$>CH_2$, in order to obtain the known derivative of Lions and Martins. Reduction with zinc dust in dilute acetic acid yielded a product, the analysis of which closely agreed with that calculated for bis[2-(2′-pyridylmethyleneaminomethyl)pyridine]iron(II) perchlorate. Its absorption spectrum (λ_{max} 568 mμ), however, was slightly different from the spectrum of an authentic sample of the complex (λ_{max} 569 mμ) prepared according to the Lions and Martins[2] procedure. When this preparation was repeated, small changes in the absorption spectrum were again observed, suggesting formation of more than one and possibly isomeric species. Experimental conditions were finally found by which the condensation of pyridine-2-aldehyde, 2-aminomethylpyridine, and ferrous salt yielded a product whose absorption spectrum was practically identical with that of the product obtained by reduction of the hydroxy derivative (see Figure 1). The constitution of the latter therefore seems definitively established.

Experimental

(1) **Bis[2-(2′-pyridylmethyleneaminohydroxymethyl)pyridine]-iron(II) Perchlorate.**—To 2.14 g. (20 mmoles) of pyridine-2-aldehyde in 10 ml. of ethanol, kept under nitrogen, was added 15 ml. of 0.4 *M* ferrous chloride (6 mmoles) followed by 5 ml. of 2 *M* ammonium bicarbonate (10 mmoles). Copious amounts of carbon dioxide were evolved and the mixture turned dark violet. After standing for 5 min. at room temperature, 5 g. of sodium perchlorate was added and the mixture kept at 0° for 3 hr. The amorphous precipitate was filtered off and washed with a solution of sodium perchlorate and finally with water; yield, 3 g.

Anal. Calcd. for $[Fe(C_{12}H_{11}N_3O)_2](ClO_4)_2$: Fe, 8.20; N, 12.35. Found (dried over P_2O_5 *in vacuo*): Fe, 8.4; N, 12.6, 12.3.

(2) **Bis[2-(2′-pyridylmethyleneaminohydroxymethyl)pyridine]-iron(II) Chloride 6-Hydrate.**—To 2.14 g. (20 mmoles) of pyridine-2-aldehyde in 20 ml. of water, kept under nitrogen, was added 2.5 ml. of 2 *M* ferrous chloride (5 mmoles) followed by 2 g. of solid ammonium chloride. The dark violet solution was kept at 25° for 15 min. and then at 0° for 1 hr. The crystalline product was filtered off, washed with a few ml. of a solution of ammonium chloride, and air-dried; yield, 1.9 g.

Anal. Calcd. for $[Fe(C_{12}H_{11}N_3O]_2)Cl_2 \cdot 6H_2O$: H_2O, 16.35. Found: H_2O, 16.85, 16.6. Calcd. for $[Fe(C_{12}H_{11}N_3O)_2]Cl_2$: Fe, 10.09; N, 15.19; Cl, 12.82. Found (dried over P_2O_5 *in vacuo*): Fe, 10.0, 10.1; N, 15.2, 15.3; Cl, 12.75.

The filtrate, which contained unreacted pyridine-2-aldehyde as the hydrochloride, was treated with sodium bicarbonate and then sodium perchlorate. The precipitated product (1.2 g.) had the same composition and spectrum as the product obtained under (1).

(3) **Bis[2-(2′-pyridylmethyleneaminomethyl)pyridine]iron(II) Perchlorate.** (A).—A solution of 1.07 g. (10 mmoles) of pyridine-2-aldehyde in 5 ml. of ethanol was mixed with 1.08 g. (10 mmoles) of 2-aminomethylpyridine, and the mixture was kept at 25° for 20 min.; 25 ml. of 0.2 *M* ferrous chloride (5 mmoles) was then added under nitrogen and the mixture kept at 0° for 1 hr. The crystalline chloride was filtered off and dissolved in 20 ml. of water, and the perchlorate of the complex was precipitated by slowly adding a solution of sodium perchlorate. The amorphous product was filtered off, washed with a diluted solution of sodium perchlorate and then with water, and air-dried; yield, 1.2 g.

Anal. Calcd. for $[Fe(C_{12}H_{11}N_3)_2](ClO_4)_2$: Fe, 8.60; N, 12.95. Found (dried over P_2O_5 *in vacuo*): Fe, 8.5; N, 13.05. (The air-dry product contained 3.35% H_2O.)

Addition of sodium perchlorate to the filtrate from the complex chloride precipitated 2 g. of a less pure product. *Anal.* Found: Fe, 8.8; N, 12.2. Its absorption spectrum had slightly shifted and broadened toward longer wave lengths, but was otherwise very similar to the spectrum of the first fraction.

