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

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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

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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 1,1,1tris(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 warning³ that azides with an (C+O)/N ratio smaller than 3(in I it is 0.25) are very explosive, our familiarity with azides⁴ coupled with the experimentally tedious - and sometimes incomplete - reduction with

 $(H_3C(CH_2OSO_2R)_3 \xrightarrow{NaN_3} CH_3C(CH_2N_3)_3 \xrightarrow{H_2, Pd/C} CH_3C(CH_2NH_2)_3$ $(R = Ph; CH_3) \qquad I \qquad II$

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

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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

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1,1,1-TRIS(AMINOMETHYL)ETHANE

-log Ka

Hatamm³⁺

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 (D₂O-TMS) δ 1.84 (s, 1, CH₃) and 3.87 (s, 2, CH₂). The molecular weight determined by titration of the hydrochloride with base was 226; theory 226.4.

<u>Anal</u>. Calcd for C₅H₁₈N₃Cl₃: C, 26.50; H, 8.01; N, 18.54. Found: C, 26.25; H, 7.88; N, 18.06.

The acidity constants of the H₃tameCl₃ at 25° in 0.1M KNO₃ were determined by previously described methods.⁵ A comparison of the acidity constants of H₃tame³⁺ with the amine salt of the related tris(aminomethyl)methane(tamm)⁶ corrected for difference in temperature of measurement⁷ indicates that H₃tame³⁺ is more acidic (Table 1).

TABLE 1

 Reac	tion

 H_3L^{3+} H_2L^{2+} H_1^+ H_3tame^{3+} H_3tamm^{3+}
 H_2L^{2+} H_L^+ H_1^+ H_1^+ H_1^+
 H_L L H_1^+ H_1^+ $H_1^ H_2$ L H_1^+ $H_1^ H_1^ H_2$ H_1^+ H_1^+ $H_1^ H_1^ H_1$ $H_1^ H_1^ H_1^ H_1^-$ </td

This increased acidity is presumably caused by the methyl group on H_3 tame³⁺ which forces the ammonium groups closer

 $CH_3-C(CH_2NH_3^+)_3$ $H-C(CH_NH_3^+)_3$

H₃tame³⁺

together creating a greater charge interaction than in the case of $H_3 tamm^{3+}$.

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