

TITLE

SYNTHESIS OF UNSATURATED NITRILES FROM LACTONES

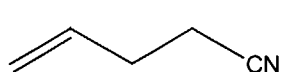
FIELD OF INVENTION

5 The synthesis of unsaturated nitriles from lactone and ammonia is described.

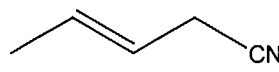
TECHNICAL BACKGROUND

Unsaturated nitriles are valuable precursors and monomers in many processes, such as the production of polyamide intermediates. One unsaturated nitrile, pentenenitrile (PN), is particularly important, as it is a precursor for the production of the nylon intermediates adiponitrile (by further hydrocyanation), adipic acid and caprolactam (by carbonylation to 5-cyanovaleric acid). It is typically produced via the hydrocyanation of butadiene. This process, however, produces a broad distribution of the various isomers of pentenenitrile:

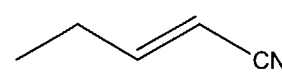
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4-pentenenitrile



3-pentenenitrile



2-pentenenitrile

Although each pentenenitrile isomer can be converted to another isomer, a simple process that produces the desired isomer as the major product would have many advantages.

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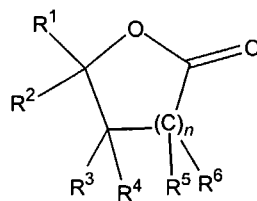
Lactones are a common and inexpensive feedstock for many processes, and many are commercially available. The reaction of ammonia with lactones typically produces a lactam or hydroxynitrile (U.S. Patent No. 3,775,431, U.S. Patent No. 3,560,550). It has been shown (U.S. Patent No. 3,043,860) that the reaction of unsubstituted caprolactone with anhydrous ammonia in the presence of acid-activated alumina catalysts produced the unsaturated nitrile with a terminal olefin. It has also been shown (U.S. Patent No. 4,904,812) that acidic zeolites can catalyze the reaction of unsubstituted caprolactone and valerolactone to produce a broad distribution of the corresponding unsaturated nitriles.

30

Magnesium silicate has been used as a catalyst in the reaction of lactams with ammonia to produce the aminonitrile (U.S. Patent No. 3,578, 558) and in the reaction of butyrolactone with ammonia to produce 2-pyrrolidone (U.S. Patent No. 4,824,967).

SUMMARY OF THE INVENTION

Disclosed is a process for the preparation of one or more unsaturated nitriles comprising:



Formula I

with ammonia in the presence of a heterogeneous base catalyst to form a reaction mixture containing the corresponding unsaturated nitriles wherein:

$n=0-11$;

- 10 R^1 , R^2 , R^3 , R^4 , R^5 and R^6 taken independently are hydrogen, hydrocarbyl or substituted hydrocarbyl, C1 to C18 unsubstituted or substituted alkyl, unsubstituted or substituted alkenyl, unsubstituted or substituted cycloalkyl, unsubstituted or substituted cycloalkyl containing at least one heteroatom, unsubstituted or substituted aryl, and unsubstituted or substituted heteroaryl.

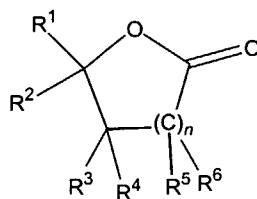
The base catalyst is selected from the group consisting of a metal silicate, a metal carbonate, a metal oxide, a metal hydroxide, a metal phosphate, a metal aluminate and a mixture thereof.

- 15 In a preferred embodiment, the base catalyst is a metal silicate; metal oxide or a metal carbonate, or a mixture thereof; more preferred is where the base catalyst is a Group 1, Group 2 or rare earth silicate, oxide or carbonate, or a mixture thereof. Preferred metals are Ba, Cs, Rb and Mg. The catalyst is optionally supported on a suitable support.

- 20 A preferred embodiment is where $n=1-7$ and R^1 , R^2 , R^3 , R^4 , R^5 and R^6 taken independently are hydrogen or alkyl. More preferred is where $n=1$, R^1 is methyl and R^2 , R^3 , R^4 , R^5 and R^6 are hydrogen.