(B).—Bis[2-(2′-pyridylmethyleneaminohydroxymethyl)pyridine]iron(II) chloride 6-hydrate (1 g.) was dissolved in 40 ml. of 4 *M* acetic acid. Under vigorous stirring 1 g. of zinc dust was added, the temperature being kept at 30–35°. After 10 min., 1 g. of zinc dust was added, and stirring was continued for 10 min. Excess zinc dust was filtered off and washed with 50 ml. of water. The combined filtrates were treated with sodium perchlorate, thereby precipitating a red, amorphous product. After 1 hr. the precipitate was filtered off, washed with a solution of sodium perchlorate and then with water, and air-dried; yield, 0.5 g.

Anal. Calcd. for $[Fe(C_{12}H_{11}N_3)_2](ClO_4)_2$: Fe, 8.60; N, 12.95. Found (dried over P_2O_5 *in vacuo*): Fe, 8.55, 8.6; N, 13.0, 13.05. (The air-dry product contained 3.5% H_2O.)

Contribution from the Chemistry Department, Reaction
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The Chemistry of Alane. III.[1] Quaternary Ammonium Aluminohydrides[2]

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Received October 26, 1964

The first compound containing the aluminohydride group, $LiAlH_4$, was prepared by Finholt, Bond, and Schlesinger[3] in 1947. Since that time many metal aluminohydrides have been prepared, but no report has been made of the synthesis of nonmetallic aluminohydrides such as the quaternary ammonium salts. We wish to report the synthesis of two quaternary ammonium aluminohydrides, tri-*n*-octyl-*n*-propylammonium aluminohydride, $(C_8H_{17})_3(C_3H_7)NAlH_4$ (I) and tetramethylammonium aluminohydride, $(CH_3)_4NAlH_4$ (II). The former is very soluble in benzene, toluene, and diethyl ether, and slightly soluble in hexane and pentane, while the latter is insoluble in all organic solvents. Both exhibit considerably greater hydrolytic stability than lithium aluminum hydride.

Experimental

Reagents were handled in a nitrogen-atomosphere vacuum drybox and all reactions were conducted under dry nitrogen. Filtrations were also conducted in the drybox. Solvents were purified and dried by refluxing over $LiAlH_4$; after distillation they were stored over $LiAlH_4$ (benzene, hexane, pentane, and toluene) or LiH (diethyl ether and tetrahydrofuran). Commercial grade $LiAlH_4$ (Metal Hydrides, Inc., Beverly, Mass.) was used without further purification. Quantitative hydrolyses were performed on a Toepler pump system.

Tri-*n*-octyl-*n*-propylammonium bromide was specially prepared by Distillation Products Industries, Division of Eastman

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[1] Paper II: *Inorg. Chem.*, **3**, 628 (1964).

[2] This research was supported by the Advanced Research Projects Agency under ARPA Order No. 24. Additional support was provided by the Air Force Flight Test Center, Air Force Systems Command, Edwards Air Force Base, Calif., under Contracts AF33(616)-5935 and AF04(611)-7046. Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

[3] A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).

Kodak Co., Rochester, N. Y. The white solid melted at 70–72° with decomposition. The following analysis was obtained on this material in our laboratories.

Anal. Calcd. for $C_{27}H_{58}NBr$: C, 68.03; H, 12.27; N, 2.94; Br, 16.77. Found: C, 67.63; H, 12.48; N, 3.01; Br, 16.50.

Tri-*n*-octyl-*n*-propylammonium Aluminohydride (I).—A solution of 47.67 g. (0.10 mole) of tri-*n*-octyl-*n*-propylammonium bromide in 300 ml. of anhydrous benzene was added to a suspension of 5.0 g. of powdered $LiAlH_4$ in 100 ml. of benzene. The mixture was stirred at room temperature for 3 days, after which time a filtered sample of the benzene solution gave a negative halogen test. The suspension was filtered and the filtrate was freeze-dried to yield 21.25 g. of white, crystalline solid, m.p. 61–63° dec. after purification by precipitation from benzene solution with pentane.

Anal. Calcd. for $C_{27}H_{62}NAl$: C, 75.81; H, 14.61; N, 3.27; Al, 6.31. Found: C, 75.51; H, 14.49; N, 3.48; Al, 6.38.

Tetramethylammonium Thiophenoxide (III).—A 10% aqueous solution containing 0.050 mole of tetramethylammonium hydroxide was mixed with 5.51 g. (0.050 mole) of thiophenol and stirred at room temperature until all of the thiophenol had dissolved (approximately 3 days). A small amount of white solid (0.357 g.), which precipitated during the reaction, was isolated by filtration and identified as diphenyl disulfide by its melting point and infrared spectrum. The aqueous filtrate was evaporated to dryness *in vacuo* at 45°, and the resultant off-white solid was dried for 24 hr. at 70° (0.007 mm.) to give 8.98 g. (98% yield) of III. The thiophenoxide melted at 144–145° with decomposition, was extremely hygroscopic, and partially hydrolyzed on standing in moist air as evidenced by the typical odor of thiophenol. The infrared spectrum of III showed no –OH or –SH absorptions.

