

Butadiene Hydroamination with Aqueous Ammonia Catalyzed by Palladium(II) Sulfoxide Complexes

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Hydroamination of 1,3-dienes with ammonia underlie the promising preparation methods for higher amines. The most interesting product of butadiene hydroamination with NH₃ is tris(2,7-octadienyl)amine (**I**) that can be easily hydrogenated to obtain a valuable extractant trioctylamine extensively applied in isolation processes of a large number of noble and rare metals and of fatty acids, and also as water softener, corrosion inhibitor, and flotation agent [1].

The butadiene hydroamination in the early studies was performed in the presence of Pd catalyst with triarylphosphine or dialkylarylphosphine oxide ligands, applying anhydrous ammonia under pressure which depended on the ratio [butadiene]:[NH₃] and on the character of the inert solvent and NH₃ concentration. The pressure in the reactor depending on the above factors and on the temperature attained up to 15–60 atmosphere, therefore the processing was complex and required the use of high-pressure reactors [2, 3].

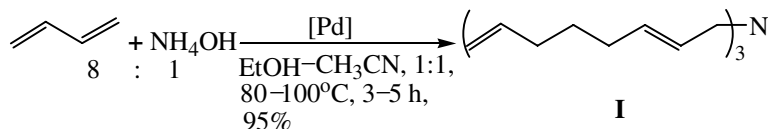
For practical application the most interesting process would be production of tris(2,7-octadienyl)amine (**I**) from butadiene and aqueous ammonia (ammonium hydroxide) that is a cheap and available product. To catalyze the hydroamination of butadiene which is insoluble in water with the water solution of ammonia a catalyst is required unaffected by water or (still better) soluble in water.

The butadiene hydroamination with aqueous 28% ammonia in the presence of a catalytic system Pd(OAc)₂–Ph₃P occurred homogeneously because of application as an environment of acetonitrile miscible with water in any ratio. The going over to aqueous ammonia essentially simplified the processing, but the conversion and the

overall yield of the unsaturated amines decreased, and also the selectivity of the reaction was reduced with respect to tris(2,7-octadienyl)amine (**I**) and the fraction of mono-octadienylamines grew. A palladium catalyst containing a water-soluble phosphine ligand [P(C₆H₃-2-CH₃, 4-SO₃Na)₃] proved to be sufficiently effective in butadiene hydroamination with aqueous ammonia in a two-phase system [pentane(toluene)–water, 1:1.6] at 80°C to give a mixture of 2,7-octadienyl-1-amine (**II**) and 1,7-octadienyl-3-amine (**III**) in an overall yield 55–61%, and the yield of the tris(2,7-octadienyl)amine under these conditions did not exceed 3–8% [4, 5].

We succeeded in butadiene hydroamination with aqueous ammonia in the presence of catalysts consisting of water-soluble complexes Pd(II) with sulfoxides: dimethyl sulfoxide and petroleum sulfoxides (PSO), PdCl₂·2DMSO and PdCl₂·*n*(PSO). The reaction proceeded at 80°C within 5 h (or at 100°C within 3 h) and led to the formation of tris(2,7-octadienyl)amine (**I**) in 95% yield at a complete ammonia conversion. The molar ratio of catalyst and reagents was [Pd]–[NH₄OH]–[butadiene] 0.5...1:100:800.

The excess butadiene is not consumed and can be returned into the process. The yield of tris(2,7-octadienyl)amine (**I**) essentially depends on the solvent character. The butadiene hydroamination with aqueous ammonia occurred cleanly in a hydroxy-containing solvents (MeOH, EtOH, PrOH, ethylene glycol) or acetonitrile. When the hydroxy-containing solvent is miscible with water, the butadiene forms an organic phase. Under these conditions the yield of the target product was 90–95%, and in dimethylformamide or dimethyl



sulfoxide, 75–80%. However on adding alcohol to DMF (DMSO) to a ratio 1:1 the yield of tris(2,7-octadienyl)-amine grew to 92%. In aromatic solvents (benzene, toluene) the yield of amine was 30%.