Preferably the unsaturated nitriles are comprised of at least 20% 4-pentenitrile.

- 25 Also disclosed is a process for the preparation of one or more unsaturated nitriles comprising: contacting lactones of Formula I



Formula I

with ammonia in the presence of a heterogeneous base catalyst to form a reaction mixture containing the corresponding unsaturated nitriles wherein:

$n=1-2$;

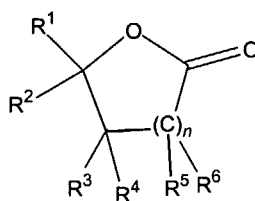
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R1 is a methyl;

R2, R3, R4, R4 and R6 taken independently are hydrogen, or C1-C18 unsubstituted or substituted alkyl.

DETAILED DESCRIPTION OF THE INVENTION

10 The present invention provides a process for the preparation of one or more unsaturated nitriles comprising contacting lactones of Formula I



Formula I

15 with ammonia in the presence of a heterogeneous base catalyst to form a reaction mixture containing the corresponding unsaturated nitriles wherein $n=0-11$; R1, R2, R3, R4, R4 and R6 taken independently are hydrogen, hydrocarbyl or substituted hydrocarbyl, C₁-C₁₈ unsubstituted or substituted alkyl, unsubstituted or substituted alkenyl, unsubstituted or substituted cycloalkyl, unsubstituted or substituted cycloalkyl containing at least one heteroatom, unsubstituted or substituted aryl, and unsubstituted or substituted heteroaryl.

20 By "unsaturated nitriles" it is meant a compound containing at least one double bond and at least one nitrile (-CN) group.

"Alkyl" means an alkyl group up to and including 12 carbons.

25 Common examples of such alkyl groups include methyl, ethyl, propyl, isopropyl, butyl, s-butyl, isobutyl, pentyl, neopentyl, hexyl, heptyl, isoheptyl, 2-ethylhexyl, cyclohexyl and octyl.

"Aryl" means a group defined as a monovalent radical formed conceptually by removal of a hydrogen atom from a hydrocarbon that is

structurally composed entirely of one or more benzene rings. Common examples of such hydrocarbons include benzene, biphenyl, terphenyl, naphthalene, phenyl naphthalene, and naphthylbenzene.

“Heteroaryl” refers to unsaturated rings of 5 or 6 atoms containing one or two O and S atoms and/or one to four N atoms provided that the total number of hetero atoms in the ring is 4 or less, or bicyclic rings wherein the five or six membered ring containing O, S, and N atoms as defined above is fused to a benzene or pyridyl ring. Common examples are furan and thiophene.

“Hydrocarbyl” means a monovalent group containing only carbon and hydrogen, and may be chiral or achiral. Unless otherwise stated, it is preferred that hydrocarbyl (and substituted hydrocarbyl) groups contain 1 to 30 carbon atoms.

“Substituted” means a group that is substituted and contains one or more substituent groups that do not cause the compound to be unstable or unsuitable for the use or reaction intended. Substituent groups which are generally useful include nitrile, ether, ester, halo, amino (including primary, secondary and tertiary amino), hydroxy, oxo, vinylidene or substituted vinylidene, silyl or substituted silyl, nitro, nitroso, sulfinyl, sulfonyl, sulfonic acid alkali metal salt, boranyl or substituted boranyl, and thioether.

The ammonia used in the process can be in any form and includes NH_3 and NH_4OH .

Preferably, $n=1-7$; R^1 , R^2 , R^3 , R^4 , R^4 and R^6 taken independently are hydrogen and alkyl groups. More preferably, $n=1$, R^1 is methyl, and R^2 , R^3 , R^4 , R^4 and R^6 are hydrogen.

