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Letter

Allylamine from Allyl Alcohol

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Introduction

Allyl amine, a versatile organic intermediate, is typically prepared by ammonolysis of allyl chloride [1 - 4]. Amination of π-allyl palladium complexes has also been investigated, especially as a route to *N*-substituted allyl amines [5 - 8]. We now report that reaction of allyl alcohol with ammonia in the presence of acid phosphate catalysts provides allylamine in high selectivity.

Experimental

Allyl alcohol was purchased from Aldrich Chemical Co. Ammonia (high purity; >99.9%) was obtained from Air Products and Chemicals. Phosphoric acid on silica (0.3 g cm^{-3}) was obtained from Davison Chemical Co. Lanthanum nitrate hexahydrate and ammonium dihydrogen phosphate were obtained from Alfa Products. Unless otherwise specified, all chemicals were ACS reagent grade; all were used without further purification. Crushed vicor quartz chips were obtained from Arthur H. Thomas Co., and were used without further treatment.

The lanthanum phosphate catalyst was prepared by addition, with stirring, of a solution of ammonium dihydrogen phosphate (172.5 g, 1.50 mol) in 300 ml deionized water to a solution of lanthanum nitrate hexahydrate (216.5 g, 0.50 mol) in 300 ml deionized water. The resulting thick precipitate was collected by filtration, washed (3 × 100 ml) with deionized water to remove soluble nitrates, and dried on a Teflon® sheet (80 - 90 °C/ 50 min) to constant weight. Analysis of the dried catalyst by ICP–AES showed lanthanum, 40.0 ± 0.3 wt.%, and phosphorus, 15.7 ± 0.2 wt.%.

All reactions of allyl alcohol and ammonia were carried out in a 20 cm^3 fixed bed stainless steel tubular reactor. Temperature was controlled with an ECS 6401 Time Proportioning Control Module. Feeds were individually

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metered to the reactor as liquids using Isco Model 314 high pressure syringe pumps. Pressure was maintained with a Grove Model SD-91LW back pressure regulator, and monitored with a Validyne Model DP 15-62 pressure transducer. Pressure and temperature readings were continuously recorded with a strip chart recorder.

Typically, the reactor was charged with crushed vicor (5 cm^3 of −12 to −18 mesh particles), followed by a mixture of catalyst (5 cm^3 of −12 to −18 mesh particles) and crushed vicor (5 cm^3 of −12 to −18 mesh particles). The catalyst charge was overlaid with an additional 2 cm^3 of vicor (−12 to −18 mesh particles). A slow flow of nitrogen (40 cm^3 min^{-1}) was passed over the catalyst while it was heated to the desired temperature. When the desired temperature was attained, system pressure was increased to the operating setpoint over 30 - 45 min. With the reactor at operating temperature and pressure, nitrogen was shut off, and allyl alcohol and ammonia were metered to the reactor. Flow rates of ammonia and allyl alcohol were adjusted to obtain the desired mole ratio of reactants. The feed also contained triethylene glycol dimethyl ether (6 wt.%, based on allyl alcohol) as an internal standard for glc analysis.

Analyses were carried out on a Varian Model 3700 gas chromatograph equipped with a capillary injection port for use with fused-silica columns, Model 8000 autosampler, and a flame ionization detector. Separations were effected with a fused-silica DB-5 wall-coated open-tubular column (30 m × 0.32 mm; 1.0 μm film thickness). Quantitation was based on use of triethylene glycol dimethyl ether as an internal standard. The autosampler was controlled, and integrations were performed by a Varian VISTA 402 chromatography data system. Identities of major products were confirmed by GC–MS.

Results and discussion

Treatment of allyl alcohol with ammonia in the presence of phosphoric acid on silica provided significant conversions to allylamine at temperatures of at least 250 °C (molar feed ratio of ammonia/allyl alcohol = 8/1; 300 psig; LHSV = 0.5 h^{-1}, based on allyl alcohol, see Table 1, runs 1 - 3). Similar results were obtained with the lanthanum phosphate catalyst (molar feed ratio of ammonia/allyl alcohol = 4/1; 450 psig; LHSV = 0.3 h^{-1}, based on allyl alcohol; see Table 1, runs 4 - 7). In general, selectivities to allylamine were high. Lesser amounts of diallyl- and triallylamine were formed; β-picoline was the major byproduct.

Lanthanum phosphate is less reactive for amination of allyl alcohol, as evidenced by the higher pressure and slower space velocity needed to obtain conversions comparable to those found with phosphoric acid on silica. With either catalyst, conversion of allyl alcohol to allylamine is directly proportional to temperature (*cf*. runs 1 - 3, 4 - 7, Table 1).

The best yields of allylamine are obtained at 320 °C. However, at higher temperatures, acid-catalyzed oligomerization and cyclization to β-picoline intervene, and selectivity to total allylamines decreases rapidly. Poor selectiv-

TABLE 1

Amination of allyl alcohol with acid phosphate catalysts

Run	Catalyst	Temperature (°C)	Conversion (%)[a]	Selectivity[d]			
				MAA[c]	DAA[b]	TAA[e]	β-picoline
1	H_3PO_4/SiO_2	250	4.5	95	4	—	1
2	H_3PO_4/SiO_2	277	11.0	85	4	3	7
3	H_3PO_4/SiO_2	320	23.0	81	4	2	13
4	$LaPO_4$	240	6.9	95	3	1	1
5	$LaPO_4$	280	8.7	87	5	2	6
6	$LaPO_4$	300	12.9	84	7	2	7
7	$LaPO_4$	320	21.7	79	9	2	10

[a] Based on allyl alcohol.

[b] Weight percent, determined by GC analysis of product stream with triethylene glycol dimethyl ether as an internal standard.

[c] Monoallylamine.

[d] Diallylamine.

[e] Triallylamine.

ities to allylamine also result from use of lower ammonia/allyl alcohol feed ratios.

In conclusion, phosphate-catalyzed amination of allyl alcohol provides allylamine in high selectivity. Moreover, coproduction of inorganic chloride salts, a disadvantage of the current commercial route to allylamine, is avoided.

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