In the second scheme, compound III, prepared as previously described,[2] was refluxed in toluene for 7 days in the presence of sufficient KOC_6H_5 to react with all the chlorine. The reaction product was washed with dilute KOH and H_2O and dried over $CaSO_4$, and the solvent was distilled off. The residue was an oil which was dissolved in *n*-hexane and decolorized. By concentrating and chilling the residual solution, compound IV was obtained in 60% yield, melting at 90–92°.

Anal. Calcd. for compound I: C, 41.52; H, 2.90; Cl, 20.43; N, 8.07; P, 17.85. Found: C, 38.92; H, 2.80; Cl, 20.76; N, 8.31; P, 18.38. Calcd. for compound III: C, 19.29; H, 4.86; Cl, 28.48; N, 22.50; P, 24.88. Found: C, 19.18; H, 4.61; Cl, 28.56; N, 22.85; P, 24.86. Calcd. for compounds II and IV: C, 52.74; H, 6.09; N, 15.38; P, 17.01. Found (compound II): C, 52.57; H, 6.11; N, 15.58; P, 16.85. Found (compound IV): C, 52.70; H, 6.37; N, 15.43; P, 16.95.

The melting point of a mixture of compounds II and IV was undepressed and their infrared spectra were superimposable. Because the configuration of compound III had been established previously[2] by H^1 n.m.r. spectra as that in which each $-N(CH_3)_2$ group is attached to a separate P atom and in a *trans* arrangement with respect to the PN ring, the identity of compounds II and IV was sufficient to establish the configuration of compound I, with the reservation that no configurational changes take place in the formation of compounds II and IV.

As further confirmation of the structure of compounds II and IV, their H^1 n.m.r. spectra were obtained on a Varian A-60 n.m.r. spectrometer in 20% deuterated chloroform solution with tetramethylsilane as an internal reference. The spectrum of each compound consisted of two sets of doublets in the ratio of 2:1. The high-field doublet had a chemical shift of 138.8 c.p.s. from TMS while that of the low-field doublet was 154.2 c.p.s. The coupling constant in each case was 12.5 ± 0.1 c.p.s., a value taken to be indicative of the $\equiv P(OC_6H_5)N(CH_3)_2$ grouping. The outside possibility that a $-N(CH_3)_2$ group migrated during formation of II and IV is contraindicated by the previously-established J'_{PH} value of 11.8 c.p.s. for the $\equiv P[N(CH_3)_2]_2$ grouping. Both spectra were identical and confirmed that both reaction routes produced the same compound. The fact that there are two doublets in a ratio of 2:1 indicates that the $-N(CH_3)_2$ groups are in a *cis-cis-trans* configuration about the ring and that no rearrangement takes place when III is converted to IV.

In addition to this evidence for the nongeminal substitution pattern in the formation of phenoxy esters of $(NPCl_2)_3$, some intimation of this was given by the fact that only 3 of the 4 moles of KOC_6H_5 reacted in the synthesis of compound I. Evidently, the formation of $\equiv P(Cl)(OC_6H_5)$ deactivates the remaining Cl so that the second $-OC_6H_5$ substitution takes place on another $\equiv PCl_2$ group. This pattern is similar to that observed for strongly basic amines such as H_2NCH_3 and $HN(CH_3)_2$.[3,4]

Acknowledgment.—This work was carried out for the Armstrong Cork Company, Lancaster, Pa., to whom we are indebted for long-term financial assistance.

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Contribution from the W. A. Noyes Laboratory,
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Decomposition of the Adducts of Diethylamine and Isopropylamine with Nitrogen(II) Oxide

By Ronald O. Ragsdale, Bruce R. Karstetter,
and Russell S. Drago

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It has been demonstrated[1-3] that nitric oxide behaves as a Lewis acid toward a large number of primary and secondary amines and some diamines. The products are diamagnetic and their infrared and nuclear magnetic resonance spectra support the formulation $R_2NH_2^+R_2NN_2O_2^-$ for secondary amines and $RNH_3^+RNHN_2O_2^-$ for primary amine products. Products of widely varying stability are obtained. It was observed[2] that the diethylamine–nitric oxide addition compound in a closed bottle undergoes slow decomposition over a period of several days in the presence of air, producing a brown oil. The compound has a slight vapor pressure at room temperature and if left on the desk top will eventually disappear. However, it can be stored indefinitely at −78° or under ether at room temperature. It was of interest to study the decomposition of the diethylamine–nitric oxide addition compound in the presence and absence of oxygen. This study was also extended to the decomposition of the isopropylamine–nitric oxide product in the presence of oxygen.

