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# The preparation of quinuclidine-fluoroboranes by base displacements reactions

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Amine-adducts of mono- and difluoroborane were first prepared by the fluorination of $(CH_3)_3NBH_3$ using anhydrous HF[1]. Later preparations involved the direct reaction of amines with difluoroborane[2] and by base displacement reactions on trimethylamine-fluoroboranes[3]. We wish to report here the synthesis of fluoroborane adducts of quinuclidine via base displacement reactions.

*Syntheses*

Trimethylamine-borane was obtained from Callery Chemical Co. and used without purification. The adducts $(CH_3)_3NBH_2F$ and $(CH_3)_3NBHF_2$ were prepared by the method of VanPaasschen and Geanangel[1]. Trimethylamine-trifluoroborane was prepared by the direct combination of the components. About 5 ml of trimethylamine was condensed on the vacuum line into a tubular glass vessel fitted with a standard taper joint and Teflon valve adapter. Small quantities of $BF_3$ were sequentially condensed into the reaction vessel and the contents warmed until the added $BF_3$ had reacted. When all the $(CH_3)_3N$ had been consumed, the vessel was warmed to room temperature and held under dynamic vacuum for 2 hr. The solid $(CH_3)_3NBF_3$ was sublimed *in vacuo* at 90° to a coldfinger at 0°.

Quinuclidine (azabicyclo[2.2.2]octane) was obtained as the hydrochloride from Aldrich. Attempts to prepare free quinuclidine by treating the hydrochloride with 40% aqueous NaOH followed by vacuum distillation resulted in yields of less than 40%. Separation of quinuclidine from water proved difficult. The high cost of this compound dictated that a more efficient method of liberating it from the hydrochloride be developed. Sodium methoxide in methanol was used as a dehydrochlorinating agent. In a typical reaction 1.09 g (47 mmol) of sodium was weighed into a dry 200 ml round bottom flask equipped with a $\overline{\S}$ 24/40 inner joint, magnetic stirbar and flushed with dry nitrogen. A sample of quinuclidine hydrochloride (3.84 g, 26 mmol) was added to the reaction vessel, which was then connected to the vacuum line via a Teflon valve adapter. The vacuum line port was equipped with a mercury blowout tube. The reaction vessel was cooled to −196° and 10 ml of methanol condensed in from another vessel on the vacuum line. The Teflon valve was then closed, the reaction vessel was warmed to −78° and vigorous stirring started. The hydrogen evolved in the reaction escaped slowly through the blowout tube as the reaction vessel was allowed to warm slowly to room temperature and remain there for 1 hr. Then the vessel was cooled to 0° and the volatile components fractionated through traps at −20 and −196°. After transfer of all the liquid phase, the reaction vessel was warmed to 60° for 1 hr. The −20° trap yielded 2.6 g (23.4 mmol) of quinuclidine, m.p. 158° (lit.[4], 156°) for a 90% conversion.

*Base displacement reactions*

Base displacement reactions were carried out in tubular glass vessels fitted with demountable 15 mm. O-ring joint, Teflon valve adapter and either magnetic or solenoid actuated stirrer. Approximately equimolar quantities (10–12 mmol) of quinuclidine and the appropriate trimethylamine adduct were weighed into a dry vessel which was then attached to the vacuum line and evacuated. About 10 ml of dry benzene was condensed into the vessel, the Teflon valve closed and the reaction mixture allowed to warm slowly to room temperature with stirring. After 48 hr the volatiles were fractionated through traps at −78 and −196°. The trimethylamine (−196° trap) was measured and discarded then the benzene (−78° trap) was condensed back into the reaction vessel. The sequence was repeated until no additional $(CH_3)_3N$ was liberated. The solid residue was then removed from the reaction vessel, sublimed and the yield calculated.

*Quinuclidine-borane*

In a typical reaction 1.0111 g (9.1 mmol) of quinuclidine and 0.6655 g (9.1 mmol) of $(CH_3)_3NBH_3$ were combined using the procedure previously described. After 48 hr 6.52 mmol (72%) of $(CH_3)_3N$ was isolated by fractionation, then the benzene was returned and the reaction continued until no more trimethylamine was released. The solid residue was sublimed at 70° resulting in a 1.068 g (93%) yield of quinuclidine-borane. The m.p. of the product was 159–163°, the same as that of a sample of quinuclidine-borane prepared from quinuclidine hydrochloride and sodium borohydride in tetrahydrofuran. The $^{11}B$ NMR spectrum of the product was a quartet with a chemical shift of the product found to be $\delta + 28.6$ ppm (ref. external $B(OCH_3)_3$) ($J_{BH} = 94$ Hz).

