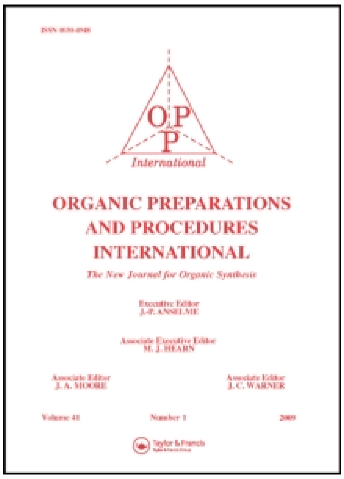

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CATALYTIC REDUCTION OF 1,1,1-TRIS(AZIDOMETHYL)ETHANE TO 1,1,1-TRIS(AMINOMETHYL)ETHANE

L. J. Zompa[a]; J. P. Anselme[a]
[a] Department of Chemistry, University of Massachusetts, Boston Boston, Massachusetts, USA

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CATALYTIC REDUCTION OF 1,1,1-TRIS(AZIDOMETHYL)ETHANE TO 1,1,1-TRIS(AMINOMETHYL)ETHANE

L. J. Zompa and J.-P. Anselme

Department of Chemistry
University of Massachusetts at Boston
Boston, Massachusetts 02125, USA

Suitably structured polyamines have received increased attention as ligands for transition metal ions. One such polyamine is 1,1,1-tris(aminomethyl)ethane(tame)(II) which has recently been prepared by the LAH reduction of 1,1,1-tris(azidomethyl)ethane(I).[1] Although azides are properly considered as extremely hazardous and explosive compounds, their reduction particularly by the catalytic method, makes them excellent precursors of primary amines.[2] In spite of the general warning[3] that azides with an (C+O)/N ratio smaller than 3(in I it is 0.25) are very explosive, our familiarity with azides[4] coupled with the experimentally tedious - and sometimes incomplete - reduction with

$$\underset{(R = Ph;\ CH_3)}{CH_3C(CH_2OSO_2R)_3} \xrightarrow{NaN_3} \underset{I}{CH_3C(CH_2N_3)_3} \xrightarrow{H_2,\ Pd/C} \underset{II}{CH_3C(CH_2NH_2)_3}$$

LAH prompted us to hydrogenate I catalytically. We have successfully reduced crude I routinely with better than 83% yield of pure isolated as its trihydrochloride salt. No attempt was made to optimize the yield which should be practically quantitative starting from the pure azide. These results suggest that with proper handling, even potentially very explosive azides are excellent and practical sources of primary amines.

EXPERIMENTAL

CAUTION! ALL OPERATIONS INVOLVING ANY AZIDE SHOULD ALWAYS BE CARRIED OUT WITH EXTREME CARE. PROTECTIVE CLOTHING SHOULD BE WORN AND ALL WORK SHOULD BE CARRIED OUT BEHIND A SHIELD.

1,1,1-Tris(azidomethyl)ethane(I).- This preparation was repeated several times according to the literature procedure.[1] In no case - including modified conditions - did the azide separate as an oil. Ether extraction of the dark brown heterogeneous reaction mixture formed after addition to water was necessary to obtain the crude azide as an amber colored material with the reported spectral properties.

1,1,1-Tris(aminomethyl)ethane(II).- Although we have never experienced any explosion with I, it is recommended that this procedure be followed exactly as described). To 50 ml of ethanol in a Parr hydrogenation bottle was added 0.2 g. of 5% Pd/C. After the catalyst was well dispersed by swirling, a solution of 1.95 g. (0.01 mole) of the azide in 100 ml. of ethanol was added slowly from a separatory funnel. The mixture was then hydrogenated at 30 psi (after proper venting of the hydrogenation bottle). Since after the initial small drop caused by adsorption of hydrogen on the catalyst there is no change in pressure, the hydrogenation was allowed to proceed overnight to insure complete reduction. Filtration of the catalyst and evaporation of the solvent gave II as a pale yellow oil, the infrared and nmr spectra of which agreed with those reported. Introduction of gaseous hydrogen chloride into an ethereal solution of the amine gave 1.87 g (83%) of the hydrochloride salt, mp. 350° (dec.); nmr (D_2O-TMS) δ 1.84 (s, 1, CH_3) and 3.87 (s, 2, CH_2). The molecular weight determined by titration of the hydrochloride with base was 226; theory 226.4.

Anal. Calcd for $C_5H_{18}N_3Cl_3$: C, 26.50; H, 8.01; N, 18.54. Found: C, 26.25; H, 7.88; N, 18.06.

The acidity constants of the $H_3tameCl_3$ at 25° in 0.1M KNO_3 were determined by previously described methods.[5] A comparison of the acidity constants of H_3tame^{3+} with the amine salt of the related tris(aminomethyl)methane(tamm)[6] corrected for difference in temperature of measurement[7] indicates that H_3tame^{3+} is more acidic (Table 1).

TABLE 1

Reaction	-log Ka H_3tame^{3+}	H_3tamm^{3+}[6]
$H_3L^{3+} \rightleftharpoons H_2L^{2+} + H^+$	5.60 ± 0.01	6.28
$H_2L^{2+} \rightleftharpoons HL^+ + H^+$	8.10 ± 0.01	8.41
$HL \rightleftharpoons L + H^+$	10.07 ± 0.01	10.23

This increased acidity is presumably caused by the methyl group on H_3tame^{3+} which forces the ammonium groups closer

CH_3-$C(CH_2NH_3^+)_3$ H_3tame^{3+}

H-C(CH $NH_3^+)_3$ H_3tamm^{3+}

together creating a greater charge interaction than in the case of H_3tamm^{3+}.

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