genolysis and is completely cleaved by reducing agents,[6] one could expect that complete phenoxy substitution would render the PN ring less vulnerable to hydrogenation and thus would permit exclusive conversion of the nitro groups to amino groups. We found indeed that catalytic hydrogenation of 2,2,4,4,-6,6-hexakis(*p*-nitrophenoxy)phosphonitrile (I) with Raney nickel does not attack the PN nucleus to any appreciable extent. 2,2,4,4,6,6-Hexakis(*p*-aminophenoxy)phosphonitrile (II) was obtained in high yields using aniline as solvent.

Phosgenation of 2,2,4,4,6,6-hexakis(*p*-aminophenoxy)phosphonitrile (II) in refluxing *o*-dichlorobenzene, utilizing a high dilution factor to suppress reaction between amino and isocyanato groups, and recrystallization of the crude reaction product gave pure 2,2,4,-4,6,6-hexakis(*p*-isocyanatophenoxy)phosphonitrile (III) in 46% yield. Higher polymeric PN compounds of the urea type were obtained as by-products, but not further identified. All six isocyanato groups of compound III reacted readily with methanol and 1-butanol to give the expected hexamethyl- and hexabutylcarbamates (IV, V) in quantitative yields. With glycols such as diethylene glycol, high polymeric urethanes were obtained.

Experimental Section

2,2,4,4,6,6-Hexakis(*p*-aminophenoxy)phosphonitrile (II).—A 1000-ml stirring autoclave was charged with 77.0 g of 2,2,4,4,6,6-hexakis(*p*-nitrophenoxy)phosphonitrile,[5] 550 g of aniline, and 10 g of Raney nickel catalyst. The vigorously agitated mixture was hydrogenated under 1000-psig hydrogen pressure at 80–90° until no further pressure drop was recorded (~3–4 hr). The reaction mixture was filtered, and most of the aniline solvent was removed by distillation *in vacuo*. The residue was diluted with ether to yield a gummy precipitate from which the liquid layer was decanted. The gum was treated with 250 ml of 2 *N* sulfuric acid and filtered. The solid filter cake was then added to 500 ml of 2 *N* sodium hydroxide and, with stirring, heated to 80–100° for 15 min. After filtration, the crude compound II was washed with water to neutrality, dried *in vacuo* over P_2O_5, and finally recrystallized from *o*-dichlorobenzene; yield 37.0 g (60%) of pure II, mp 189–190°. Additional amounts of II were obtained by working up the mother liquors. *Anal.* Calcd for $C_{36}H_{36}N_9O_6P_3$: C, 55.17; H, 4.63; N, 16.11; P, 11.80. Found: C, 55.17; H, 4.91; N, 16.11; P, 11.61.

2,2,4,4,6,6-Hexakis(*p*-isocyanatophenoxy)phosponitrile (III).—Phosgene was passed into 250 ml of boiling *o*-dichlorobenzene at a rate of approximately 10 g/hr. To this mixture was slowly added a hot solution of 20 g of 2,2,4,4,6,6-hexakis(*p*-aminophenoxy)phosphonitrile (II) in 1500 ml of *o*-dichlorobenzene over a period of 4.5 hr. After complete addition, heating and slow passage of $COCl_2$ was continued overnight. The solution was then filtered from 6.5 g of insoluble material. The solvent was distilled *in vacuo* to render 17 g of a brown solid which was recrystallized, first from toluene and then from acetonitrile, to yield 11 g (46%) of pure III, mp 149–150°. *Anal.* Calcd for $C_{42}H_{24}N_9O_{12}P_3$: C, 53.68; H, 2.57; N, 13.42; P, 9.90. Found: C, 53.85; H, 2.60; N, 13.16; P, 9.24.

The hexamethylcarbamate (IV), mp 148°, was prepared from III and boiling methanol in 98% yield. *Anal.* Calcd for $C_{48}H_{48}N_9O_{18}P_3$: C, 50.93; H, 4.27; N, 11.13; P, 8.22. Found: C, 50.73; H, 4.25; N, 11.02; P, 8.22.