The unsaturated nitriles that are produced by the instant process can be one particular compound of a mixture of isomers. For example, when $n=1$, R^1 is methyl, and R^2 , R^3 , R^4 , R^4 and R^6 are hydrogen, the lactone is gamma-valerolactone (also known as gamma-methylbutyrolactone, gamma-pentalactone, and 4-methylbutyrolactone) then one or more of the following unsaturated nitriles could be produced:

	cis-2-pentenitrile	trans-2-pentenitrile
	cis-3-pentenitrile	trans-3-pentenitrile
	4-pentenitrile	

A preferred process is where the lactone is gamma-valerolactone and more than 20% of the unsaturated nitriles produced are 4-pentenitrile.

"Heterogeneous catalyst" refers to a catalyst that operates on reactions taking place on surfaces where the reacting species are held on the surface of the catalyst by adsorption. Typically heterogeneous catalysts are not in solution and do not exist in the same phase (solid,
5 liquid or gas) as the reactants.

A suitable base catalyst can be defined either as a substance which has the ability to accept protons as defined by Brönsted, or as a substance which has an unshared electron pair with which it can form a covalent bond with an atom, molecule or ion as defined by Lewis. A further
10 definition of base catalysts and how to determine if a particular substance is base is explained in Tanabe, K., *Catalysis : Science and Technology*, Vol. 2, pg 232-273, ed. Anderson, J. and Boudart, M., Springer-Verlag, N.Y., 1981.

Examples of suitable base catalysts include, but are not limited to,
15 metal oxides, hydroxides, carbonates, silicates, phosphates, aluminates and mixtures thereof. Preferred are metal oxides, carbonates, and silicates. More preferred are Group 1, Group 2, and rare earth oxides, carbonates, and silicates. The catalysts of the invention can be obtained already prepared from manufacturers, or they can be prepared from
20 suitable starting materials using methods known in the art.

The catalysts employed herein may be used as powders, granules, or other particulate forms, or may be supported on an essentially inert support as is common in the art of catalysis. Selection of an optimal average particle size for the catalyst will depend upon such process
25 parameters as reactor residence time and desired reactor flow rates

Suitable supports include but are not limited to alumina, titania, silica, zirconia, zeolites, carbon, clays, or mixtures thereof. Any method known in the art to prepare the supported catalyst can be used. The support can be neutral, acidic or basic, as long as the surface of the
30 catalyst/support combination is basic. Preferred supports are those which are neutral. Commonly used techniques for treatment of supports with metal catalysts can be found in B. C. Gates, *Heterogeneous Catalysis*, Vol. 2, pp. 1-29, Ed. B. L. Shapiro, Texas A & M University Press, College Station, TX, 1984.

35 The catalysts of the present invention may further comprise catalyst additives and promoters, which will enhance the efficiency of the catalyst. Use of these materials are common and well known in the art (see for

example, Kirk-Othmer Encyclopedia of Chemical Technology, Howe-Grant Ed., Vol. 5, pp 326-346, (1993), John Wiley & Sons, New York and Ullmann's Encyclopedia of Industrial Chemistry, Vol. A5, Gerhartz et al., Eds., pp. 337-346, (1986), VCH Publishers, New York). The relative percentages of the catalyst promoter may vary. Useful amounts of promoter can be from about 0.01% to about 5.00% by weight of catalyst.

A preferred catalyst is a metal silicate. By "silicate" is meant an anion consisting of Si, O, and optionally H. These include but are not limited to SiO_3^{2-} , $\text{Si}_2\text{O}_7^{6-}$, and SiO_4^{4-} , and their various hydrated forms. More preferred are silicate salts of Group 2 metals; most preferred is magnesium silicate.

One particularly preferred catalyst is Magnesol®, a hydrated, synthetic, amorphous form of magnesium silicate produced by The Dallas Group of America, Inc.

Another preferred catalyst is an oxide, carbonate, or mixture thereof of a Group 1, 2, or rare earth metal, optionally supported on a suitable support. One method to prepare these is to dissolve a metal acetate salt in water. A support such as silica is wet with the solution, then calcined. This oxidizes the acetate to an oxide, carbonate, or a mixture thereof. More preferred is where the metal is from Group 1 or 2, most preferred is where the metal is Ba, Cs, or Rb.