Experimental

Purification of Materials.—Matheson commercial grade nitric oxide was used directly in the high pressure preparation of the nitric oxide products. In the atmospheric pressure method nitric oxide was purified by bubbling through 10 *M* potassium hydroxide and dried by passing through columns of sodium hydroxide pellets. The amines were purified by distillation from anhydrous barium oxide.

Preparation of $(C_2H_5)_2NH_2^+(C_2H_5)_2NN_2O_2^-$ and $(CH_3)_2CHNH_3^+$-$(CH_3)_2CHNHN_2O_2^-$.—The compounds were prepared by both high pressure and atmospheric pressure methods as described in earlier publications[1,2] and were checked by means of elemental analyses.

Decomposition of $(C_2H_5)_2NH_2^+(C_2H_5)_2NN_2O_2^-$.—A weighed sample (11.2 g.) was placed in a loosely-capped bottle and al-

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lowed to decompose in the presence of air. After 3 days, the sample had decomposed to a dark amber oil and a weight increase of 0.7 g. was observed. Distillation of the sample showed that the first fraction was water. The second and larger fraction distilled over at 175°. Redistillation of the second fraction gave a pure product which was identified as diethylnitrosamine. The compound was identified by its boiling point (found 177°, reported 176.9°), refractive index (found 1.4381 at 20°, reported 1.4386 at 19.9°), and analysis.

Anal. Calcd. for $(C_2H_5)_2NNO$: C, 47.20; H, 9.89; N, 27.43. Found: C, 47.01; H, 9.71; N, 27.31.

The amount of diethylnitrosamine obtained by decomposition and distillation was 6.8 g., which represents a 62% conversion of all the diethylamine in the starting material to diethylnitrosamine.

The decomposition of the diethylamine product was also carried out over a 3-day period in an atmosphere of pure, dry oxygen which was replenished as reaction occurred. Again an amber-to-red oil was formed, but a large mass of solid material was also produced. During the next 10 days there was no further uptake of oxygen, and the solid remained. The oil was identified as diethylnitrosamine. The solid material was filtered from the oil and washed with ether. It was recrystallized from chloroform by flooding the saturated solution with ether, and pale-yellow, needle-like hygroscopic crystals were recovered. The product gives a positive nitrite test,[4] reacts with hydrochloric acid to evolve nitric oxide, melts at 79–81°, and when heated above the melting point it decomposes to a yellow oil having the characteristic odor of diethylnitrosamine. Its infrared spectrum shows strong absorption in the 2950–2400 $cm.^{-1}$ region, indicating the presence of the substituted ammonium ion, and the elemental analyses are in agreement with theoretical calculations for diethylammonium nitrite.

Anal. Calcd. for $(C_2H_5)_2NH_2^+NO_2^-$: C, 39.97; H, 10.08; N, 23.32. Found: C, 39.48; H, 10.17; N, 23.19.

In the absence of oxygen the decomposition of the diethylamine addition compound is very slow at room temperature as the compound failed to reach an equilibrium vapor pressure in 28 days at 30°. The compound was decomposed rapidly at 90° (a 1.0-g. sample decomposed completely in approximately 1 hr.) in a vacuum system and a white solid condensed in a −78° trap. The noncondensable gas (nitric oxide) was bubbled through a saturated ferrous sulfate solution acidified with H_2SO_4, and a positive test for nitric oxide was obtained.[5,6] The solid in the −78° trap was allowed to melt (a liquid is obtained at room temperature) and was dissolved in ether. Dry hydrogen chloride gas was bubbled through the solution. A solid was formed and was identified as diethylammonium chloride by infrared and elemental analyses.

In a second experiment the addition compound was decomposed in a vacuum system and the products were transferred to a 5-cm. NaCl gas cell at 140 mm. pressure. The infrared spectrum showed the presence of only two products, diethylamine and nitric oxide. This analysis was confirmed by experiments in which the infrared spectra of nitric oxide, diethylamine, and nitric oxide and diethylamine together were recorded and compared with the spectrum of the decomposition products.