The hexa-*n*-butylcarbamate (V), mp 163.5–164°, was prepared from III and *n*-butyl alcohol in quantitative yield. *Anal.* Calcd for $C_{66}H_{84}N_9O_{18}P_3$: C, 57.26; H, 6.12; N, 9.11; P, 6.72. Found: C, 57.24; H, 6.12; N, 9.15; P, 6.67.

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CONTRIBUTION FROM THE CHEMISTRY RESEARCH SECTION, ROCKETDYNE, A DIVISION OF NORTH AMERICAN AVIATION, INC., CANOGA PARK, CALIFORNIA

Tautomerism Exchange in $B_3H_7 \cdot N(CH_3)_3$ and $B_3H_7 \cdot THF$

BY MOREY A. RING, EDWARD F. WITUCKI, AND R. CLIVE GREENOUGH

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Hydrogen tautomerism in boron hydride like compounds was first deduced from the nmr spectrum of aluminum borohydride.[1] Discovery of hydrogen tautomerism in many other boron hydrides and derivatives followed.[2,3] The B^{11} nmr spectrum of $B_3H_7 \cdot O(C_2H_5)_2$ indicated that all borons were identical (single chemical shift value)[4] and that hydrogen tautomerism was taking place (all borons were equally spin–spin coupled to all seven protons).[2] In order to account for the single chemical shift value it is necessary to assume that rapid Lewis base exchange is taking place (possibly synchronized with the hydrogen tautomerism).

Lewis base exchange would not be expected when the ligand is a much stronger Lewis base than the solvent. In this case, the B^{11} nmr spectrum of a $B_3H_7 \cdot LB$ (LB = Lewis base) should show at least one nonequivalent boron. In order to check this, we obtained the B^{11} nmr spectra of $B_3H_7 \cdot N(CH_3)_3$ in benzene and in ether and the spectra of $B_3H_7 \cdot THF$ (tetrahydrofuran) in benzene and in THF.

Trimethylamine triborane ($B_3H_7 \cdot N(CH_3)_3$) was prepared according to the method of Graybill, Ruff, and Hawthorne.[5] The THF adduct was synthesized by a slight modification of the method of Kodama.[6] B^{11} nmr spectra were obtained with Varian nmr spectrometers, Models V-4300 (12.83 Mc) and DP-60 (19.3 Mc). Chemical shifts and coupling constants were determined using boron trichloride, boron triethyl, and aqueous sodium borohydride as external standards. The spectrum of trimethylamine triborane in benzene is compatible with the superposition of two octets, both with *J* values of about 35 cps. One octet appears to be centered about 35 cps upfield and is half the intensity

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of the other octet. The data are compatible with a model in which only hydrogen tautomerism is taking place and Lewis base exchange, if any, is too slow to be detected. There are, therefore, two types of boron in the ratio of 2:1 which would be expected to have different chemical shift values. These two kinds of boron would be expected to couple to the seven hydrogens by similar (but not identical) amounts. Assuming that both kinds of boron spin couple to the seven hydrogens equally, agreement between the intensities predicted and the intensities observed can be shown (Table I).

TABLE I

PREDICTED *vs.* OBSERVED INTENSITIES

Low-field borons	0.02	0.13	0.40	0.67	0.67	0.40	0.13	0.02	
High-field borons		0.01	0.07	0.20	0.33	0.33	0.20	0.07	0.01
Predicted (calcd) intens	0.02	0.14	0.47	0.87	1.00	0.73	0.33	0.09	0.01
Obsd intens (octet)		0.14[a]	0.49	0.88	1.00	0.71	0.29	0.08[a]	
Predicted (calcd) intens (sextet)			0.37	0.83	1.00	0.67	0.67	0.23	

[a] Weakest peaks rather broad.