The process is preferably in the vapor phase. The process can be performed in any suitable reactor such as but limited to a pulse, fluidized bed, fixed bed, steady state riser reactor, and a recirculating solids reactor system. The reaction temperature is preferably about 250°C to about 500°C, more preferably about 350°C to about 500°C, most preferably 400°C. The process is preferably performed at pressures of ambient to about 1000 psi (6.9 MPa).

It will be appreciated that the selectivities and yields of product may be enhanced by additional contact with the catalyst. For example, yields and selectivities may be increase where the reactor effluent containing a mixture of reactant and product may be passed one or more times over the catalyst under the reaction conditions to enhance the conversion of reactant to product.

The process may be performed in one step, or in two steps wherein an intermediate such as the hydroxyamide, pyrrolidone, or lactam is produced, which is then further reacted to the unsaturated nitrile.

The process of the instant invention may additionally comprise the recovery or isolation of one or more of the unsaturated nitriles. This can be done by any method known in the art, such as distillation, decantation, recrystallization, or extraction.

5 The process of the instant invention may also additionally comprise the further conversion of one or more of the unsaturated nitriles to other useful compounds, especially the conversion of pentenenitrile to caprolactam or adiponitrile. This conversion can be done by any method known in the art (see for example, Kirk-Othmer Encyclopedia of Chemical
10 Technology, Howe-Grant Ed., Vol. 19, pp 489-491, (1993), John Wiley & Sons, New York and Ullmann's Encyclopedia of Industrial Chemistry, Vol. A5, Gerhartz et al., Eds., pp. 44-46, (1986), VCH Publishers, New York).

15 **Materials and Methods**

The following abbreviations are used herein:

20	3APN	3-aminopentanitrile
	4HPAm	4-hydroxypentamide
	4-PN	4-pentenitrile
	c-2PN	cis-2-pentenitrile
	c-3PN	cis-3-pentenitrile
	cc	cubic centimeters
25	FID	flame ionization detector
	GC	gas chromatograph
	ID	inner diameter
	MePYR	methyl pyrrolidone
	OD	outer diameter
30	PN	pentenenitriles
	Rctr	reaction
	t-2PN	trans-2-pentenitrile
	t-3PN	trans-3-pentenitrile
	Temp	temperature
	TOS	time on stream
	VL	gamma-valerolactone

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The following procedure is illustrative of the procedure used to prepare base catalysts on silica supports. All metals were used as the acetate salts.

Procedure for preparation of 20%Cs on Silica

40 Cesium acetate (2.91 g, Aldrich, Milwaukee, WI) was dissolved in H₂O (14 ml) and the solution was added dropwise into silica (8.07 g, W.R. Grace, Columbia, MD, Grade 55, 12 x 20 mesh). The mixture was allowed

to stand at room temperature for 2hr and then the mixture was transferred into an alumina boat. The boat was placed in a horizontal quartz tube with purged with air. The supported catalyst was heated at 120°C for 4hr and then at 450°C for 16 hours in a stream of air. The sample was then cooled to yield 9.87g of 20%Cs on silica.

EXAMPLES

8 cc of a 50% by weight (molar ratio = 20:1/NH₃:VL) of an aqueous solution of gamma-valerolactone and ammonia (metered through a mass flow controller at 74.8 cc/minute) was passed into a ½" OD Inconel tubular reactor heated by a tube furnace at a rate of 2 cc/hour. The reactor contained 8 cc of Magnesol® magnesium silicate catalyst that had been pressed into 20-30 mesh size pellets. The reactor effluent was quenched in a cold solution of methanol (-10°C). The sample was then analyzed on a HP 5890 GC using a FID (with a RTX-1701 column 30 m x 0.53 mm ID from Restek). The detector was held at 50°C for 3 minutes then heated to 165°C at a rate of 30°C/min and held for 8 minutes. The selectivity and conversion were then calculated based on normalized area percents. The results are shown in Table 1 below. The table includes the percent VL converted, the % selectivity to total pentenenitriles, and the distribution of the various pentenenitrile isomers in the total pentenenitriles.

