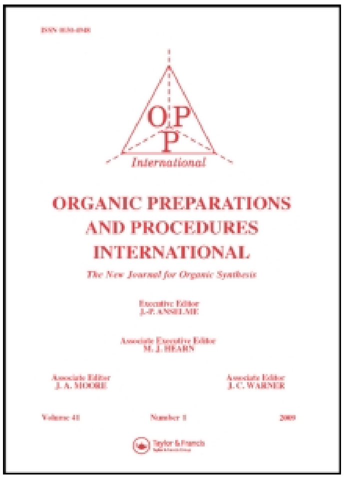


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

SYNTHESIS OF PURE ALKALI METAL LACTAMATES

J. Šebenda[a]; A. Stiborová[a]; L. Lochmann[a]; Z. Bukač[a]
[a] Institute of Macromolecular Chemistry Czechoslovak Academy of Sciences, Prague, CZECHOSLOVAKIA

To cite this Article Šebenda, J. , Stiborová, A. , Lochmann, L. and Bukač, Z.(1980) 'SYNTHESIS OF PURE ALKALI METAL LACTAMATES', Organic Preparations and Procedures International, 12: 5, 289 — 295
To link to this Article: DOI: 10.1080/00304948009356481
URL: http://dx.doi.org/10.1080/00304948009356481

ORGANIC PREPARATIONS AND PROCEDURES INT. 12(5), 289-295 (1980)

SYNTHESIS OF PURE ALKALI METAL LACTAMATES

J. Šebenda*, A. Stiborová, L. Lochmann and Z. Bukač

Institute of Macromolecular Chemistry
Czechoslovak Academy of Sciences
162 06 Prague, CZECHOSLOVAKIA

Dedicated to Professor C.G. Overberger on the Occasion of his 60th Birthday

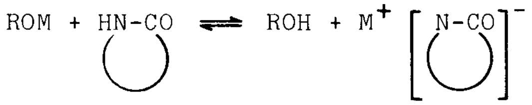
Reproducible results and maximum rates of anionic lactam polymerization can be achieved only if very pure lactam salts are used as initiators.[1] The increasing interest in the polymerization of lactams other than caprolactam has stimulated us to check whether the methods used for the preparation of very pure sodium caprolactamate can also be used for other lactams in general.

So far, pure alkali metal salts of caprolactam for anionic lactam polymerizations have been prepared under defined conditions from alkali metal methoxide and caprolactam.[2] However, preliminary experiments revealed that optimum conditions for the conversion of sodium methoxide into sodium caprolactamate are not suitable for dodecane lactam.

During the preparation of lactamates from alkoxides, it is important that both components should be in solution. For methoxide, this condition can be fulfilled by using a slight excess of lactam which then maintains the reactants in solution.[2]

The same effect can be attained by adding inert solvents, e.g. dimethylsulfoxide.[3] However, a large excess of lactam or solvent retains methanol and renders its complete removal more difficult. Moreover, the excess of lactam may react with the lactamate to yield N-acylated lactam[4] which is an effective activator of anionic lactam polymerization. This reaction may interfere particularly in the case of the five- and six-membered lactams which already polymerize at room temperature.[5]

The disadvantages of methoxides are their poor solubility in aprotic solvents and the rather weak basicity of the alkoxide anion which affects the equilibrium. This equilibrium



can be shifted in favor of lactamate formation by the use of stronger bases (e.g. hydrides or amides) or of solvents in which the initial base is easily soluble but in which the lactamate is not.

Although alkali metal salts of dialkylamines or hexamethyldisilazane are very strong bases (pK_a[6] of dialkylamines □ 36) they cannot be used for our purpose because traces of amines contaminating the product, react with the growth centers and thus interfere with the polymerization process. Salts derived from triphenylmethane (pK_a[6] = 28-33) have also been rejected, because triphenylmethane cannot be removed easily from the reaction products. We focused our attention on alkali metal salts of t-butyl alcohol which can be obtained in a very pure state.[7] Their solubility in aprotic solvents coupled with the insolubility of lactamates allowed the quantitative conversion of alkoxide into pure lactamate.