Decomposition of $(CH_3)_2CHNH_3^+(CH_3)_2CHNHN_2O_2^-$.—The primary amine–nitric oxide adduct was allowed to decompose in the presence of dry oxygen. No signs of decomposition are observed within 48 hr. at ice temperature. At room temperature the compound remained for 0.5–2 hr. before any decomposition occurred. After decomposition begins, it is very rapid and 4–5 g. of product will decompose within 3 min. A Dry Ice trap was connected to the reaction flask to collect any volatile gases which are condensable at −78°. A gas was trapped which gave a Baeyer's test for unsaturation. The decomposition liquid in the reaction flask was collected and attempts were made to fractionate the liquid with a small spinning-band column. The first fraction was collected at 35–45° and a phenylthiourea derivative was formed which melted sharply at 101°. This derivative identified isopropylamine as one of the products.[7]

The second fraction was collected from 45 to 60°, and as it passed through the condenser into the receiver it crystallized. On the basis of the infrared spectrum and a positive test with the Griess reagent[8] it is suggested that this compound is a nitrite.

On collecting higher fractions it was observed that further decomposition occurred. In fraction 4 (70–80°) the presence of alcohol was indicated by means of a positive periodic acid test.[9] Water was definitely identified by its infrared spectrum and elemental analyses in fraction 5 (80–95°). Attempts to make derivatives in the latter fractions were hampered by the small amounts obtained in each fraction and also by the fact that each fraction contained more than one component, as shown by gas chromatography.

Discussion

The diethylamine–nitric oxide addition compound has been shown to decompose to diethylamine and nitric oxide in the absence of oxygen. The decomposition is very slow at room temperature and the rate does not become rapid until the temperature is above 80°. The decomposition is assumed to proceed by a path which is the reverse of the path by which the addition compound is formed.[10]

In the presence of oxygen, the diethylamine compound is slowly oxidized to diethylammonium nitrite and diethylnitrosamine according to the equation

$$(C_2H_5)_2NH_2^+(C_2H_5)_2NN_2O_2^- + {}^1/_2O_2 \longrightarrow (C_2H_5)_2NH_2^+NO_2^- + (C_2H_5)_2NNO \quad (1)$$

It seems likely that the amine and nitric oxide are oxidized to the nitrite and the nitrosamine after dissociation of the adduct since gaseous mixtures of dimethylamine, oxygen, and nitric oxide in the ratio 4:1:4 yield dimethylnitrosamine and dimethylammonium nitrite.[11] In one experiment we prepared diethylnitrosamine and diethylammonium nitrite directly from the gas-phase reaction of diethylamine, nitric oxide, and air. The preparation of various nitrosamines has also been accomplished by reaction of the corresponding amines with a mixture of nitrogen dioxide and nitric oxide.[12]

When the oxidation of the diethylamine–nitric oxide product is allowed to proceed in the presence of air, the solid diethylammonium nitrite does not appear in the reaction product since moisture from the atmosphere brings about its dissolution in the liquid product. Subsequent distillation of the oil results in a yield of diethylnitrosamine of better than 100%, based upon eq. 1 for the oxidation of the addition compound. During the distillation the nitrite apparently decomposes to diethylnitrosamine and water.

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[9] R. Shriner, R. Fuson, and D. Curtin, ref. 8, pp. 129 and 130.

[10] R. S. Drago, Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, p. 143.

[11] British Patent 772,331 (Oct. 26, 1955), to Olin Mathieson Chemical Corp.

[12] German Patent 1,011,431 (July 4, 1957), to E. I. du Pont de Nemours and Co.

The decomposition of the isopropylamine–nitric oxide product in the presence of oxygen gave several decomposition products. Water and isopropylamine were definitely identified as products. Qualitative indications were obtained for the presence of an olefin, a nitrite, and an alcohol. Some of these products can be accounted for if it is considered that some of the addition compound decomposes into starting materials (isopropylamine and nitric oxide). The nitric oxide is oxidized by oxygen to nitrogen dioxide, and a mixture of NO and NO_2 in the presence of moisture forms some nitrous acid. The nitrous acid can then form an isopropylammonium diazonium compound which is unstable and will decompose to an alcohol, an olefin, and nitrogen. Water can be accounted for as one of the products of decomposition of isopropylammonium nitrite.[13]

Acknowledgment.—The authors are grateful to the U. S. Army Research Office (Durham) for financial support of this research under Grant No. USDA-G-72.