TABLE 1

Ex.	Catalyst	Rctr Temp (°C)	TOS (hrs)	% VL Conv.	% PN Sel.	% MePYR Sel.	% 4HPA m Sel.	% 3APN Sel.	% c-2PN Dist.	% 4-PN Dist.	% t-2PN Dist.	% t-3PN Dist.	% c-3PN Dist.
1	Magnesol®	250	0.75	16.3	0.0	18.0	32.4	0.0	0.0	0.0	0.0	0.0	0.0
2	Magnesol®	300	0.5	43.6	9.7	38.3	21.4	12.8	7.7	59.1	8.6	19.6	5.0
3	Magnesol®	350	1	81.6	41.2	32.2	5.5	6.6	10.6	53.5	10.2	19.2	6.5
4	Magnesol®	400	1	99.8	66.8	21.2	0.0	0.0	13.2	56.6	10.6	13.5	6.2
5	Magnesol®	450	0.5	100.0	89.5	0.0	0.0	0.0	18.4	43.5	11.9	18.8	7.4
6	Magnesol®	500	0.75	99.8	75.6	1.0	0.0	0.2	17.8	40.8	14.4	18.5	8.4
7	15%Ba on silica	300	1	14.6	4.9	11.6	38.8	23.0	2.8	81.7	0.0	12.8	2.7
8	15%Ba on silica	350	1	59.5	19.0	3.3	44.4	13.0	6.4	74.8	5.8	9.6	3.3
9	15%Ba on silica	400	1	80.0	72.9	2.9	6.4	3.6	12.2	58.6	9.7	13.6	5.9
10	15%Ba on silica	450	1	99.8	64.4	0.0	0.0	1.0	18.9	39.7	13.7	19.4	8.3
11	20%Cs on silica	300	1	53.8	10.8	0.0	77.2	2.4	7.2	77.2	4.7	8.4	2.4
12	20%Cs on silica	350	1	47.9	41.3	0.8	42.2	2.5	19.0	42.8	11.9	19.8	6.5

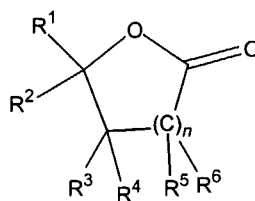
Ex.	Catalyst	Rctr Temp (°C)	TOS (hrs)	% VL Conv.	% PN Sel.	% MePYR Sel.	% 4HPA m Sel.	% 3APN Sel.	% c-2PN Dist.	% 4-PN Dist.	% t-2PN Dist.	% t-3PN Dist.	% c-3PN Dist.
13	20%Cs on silica	400	1	99.7	17.5	0.0	0.0	0.0	19.4	32.9	17.5	20.4	9.8
14	20%Cs on silica	450	1	99.6	22.8	0.0	0.0	0.8	16.9	35.1	15.2	21.9	10.8
15	20%Rb on silica	350	1	14.0	23.1	0.0	32.0	5.5	21.8	32.2	13.8	24.2	8.0
16	20%Rb on silica	400	1	51.4	81.9	0.0	5.0	0.8	26.6	19.6	16.8	27.1	9.9
17	20%Rb on silica	500	1	99.3	27.9	0.0	0.0	0.2	14.7	36.9	15.0	22.3	11.2

CLAIMS

What is claimed is:

1. A process for the preparation of one or more unsaturated nitriles comprising: contacting lactones of Formula I

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Formula I

with ammonia in the presence of a heterogeneous base catalyst to form a reaction mixture containing the corresponding unsaturated nitriles wherein:

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$n=0-11$;

R^1 , R^2 , R^3 , R^4 , R^5 and R^6 taken independently are hydrogen, hydrocarbyl or substituted hydrocarbyl, C1-C18 unsubstituted or substituted alkyl, unsubstituted or substituted alkenyl, unsubstituted or substituted cycloalkyl, unsubstituted or substituted cycloalkyl containing at least one heteroatom, unsubstituted or substituted aryl, and unsubstituted or substituted heteroaryl.

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2. The process as in Claim 1 wherein the base catalyst is selected from the group consisting of a metal silicate, a metal carbonate, a metal oxide, a metal hydroxide, a metal phosphate, a metal aluminate and a mixture thereof.