Anal. Calcd. for $C_{10}H_{17}NS$: C, 65.52; H, 9.35; N, 7.64; S, 17.49. Found: C, 65.80; H, 9.73; N, 8.00; S, 16.80.

Tetramethylammonium Aluminohydride (II).—A suspension of 8.98 g. of III in 110 ml. of THF was mixed with 240 ml. of a 0.233 *M* solution of $LiAlH_4$ in THF and stirred for 2 days at 63°. The suspended solid, which changed from an egg-shell to a bright white color, was isolated by filtration, washed thoroughly with THF, and dried at room temperature *in vacuo* for 5 hr. This procedure afforded 4.52 g. of II (86% over-all yield, based on tetramethylammonium hydroxide). The aluminohydride decomposed above 173° without melting, forming an aluminum mirror in the melting point capillary. It ignited when dropped into water but did not flame in moist air. The density was 0.990 g./cm.^{3} (displacement of *n*-hexane).

Anal. Calcd. for $C_4H_{16}NAl$: C, 45.69; H, 15.34; N, 13.32; Al, 25.65. Found: C, 45.99; H, 15.69; N, 13.01; Al, 25.30; Li, <0.5; S, 0.0.

Results and Discussion

The infrared spectrum of I, taken as a differential in benzene, showed only a simple, relatively sharp, Al–H absorption at 6.03 μ (1660 cm.$^{-1}$). Cryoscopic molecular weight determinations in benzene showed anomalous behavior in that the apparent molecular weight increased with increasing dilution. In tetrahydrofuran (THF), however, ebullioscopic measurements showed decreasing apparent molecular weights with increasing dilution, the values ranging from 12,570 to 285 (5.73% to 0.52% by weight). Isopiestic molecular weight determinations in THF also showed a normal effect of concentration. At 5.33 and 2.66 wt. % concentrations values of 418 and 180, respectively, were obtained. The formula weight of tri-*n*-octyl-*n*-propylammonium aluminohydride is 428.

Tri-*n*-octyl-*n*-propylammonium aluminohydride reacted readily, but not vigorously or completely, with water. Only by incubation in a sealed tube for 2 weeks at 100° with 6 *N* hydrochloric acid could quantitative hydrolysis be effected. A sample of I was heated *in vacuo*, maintained by the continuous pumping of a Toepler pump. No decomposition occurred below 75°; at 90° decomposition was slow. Evolution of hydrogen ceased after several days at 100–109° and the total quantity of hydrogen collected represented 72.4% of the total hydridic hydrogen present in the compound. Another 18.6% was accounted for by the formation of a mixture of condensable gases consisting of 79.5% of *n*-propane and 19.8% of *n*-octane. The residue consisted of metallic aluminum and 95.4% of the theoretical quantity of tri-*n*-octylamine.

Tetramethylammonium aluminohydride (II) was more difficult to prepare than I, since no suitable starting material (soluble in an aprotic solvent) was available. The synthesis was accomplished by using tetramethylammonium thiophenoxide (III), which was found to be slightly soluble in THF. The infrared spectrum of II showed a broad Al–H absorption at 6.03 μ (1660 cm.$^{-1}$) with a shoulder at 5.90 μ (1695 cm.$^{-1}$). Elemental analysis showed that II was quite pure, although it could not be purified by recrystallization because of its insolubility. It was free of sulfur and contained less than 0.5% lithium. The tetramethylammonium aluminohydride was also very difficult to hydrolyze, requiring 14 days of incubation with 6 *N* hydrochloric acid in a sealed tube at 95° to produce 92% of the theoretical quantity of hydrogen.

Both quaternary ammonium aluminohydrides exhibit their principal Al–H absorption near 6 μ in the infrared, suggesting that they exist primarily in the ionic form. This was confirmed in the case of I by preliminary conductivity measurements in THF which showed that the salt had approximately twice the conductivity of $LiAlH_4$ in THF. In the case of II the ionic character of the solid is suggested by its insolubility in organic solvents and its relatively high decomposition temperature. The apparent greater ionic character of these quaternary ammonium aluminohydrides as compared to $LiAlH_4$ may also account for the difficulties encountered in effecting complete hydrolysis.

Contribution from the Reaction Motors Division
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The Reaction of Xenon with Dioxygen Difluoride. A New Method for the Synthesis of Xenon Difluoride

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Received December 8, 1964

In the course of an investigation of the chemistry of dioxygen difluoride, we have examined its reactivity