The Table summarizes some typical optimistic and pessimistic results illustrating that pure lactamates are obtained only under selected conditions.

TABLE

Effect of Reaction Conditions on the Residual Content of t-Butoxide in Alkali Metal Lactamates (Initial Ratio Alkoxide /Lactam = 1.00-1.05)

Lactam Ring Size	Metal	Evaporation Conditions			Alkoxide Content[a] (mol%)	
		T(°C)[b]	p(mm)	t(min.)	A	B
13	Li	120	760	10	0.56	0.10
13	Li	70	1	15	23.0	0.15
13	Na	20	1	15	9.9	0.04
13	Na	120	760	15	0.12	0.02
13	Na[c]	20	760	10	10.9	0.01
13	K[c]	20	1	10	0.85	0.02
11	Na	20	1	10	10.5	0.05
9	Li	20	1	10	3.8	0.02
9	Na	20	1	10	4.9	0.03
8	Li	20	1	10	1.6	0.05
8	Na	20	1	10	1.3	0.02
7	Li	20	1	10	2.2	0.03
7	Na	20	1	10	5.6	0.02
5	Na	20	1	10	1.7	0.03
4[d]	Na	20	1	10	2.4[e]	0.02[e]

a) A is heated 15 min at 120°/1 mm after evaporation and B is added 5 ml cyclohexane, evaporated and then heated 15 min at 120°/1 mm after evaporation. b) Bath temperature. c) Alkoxide solution in THF. d) 3,3-Dibutyl-2-azetidinone. e) The salt was heated at 25° (instead at 120°).

The most difficult case represent lithium and sodium salts of the thirteen-membered lactam. Although dodecanelactam is the most acidic among the lactams investigated, its pK_a value still differs from that of t-butyl alcohol. Slow distillation of t-butyl alcohol and solvents as well as successive additions and evaporation of non-polar solvents proved to be useful.

It has to be stressed that the results obtained refer to ~0.5 mmol quantities. The purity of lactamates may be influenced by different approaches by individual operators as well as by slight modifications of the equipment. It is recommended that the alkoxide content be checked by gas chromatography.

EXPERIMENTAL

All operations with dry solvents and alkali metal salts were performed under dry argon (less than 4 ppm H_2O). The solvents and solutions were transferred with inert gas pressure by means of stainless steel capillaries. All solvents were predried by reflux with $LiAlH_4$ and distillation followed finally by reflux (benzene with sodium and benzophenone, THF with sodium and anthracene, cyclohexane with $LiAlH_4$). Solutions of lithium, sodium and potassium t-butoxides in THF or cyclohexane (0.1-0.2 M) were stored under dry argon.

Preparation of Alkali Metal Lactamates. - A precisely weighed amount of lactam (~0.5 mmol) was dried 12 hrs at 25°/1 mm in the apparatus shown in Fig. 1. After releasing the vacuum to an inert gas, flask 3 was connected to the ground joint of the buret (Fig. 2) a measured volume of the t-butoxide solution was added with stirring in a stream of argon (the ratio lactam/t-butoxide = 1.00-1.10). After connecting flask 3 with the upper part 5, the solution was immersed in a thermostatted bath and evaporated with stirring. During evaporation under the conditions given in the Table, a slow stream of dry argon was passed through stopcock 1, while stopcock 2 was connected to a vacuum source. The level of the thermostatted bath was maintained 1 cm higher than the level of the reaction mixture. After evaporation to dryness, either a 5-ml portion of cyclohexane was added or the dry residue was heated for 15 min at 120°/1 mm;during this period flask 3 was flushed 10 times with argon; the lactamate of the four-membered lactam was heated at 25° only.

Determination of *t*-Butoxide in Lactamates.- To the reaction product was added 2 ml of a chlorobenzene solution of acetic acid (22.80 mg/ml), containing toluene (0.385 mg/ml) as an internal standard for gas chromatography. After thorough homogenization and filtration the content of *tert*-butyl alcohol was determined by gas chromatography on a Perkin-Elmer F 11 instrument; 1 μl was injected into a 2 m column packed with 10% of silicone rubber (XE-60) on Chromosorb W (80-100 mesh) at a column temperature of 60° and an injection port temperature of 230°. Under the given conditions, a lower limit of 0.01 mol% of alcohol could be detected.