Table I also shows the calculated intensities where tautomerism excludes the bridge hydrogens. This model would predict two sextets in place of two octets. A better fit is obtained for the two octets. This result is in agreement with the observed intensities in the B^{11} nmr spectrum of $B_3H_8^-$ [3,5] which show better agreement for a nonet (tautomerism including bridge hydrogens) than for a septet (tautomerism excluding bridge hydrogens).

The spectrum of THF–triborane in THF consisted of an unresolved multiplet which is compatible with that of a single octet with $J = 38$ cps. These data are in agreement with the Phillips, Miller, and Muetterties data on $B_3H_7 \cdot O(C_2H_5)_2$ in diethyl ether.[4]

Two systems have been examined; in one there was Lewis base exchange and tautomerism ($B_3H_7 \cdot$THF in THF) and the other case we interpreted as only hydrogen tautomerism taking place ($B_3H_7 \cdot N(CH_3)_3$ in benzene). It was known that if $B_3H_7 \cdot N(CH_3)_3$ and $N(CH_3)_3$ were mixed further, decomposition of the B_3H_7 moiety would occur. Accordingly, $B_3H_7 \cdot N(CH_3)_3$ was dissolved in diethyl ether and the nmr spectrum was obtained. The same spectrum as $B_3H_7 \cdot N(CH_3)_3$ dissolved in benzene was obtained and we interpret this result as indicating the ether to be too weak to promote Lewis base exchange. From these results it was expected that no Lewis base exchange would occur in $B_3H_7 \cdot$THF dissolved in benzene. However, the nmr spectrum of $B_3H_7 \cdot$THF in benzene appeared to be similar to that of $B_3H_7 \cdot$THF in THF.

This latter result suggests that Lewis base exchange does occur in $B_3H_7 \cdot$THF in benzene, or, at least, that in benzene the THF molecule is able to migrate from one boron atom to another in the same molecule. Since THF is a much weaker base than trimethylamine, the fact that this observation was made for the THF adduct and not for the trimethylamine adduct is not surprising. A similar exchange reaction has been observed for the $(CH_3)_3Ga \cdot N(CH_3)_3$ adduct with both $(CH_3)_3Ga$ and $N(CH_3)_3$ in an inert solvent.[7]

Chemical shifts relative to boron trifluoride etherate as zero are listed in Table II.

TABLE II

CHEMICAL SHIFTS

Compound	Chemical shift, cps
THF·B_3H_7 in THF	10 ± 1
THF·B_3H_7 in benzene	
(position of max intens)	10 ± 2
$(CH_3)_3N \cdot B_3H_7$ in benzene	
High-field octet	16.2 ± 1
Low-field octet	14.4 ± 1
$(CH_3)_3N \cdot B_3H_7$ in ether	
High-field octet	14.4 ± 1
Low-field octet	13.0 ± 1

In summary we may conclude: Lewis base exchange in $B_3H_7 \cdot$LB is not a prerequisite to hydrogen tautomerism, or at least the rate at which H tautomerism occurs is much greater than Lewis base exchange.

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CONTRIBUTION FROM THE CRYSTALLOGRAPHY LABORATORY, UNIVERSITY OF PITTSBURGH, PITTSBURGH, PENNSYLVANIA 15213

On the Crystal Structures of the Red, Yellow, and Orange Forms of Mercuric Iodide

BY G. A. JEFFREY AND M. VLASSE

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HgI_2 has three modifications, the well-known red and yellow forms,[1] stable above and below 126°, respectively, and a metastable orange form.[2,3] No detailed single-crystal structure studies have been reported. Early powder work[4] on the red form determined the single variable positional parameter which was such that the iodine atoms are distorted somewhat from ideal close packing. The parameters of the yellow form have been inferred[1] to be similar to those of $HgBr_2$ and the structure of the orange form is unknown. In this Note we give the results of a three-dimensional single-crystal structure refinement of the parameters for the red and yellow forms and some preliminary crystal data for the orange form.

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