*Quinuclidine-monofluoroborane*

Quinuclidine (1.1985 g, 10.8 mmol) was combined with 0.9573 g (10.5 mmol) $(CH_3)_3NBH_2F$ as described above. After 48 hr 8.85 mmol (84%) of $(CH_3)_3N$ was recovered by fractionation. Continued reaction and sublimation at 105° resulted in a 90% isolated yield of white, crystalline quinuclidine-monofluoroborane, m.p. 145–7°. *Anal.* Calcd for $C_7H_{15}BFN$: C, 58.8; H, 10.5; B, 7.57; N, 9.79. Found: C, 58.8; H, 10.5; B, 7.51; N, 9.78. The $^{11}B$ resonance in $CH_2Cl_2$ solution was nearly identical in appearance to those of other amine-monofluoroboranes[1, 3] ($\delta + 9.5$ ppm; $J_{BH} = 108$ Hz, $J_{BF} = 79$ Hz).

*Quinuclidine-difluoroborane*

In a typical reaction 1.1604 g (10.6 mmol) $(CH_3)_3NBHF_2$ and 1.0712 g (9.6 mmol) of quinuclidine were combined as above resulting, after 48 hr, in 8.6 mmol (88%) of $(CH_3)_3N$. After continued reaction the solid residue was sublimed at 110° giving a 92% yield of white crystalline quinuclidine-difluoroborane (m.p. 134–6°). *Anal.* Calcd for $C_7H_{14}BF_2N$: C, 52.3; H, 8.69; B, 6.72; N, 8.69. Found: C, 52.39; H, 8.84; B, 6.77; N, 8.69. The product was found to be soluble in $CH_2Cl_2$ and $C_6H_6$. Its $^{11}B$ spectrum was virtually identical in form to that of other amine-difluoroboranes[1, 3] with $\delta + 18.0$ ppm.

*Quinuclidine-trifluoroborane*

A reaction between 1.0416 g (9.4 mmol) of quinuclidine and 1.1964 g (9.40 mmol) of $(CH_3)_3NBF_3$, carried out as described in the foregoing, produced an 88% yield (1.479 g) of quinuclidine-trifluoroborane (m.p. 161–4°) *Anal.* Calcd for $C_7H_{13}BF_3N$: C, 47.0; H, 7.27; N, 7.83. Found: C, 46.7; H, 7.59; N, 7.85. The product was soluble in $CH_2Cl_2$ and $C_6H_6$. Its $^{11}B$ spectrum consisted of a singlet at $\delta + 18.0$ ppm.

## DISCUSSION

The preparation of fluoroborane adducts by the fluorination of borane adducts with HF is applicable to most amine-boranes which are soluble in solvents such as $CH_2Cl_2$ and $C_6H_6$. It is less suitable for those which require more polar solvents such as ethers because of the strong solvation of HF by those solvents. For that reason we have been investigating other, indirect methods for preparing fluoroborane adducts. The use of base displacement reactions to prepare triethylenediamine and piperazine adducts was described earlier[3] and we wish to report here further studies of that method.

Competitive reactions as shown generally in (1) can be regarded as dynamic equilibria. The relative proportion of $(CH_3)_3N$ displaced by a given base (D) provides a measure of the relative donor abilities of the two bases towards the borane acceptor. Quinuclidine is generally believed[5] to be a stronger base than trimethylamine mainly because of the steric advantages of its

bicyclic structure. Our results confirm this since quinuclidine displaced substantially more than 50% of the trimethylamine from each of its four borane adducts. The relative proportions of $(CH_3)_3N$ released after 48 hr at room temperature in benzene are: 72% ($BH_3$), 84% ($BH_2F$), 88% ($BHF_2$), 88% ($BF_3$). The greater amounts of $(CH_3)_3N$ displaced in the case of the more fluorinated boranes probably indicates that quinuclidine is a harder base than trimethylamine and, therefore, forms more stable adducts with those acceptors.

$$(CH_3)_3NBH_{3-x}F_x + D \rightleftharpoons DBH_{3-x}F_x + (CH_3)_3N \quad (x = 0,1,2,3) \tag{1}$$

The successful use of base displacement reactions to prepare mono- and difluoroborane adducts requires that reasonable yields be accessible and that the integrity of the borane group not be lost due to disproportionation. We maximized the yield of quinuclidine boranes by periodically removing free trimethylamine, thereby driving the equilibrium represented by reaction (1) to the right. This is a variation of the transamination method[6] and it appears to work effectively in this system. The principle advantage of this approach over using an excess of displacing base is in the simpler purification of the product.