REFERENCES

1. E. Šittler and J. Šebenda, Coll.Czech.Chem.Commun., 33, 3182 (1968).
2. P. Čefelín and J. Šebenda, Coll.Czech.Chem.Commun., 26, 3028 (1961).
3. P. A. Tierney, Fr.Pat. 1,554,779 (24.1.1969); CA 71, 39622 (1969).
4. J. Šebenda, J.Macromol.Sci.-Chem. A6, 1152 (1972).

5. S. Barzakay, M. Levy, and D. Vofsi, J.Polym.Sci. A-1, 4 2211 (1966).

6. H. O. House, Modern Synthetic Reactions, W. A. Benjamin, Inc. 1972, Menlo Park, California, p.494.

7. L. Lochmann, J. Čoupek, and D. Lím, Coll.Czech.Chem.Commun., 35, 733 (1970).

8. A. Caillet, D. Bauer, G. Froyer, and H. Sekiguchi, C.R.Acad. Sci. Paris 277, Ser.C, 1211 (1973).

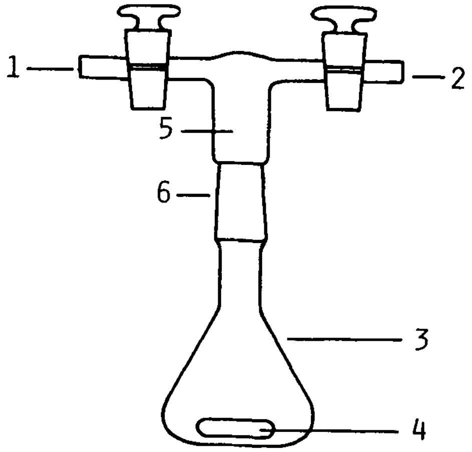


FIG. 1

Reactor for alkali metal salts: 1 inert gas inlet, 2 inert gas outlet, 3 reaction flask (20 ml), 4 Teflon or glass coated magnetic stirring bar, 5 upper part of reactor, 6 ground joint 14/23.

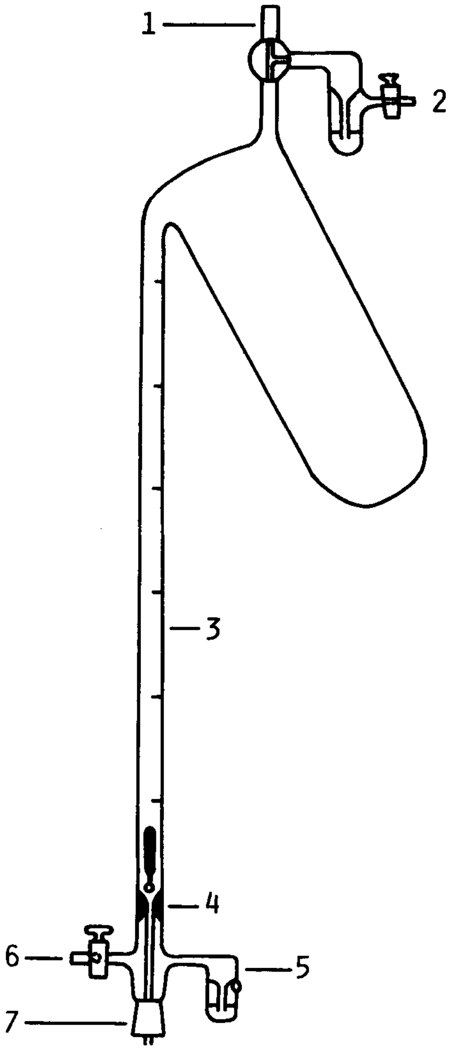


FIG. 2

Automatic Buret: 1 and 6 inlets of inert gas, 2 and 5 outlets of inert gas (through a paraffin oil bubbler), 3 buret (5 ml) with 0.02 ml divisions, 4 magnetic valve, 7 ground joint 14/23.

(Received March 3, 1980; in revised form August 29, 1980)