Reaction of Ni[P(OC_2H_5)$_3$]$_4$ with I_2 in pyridine in a closed, evacuated flask released no gas. Determination of excess I_2 in the pyridine after this reaction showed that 5 moles of I_2 per mole of Ni[P(OC_2H_5)$_3$]$_4$ was used. Known bis(triphenylphosphine)platinum hydride, $[(C_6H_5)_3P]_2PtH_2$, exhibits infrared M–H stretching bands at 1670 and 815 cm.$^{-1}$.[5] The infrared spectra of tetrakis(triethyl phosphite)nickel(0) in Nujol and in a KBr pellet are practically identical with the spectrum of purified triethyl phosphite over the range 4000 to 670 cm.$^{-1}$ showing no indication of M–H stretching frequencies. The most plausible equation which fits this stoichiometry is

$$\mathrm{Ni[P(OC_2H_5)_3]_4 + 5I_2 \longrightarrow NiI_2 + 4(C_2H_5O)_3PI_2}$$

We anticipate that this new preparation will provide a more convenient route to other Ni(0) complexes and will help clarify aspects of other reactions involving Ni(II) organophosphorus complexes.

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Contribution from the Chemistry Section,
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Synthesis of Nitrogen Trifluoride from the Elements

By Walter Maya

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It has been reported that nitrogen trifluoride cannot be synthesized from the elements by the action of an electrical discharge at low temperatures.[1] We have found that nitrogen trifluoride can be synthesized in substantial yields by the action of an electrical discharge at liquid nitrogen temperature on a gaseous mixture of fluorine and nitrogen. The synthesis of nitrogen trifluoride appears analogous to the synthesis of fluorine oxides from the elements under essentially the same conditions.[2,3] However, unlike the fluorine oxides, variations of the stoichiometry of the fluorine–nitrogen mixtures did not lead to other nitrogen–fluorine compounds such as N_2F_2.

Experimental

A 15-kv., 30-ma. luminous tube transformer was used as the power source for the discharge. The discharge cell consisted of a glass U-tube, with each leg of the U equipped with copper electrodes. The electrodes were 8 cm. apart. The whole cell was immersed in liquid nitrogen during the discharge. A mixture of fluorine and nitrogen was prepared by admitting the requisite amount of gas into an evacuated 2-l. glass bulb; the fluorine is storable in glass for days, if the glass is thoroughly dry. Mixtures of the two gases investigated were 25% F_2, 75% N_2 and 75% F_2, 25% N_2. The best yields of NF_3 were obtainable with the latter mixture. The gaseous mixture was admitted into the discharge cell at a rate that allowed the pressure in the cell to remain between 20 and 40 mm. After leaving the discharge cell, the noncondensable gases were pumped off through a bubbler manostat filled with Fluorolube oil, through a fluorine absorber made of sodium chloride–soda lime, and to a vacuum pump.

At the end of the reaction, the discharge cell was allowed to warm gradually to room temperature, and its contents were fractionated in a high-vacuum line by pumping through a −196° and a −210° (solid nitrogen) trap. In the latter trap, nitrogen trifluoride in yields of 30% was found. The NF_3 was characterized by infrared[4] and mass spectra.

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Matrix Isolation Spectra of $HBCl_2$ and $DBCl_2$

By C. D. Bass, L. Lynds, T. Wolfram, and R. E. DeWames

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In a recent paper, DeWames and Wolfram have developed a method of vibrational analysis of substituted and perturbed molecules utilizing the Green's function and partitioning techniques.[1] We have applied this method to planar XY_3 molecules and calculated the spectra of $HBCl_2$ and $DBCl_2$ from the observed frequencies of BCl_3, without invoking a force constant model.[2] Since the gas phase spectra of $HBCl_2$ and $DBCl_2$ are complicated by interference from BCl_3, which cannot be eliminated,[3] we obtained the matrix isolation spectra of $HBCl_2$–BCl_3 and $HBCl_2$–$DBCl_2$–BCl_3 mixtures in a large excess of argon at ≈ 10°K.[4] Although the matrix spectra are also quite complex, they have provided us with additional evidence in support of our gas phase calculations and assignments, as well as showing some interesting features.

Figure 1 shows some of the typical matrix isolation spectra which were observed. Table I lists the results of our calculations, and the gas phase assignments. The following correlations from the $HBCl_2$–BCl_3 spectrum are immediately apparent: a triplet with peaks at 2647, 2639, and 2625 cm.$^{-1}$ in the region where the B–H stretching band is observed (2617 cm.$^{-1}$); two bands at 1116 and 1099 cm.$^{-1}$, which are near the frequencies of the B^{10} and B^{11} components of the B–Cl asymmetric stretch (1100 and 1089 cm.$^{-1}$); and a doublet centered at 895 cm.$^{-1}$, which correlates with the frequency assigned to the B^{11}–H in-plane deforma-

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