrawing nitro group decreased the stability of the adduct.

In view of the preceding assumption, any change in the reaction system which would make the intermediate adduct less stable might favor the desired reaction and suppress anhydride formation. If a Dreiding model of a para-substituted benzoyl pyridinium adduct is fashioned and compared with the model of the analogous adduct, using triethylamine in place of pyridine, it is readily apparent that the triethylamine analog might be less stable because of steric effects which are not present in the pyridinium adduct. As a result, if triethylamine were used in place of pyridine for the preparation of *N*-4-methoxybenzoylcaprolactam, the yield of the *N*-acyllactam might be significantly improved, and the reaction might be easily reproducible. In actual experimentation, this proved to be the case (see Table I).

All *N*-acylcaprolactams prepared were screened for anti-malarial activity (5), but none was found.

The *N*-acylcaprolactams reported all function as cocatalysts for the anionic polymerization of caprolactam.

Table I. Properties of Some N-Acylcaprolactams

Method	N-Acyl Group (% Yield)	Physical Constants			Analyses				
		B.p., ° C.	$n_D^{25}$	$d_{25}$	M.p., ° C.	% C		% H	
						Calcd.	Found	Calcd.	Found
A	n-Valeryl (45%)	130(0.1) <sup>a</sup>	1.4791	1.0133		66.97	66.92	9.71	9.80
A	n-Hexanoyl (26%)	145(0.1)	1.4755	1.0582		68.21	68.32	10.02	10.28
A	n-Heptanoyl (70%)	146(3.0)	1.4777	1.0091		69.29	69.05	10.29	10.48
A	n-Octanoyl (37%)	170(0.1)	1.4719	1.0114		70.25	70.44	10.53	10.58
A	n-Nonanoyl (25%)	171(3.0)	1.4741	0.9964		71.10	71.06	10.74	10.70
A	n-Decanoyl (37%)	175(0.1)	1.4740	0.9627		71.86	71.77	10.93	11.00
A	n-Undecanoyl (40%)	199(3.0)	1.4624	0.9570		72.55	72.51	11.10	11.28
A	Lauryl (42%)	206(0.1)		0.9533		73.17	73.38	11.26	11.37
A	n-Tridecanoyl (29%)	217(0.1)		1.0315		73.73	73.83	11.40	11.51
A	Myristoyl (48%)	225(0.1)		0.9600		74.25	74.02	11.53	11.63
B	4-Methoxybenzoyl (40%)				82-4	68.00	67.68	6.93	6.79
C	4-Chlorobenzoyl (40%)				112-5	62.03	62.22	5.61	5.59
A	4-Bromobenzoyl (15%)				125-7	52.72	52.76	4.76	4.71
B	4-Iodobenzoyl (30%)				130-4	45.50	45.61	4.11	4.24

<sup>a</sup> Figure in parentheses denotes pressure in mm. of Hg.

## EXPERIMENTAL

**Preparation of N-Acyl Lactams.** PYRIDINE METHOD (A). Benzene (200 ml.), pyridine (90 ml.), caprolactam (11.3 grams; 0.1 mole), and the appropriate acyl chloride (0.1 mole) were mixed and heated at 90° to 100° C. for 30 minutes. The mixture was then poured into 500 ml. of water. The benzene layer was separated. The water layer was saturated with sodium chloride and extracted several times with chloroform. The benzene and chloroform solutions were dried (MgSO<sub>4</sub>) and the solvent was removed by distillation. The residue was recrystallized or distilled at reduced pressure.

TRIETHYLAMINE METHOD (B). This was identical to the pyridine method, except that 90 ml. of triethylamine was substituted for 90 ml. of pyridine.

SODIUM SALT METHOD (C). Toluene (600 ml.) and caprolactam (11.3 grams, 0.1 mole) were mixed and heated until 300 ml. of toluene was collected by distillation. To the remaining solution, 2.3 grams (0.1 mole) of powdered sodium was added. The mixture was heated at the reflux with good agitation for 30 minutes. The mixture was cooled to room temperature while the initial stirring rate was maintained, and 0.1 mole of the appropriate acid chloride was added. The mixture was refluxed for 12 hours, cooled, and filtered. The solvent was allowed to evaporate from the

filtrate at room temperature and the residue recrystallized from ligroin or distilled at reduced pressure.

INFRARED SPECTRA. Infrared spectra were taken in both potassium bromide wafers and chloroform solutions on a Perkin-Elmer Model 237 spectrophotometer and were consistent with the assigned structures.

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