The reaction time depended strongly on the temperature: whereas at 80°C the reaction completed in 5 h, at 100°C, in 3 h. At lower temperature (50–60°C) the reaction rate decreased 3 times (~16–18 h), and simultaneously the selectivity of the process was reduced by formation of a mixture of adducts 2,7-octadienyl-1-amine (**II**) and 1,7-octadienyl-3-amine (**III**). The yield of amine **I** fell to 32%. The raising of temperature to 130–140°C ensured complete conversion of ammonia and butadiene within 1 h, but the reaction products contained alongside bis(2,7-octadienyl)amine (**IV**) and tris(2,7-octadienyl)amine (**I**) also a considerable quantity of linear and cyclic butadiene dimers and trimers thus significantly complicating the isolation of the target product **I**.

In butadiene hydroamination with aqueous ammonia freshly-prepared palladium complexes PdCl₂·2DMSO and PdCl₂·*n*(PSO) were used.

PdCl₂·2DMSO was prepared by a known procedure [6]. The isolated yellow complex by its IR spectrum and elemental analysis was well consistent with the published data. In a similar way the PdCl₂ complex with petroleum sulfoxides (PSO) was obtained. After thorough grinding of PdCl₂ in a mortar the fine powder obtained was carefully mixed with excess petroleum sulfoxides of sulfoxide number 9.12%. After 24 h the yellow-brown complex obtained was filtered off and washed on the filter with ethanol and ether. After drying at 50°C the substance was analyzed. In the IR spectrum a band was definitely observed at 1115 cm⁻¹ corresponding to the bridging chloride and a very strong band at 1155 cm⁻¹ characteristic of the stretching vibrations of the S–O bond. Found, %: C 26.47; H 3.59; Cl 29.00; Pd 35.56; S 2.40. Calculated, %: C 26.91; H 3.85; Cl 28.31; Pd 36.02; S 2.84.

The reaction was carried out in pressure microreactors of stainless steel or titanium of 17 ml capacity. Into the microreactor at 0°C (ice-water bath, NaCl) was charged under argon 0.1 mmol of PdCl₂·2DMSO [or PdCl₂·*n*(PSO)], 10 mmol of 28% aqueous ammonia, 60–80 mmol of freshly distilled butadiene, 4 ml of ethanol (or 2 ml of ethanol and 2 ml of CH₃CN), the reactor was airtight closed and heated at 80–100°C for 3–5 h with stirring.

On completion of the reaction the microreactor was cooled to ~20°C, opened, the organic layer was separated and passed through a bed of Al₂O₃ of II grade activity, the solvent was distilled off, and the residue was distilled in a vacuum.

Tris(2,7-octadienyl)amine (I). Yield 95%, bp 175°C (1Pa) {bp 185°C (2Pa) [1]}. IR spectrum, ν, cm⁻¹: 920, 1000, 3080 (–CH=CH₂), 980, 3030 (–CH=CH–). ¹H NMR spectrum, δ, ppm: 1.43 m (6H, –CH₂–), 1.95 (12H, –CH₂C=), 2.98 m (6H, >NCH₂C=C), 4.92 m (6H, CH₂=C), 5.45 m (9H, –CH=CH–). ¹³C NMR spectrum (CDCl₃), δ, ppm: 55.94 (C¹), 126.07 (C²), 134.60 (C³), 30.82 (C⁴), 28.23 (C⁵), 32.45 (C⁶), 138.26 (C⁷), 144.63 (C⁸). Found, %: C 84.55; H 11.41; N 4.04. C₂₄H₃₉N. Calculated, %: C 84.39; H 11.51; N 4.10.

The reaction products were analyzed by GLC on chromatographs Tsvet-102 and Chrom-5 equipped with flame-ionization detectors, columns 1.2 m × 3 mm, stationary phase Silicone SE-30 (5%) on Chromaton N-AW-HMDS (0.125–0.160 mm), carrier gas helium (50 ml/min), oven temperature from 50 to 220°C. IR spectra were recorded on a spectrophotometer UR-20. ¹H and ¹³C NMR spectra were registered on a spectrometer Jeol FXG at operating frequencies 90 and 22.5 MHz respectively with TMS as reference. The elemental analysis of products was determined on an analyzer Carlo Erba, model 1106.

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