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CONTRIBUTION FROM THE REACTION MOTORS DIVISION,
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Reaction of Decaborane and Its Derivatives. II. Addition Reactions of 6,9-Bis(acetonitrile)decaborane with Hydrazine

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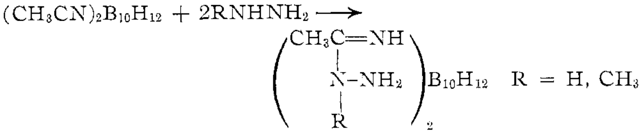
The structure of 6,9-bis(acetonitrile)decaborane (I) as reported by Reddy and Lipscomb[1] indicates that the $-B_{10}H_{12}-$ nucleus is electrophilic. Thus, the addition of an HX molecule (where H is labile and X has an unshared electron pair) to the CH_3CN moiety should be facile. That primary and secondary amines would add to I was shown by Hawthorne and Pitochelli[2] and by work in these laboratories.

We wish to report that hydrazine will react with I in a similar manner to form hydrazidine-like products.



$$(CH_3CN)_2B_{10}H_{12} + 2RNHNH_2 \longrightarrow \left(\begin{array}{c} CH_3C{=}NH \\ | \\ N{-}NH_2 \\ | \\ R \end{array}\right)_2 B_{10}H_{12} \quad R = H, CH_3$$

Treatment of I with stoichiometric quantities of hydrazine hydrate or methylhydrazine hydrate results in the formation of 6,9-bis(acethydrazidine)decaborane (II, R = H) and 6,9-bis(acet-N-methylhydrazidine)-decaborane (III, R = CH_3), respectively.

It is of interest to note that the ease with which the amines and hydrazines add to the nitrile is parallel to the ease with which R_fCN compounds (R_f = fluoroalkyl) add HX materials.[3] In both situations, the nitrile functionality is bonded to a highly electrophilic group. In the fluoroalkyl nitriles the electrophilic group is covalently bonded to the nitrile carbon, whereas in I the bonding is coordinate covalent between $\equiv N$: and $B_{10}H_{12}$. Nevertheless, both nitriles readily undergo HX addition.

Experimental

6,9-Bis(acethydrazidine)decaborane.—Hydrazine (9.1 g., 0.28 mole) was added slowly to a cooled, stirred suspension of bis(acetonitrile)decaborane (30.0 g., 0.15 mole) in 380 ml. of benzene. After addition, the mixture was heated for 16 hr. at reflux. After cooling, a white, crystalline solid (38.6 g.) was filtered, washed with benzene, and then dried under vacuum. The product does not melt up to 360°. Its infrared spectrum is consistent with that expected of a hydrazidine having N—H, NH_2, N—N, and C=N bands as well as the -BH absorption at 3.9 μ.

Anal. Calcd. for $C_4H_{26}N_6B_{10}$: C, 18.03; H, 9.83; N, 31.54; B, 40.60. Found: C, 17.6; H, 9.8; N, 31.3; B, 39.9.

6,9-Bis(acet-N-methylhydrazidine)decaborane.—Methyl hydrazine hydrate (25 ml.) was added slowly to a cooled, stirred suspension of bis(acetonitrile)decaborane (10 g.) in 100 ml. of benzene. The reaction was exothermic but there was no gas evolution. After addition, the mixture was heated for 3 hr. at reflux. On cooling, a white solid separated which was filtered, recrystallized from acetonitrile, then dried under vacuum. The solid decomposes explosively at 218–219°: its infrared spectrum is similar to that of II.

Anal. Calcd. for $C_6H_{30}N_6B_{10}$: B, 36.73. Found: B, 36.9.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Preparation and Properties of Tetrakis(trifluorophosphine)palladium(0)

BY G. F. SVATOS AND E. E. FLAGG

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We wish to report the preparation of tetrakis(trifluorophosphine)palladium(0). This compound is of particular interest since no palladium compounds of this type have previously been prepared. Its properties are generally very similar to those of $[Ni(PF_3)_4]$.[1,2]

Experimental

Preparation of $[Pd(PF_3)_4]$.—The procedure employs $[Pd(CO)_2Cl_2]$[3] and PF_3[4] as reactants in a high-pressure Pyrex bomb. The

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