3. The process as in Claim 2 wherein the base catalyst is selected from the group consisting of a Group 1, Group 2 or rare earth silicate, a Group 1, Group 2 or rare earth oxide, a Group 1, Group 2 or rare earth carbonate and a mixture thereof.

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4. The process as in Claim 3 wherein the base catalyst is a Group 1, Group 2 or rare earth silicate.

5. The process as in Claim 3 wherein the base catalyst is a Group 1 or Group 2 or rare earth oxide.

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6. The process as in Claim 3 wherein the base catalyst is a Group 1 or Group 2 or a rare earth carbonate.

7. The process as in Claim 1 wherein the catalyst is supported on a suitable support.

8. The process as in Claim 1 wherein $n=1-7$ and R^1 , R^2 , R^3 , R^4 , R^5 and R^6 taken independently are hydrogen or alkyl.

9. The process as in Claim 7 wherein $n=1$, R^1 is methyl and R^2 , R^3 , R^4 , R^5 and R^6 are hydrogen.

5 10. The process as in Claim 7 wherein the unsaturated nitriles is comprised of at least 20% 4-pentenitrile.

11. The process as in Claim 1 wherein the temperature is at least about 250°C.

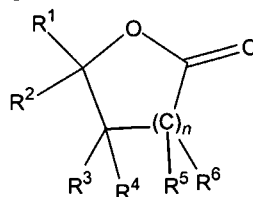
10 12. The process as in Claim 10 wherein the temperature is at least about 350°C.

13. The process as in Claim 1 wherein the process is run in the vapor phase.

14. The process as in Claim 1 further comprising the recovery of one or more of the unsaturated nitriles.

15 15. The process as in Claim 1 further comprising the conversion of one or more of the unsaturated nitriles to caprolactam or adiponitrile.

16. A process for the preparation of one or more unsaturated nitriles comprising: contacting lactones of Formula I



Formula I

20 with ammonia in the presence of a heterogeneous base catalyst to form a reaction mixture containing the corresponding unsaturated nitriles wherein:

$n=1-2$;

R^1 is a methyl;

25 R^2 , R^3 , R^4 , R^5 and R^6 taken independently are hydrogen, or C1-C18 unsubstituted or substituted alkyl.

17. The process as in Claim 16 wherein the base catalyst is selected from the group consisting of a metal silicate, a metal carbonate, a metal oxide, a metal hydroxide, a metal phosphate, a metal aluminate
30 and a mixture thereof.

18. The process as in Claim 16 wherein the base catalyst is selected from the group consisting of a Group 1, Group 2 or rare earth

silicate, Group 1, Group 2 or rare earth oxide and a Group 1, Group 2 or rare earth carbonate.

19. The process as in Claim 18 wherein the base catalyst is a Group 1, Group 2 or rare earth silicate.

5 20. The process as in Claim 18 wherein the base catalyst is a Group 1 or Group 2 or rare earth oxide.

21. The process as in Claim 18 wherein the base catalyst is a Group 1 or Group 2 or rare earth carbonate.

10 22. The process as in Claim 16 wherein the catalyst is supported on a suitable support.

23. The process as in Claim 22 wherein $n=1$, R^1 is methyl and R^2 , R^3 , R^4 , R^4 and R^6 are hydrogen.

24. The process as in Claim 23 wherein the unsaturated nitriles are comprised of at least 20% 4-pentenenitrile.

15 25. The process as in Claim 16 wherein the temperature is at least about 250°C.

26. The process as in Claim 25 wherein the temperature is at least about 350°C.

20 27. The process as in Claim 16 wherein the process is run in the vapor phase.

28. The process as in Claim 16 further comprising the recovery of one or more of the unsaturated nitriles.

29. The process as in Claim 16 further comprising the conversion of one or more of the unsaturated nitriles to caprolactam or adiponitrile.

25 30. The process of Claim 2 or Claim 17 wherein the metal of the catalyst is selected from the group consisting of Ba, Cs, Rb and Mg.