Previous investigators[7, 8] have observed apparent disproportionation of the borane moiety in attempting to prepare fluoroborane adducts. Work in this laboratory[9] involved reaction (2), an attempt to prepare free fluoroborane or possible difluorodiborane. The stronger Lewis acid, $BF_3$, as assumed to displace the weaker, $BH_2F$, from its adduct, but only diborane and trifluoroborane were detected among the products. Evidently, $BH_2F$, if formed, rapidly disproportionates.

$$(CH_3)_3NBH_2F + BF_3 \xrightarrow[25°]{CH_2Cl_2} (CH_3)_3NBF_3 + 1/3B_2H_6 + 1/3BF_3 \tag{2}$$

The fact that no detectable disproportionation of the fluoroborane group was observed in the preparation of triethylenediamine fluoroborane adducts[3] or the quinuclidine adducts described here suggests that free borane may not be involved in the reaction. This is consistent with a bimolecular nucleophilic displacement mechanism. Neither quinuclidine·$BH_2F$ nor quinuclidine·$BHF_2$ show any tendency to disproportionate at room temperature in the solid state or in solution as evidenced by their NMR spectra. The relative large melting ranges of the pure solids may indicate that disproportion begins near the melting point.

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# Nitrosation of N,N′-ethylenebis(salicylaldehydeiminato) acetylacetonate cobalt(III) monohydrate

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Recently, the reactions of coordinated organic ligands are receiving much attention, as they may open up new routes to the syntheses of new and novel complexes and as well as organic materials. In an earlier communication[1] we have reported the nitration of N,N′-ethylenebis(salicylaldehydeiminato) acetylacetonato cobalt(III) monohydrate, [Co(salen)(acac)]·$H_2O$. In this note we report the nitrosation of [Co(salen)(acac)]·$H_2O$.

## EXPERIMENTAL

Solvents and chemicals were purified and dried by usual procedures. Nitrosation of [Co(salen)(acac)]·$H_2O$[2] was done as follows:

The heterochelate [CO(salen)(acac)]$H_2O$ (0.85 g., 0.002 mole) was dissolved in 150 ml of methanol and nitric oxide[3] was passed through the solution in a slow stream for about 8 hr at room temperature. The deep brown crystals formed were filtered through suction, washed with methanol and dried over sulphuric acid in a desiccator. Yield ~50%; m.p. ~280°C (dec.).

The complex is insoluble in common organic solvents, but soluble in coordinating solvents on heating. (Found: C, 55.89; H, 4.80; N, 9.39; Co, 12.88%; Calc. for [Co(salen)(acac-No)]: C, 55.63; H, 4.42; N, 9.27; Co, 13.02%).

## RESULTS AND DISCUSSION

Slow passage of nitric oxide through a solution of [Co(salen)(acac)]·$H_2O$ in methanol yields the complex [Co(salen)(acac-No)]. Low solubility of the nitroso-product in organic solvents prevents the recrystallisation of this complex. However, the complex was thoroughly washed with methanol.

In the case of nitration of [Co(salen)(acac)]·$H_2O$[1], nitro groups enter at 5 and 5′-positions of phenyl residue and at γ-position of acetylacetone residue of the chelate depending on the concentration of $Cu(NO_3)_2 \cdot 3H_2O$ used. No 3,3′-nitrosubstituted product could be isolated. However, in the present case of nitrosation reaction, nitroso group enters only at the γ-position of the acetylacetone residue of the complex. The nitroso group then rearranges to the isonitrosoform as this form is expected to be more stable. A similar phenomenon has been recently observed by Bose and Patel[4] when they reacted N,N′-ethylenebis(acetylacetoneimino) M (where M = Cu(II) or Ni(II)) with nitric oxide in methyl alcohol.

The present nitroso complex is diamagnetic showing the presence of tervalent cobalt atom.

The IR spectrum of [Co(salen)(acac-No)] in Nujol mull shows a very sharp band at about 1720 $cm^{-1}$ which can be attributed to a free carbonyl group. The position and intensity rules out the possibility of this band being to C=N or C=C, which have been assigned around 1600 $cm^{-1}$. Tris(isonitrosoacetylacetonato) cobalt(III) gives a similar band at 1680 $cm^{-1}$ which has been attributed to a free carbonyl group[5]. Another strong band in the complex observed at 1155 $cm^{-1}$ which can be attributed to the coordinated N–O[4], the coordination being through the nitrogen