[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

# Steric Effects in Displacement Reactions. XI. The Heats of Reaction of Diborane with Pyridine Bases. Steric Strains in Homomorphs of *o*-*t*-Butyltoluene and Hemimellitene[1]

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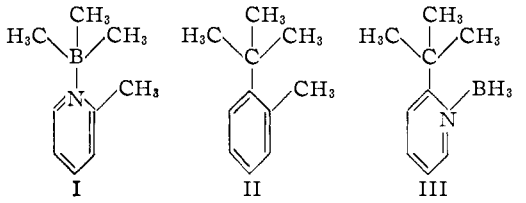
The heats of reaction of gaseous diborane with pyridine, the monoalkylpyridines and 2,6-lutidine, all in nitrobenzene solution, have been determined. The values (in kcal./mole) for the reaction, $\frac{1}{2}B_2H_6(g) + Py(soln.) = Py:BH_3(soln.)$, are: pyridine, 17.91 ± 0.24; 4-picoline, 18.45 ± 0.18; 3-picoline, 18.15 ± 0.16; 2-picoline, 17.16 ± 0.11; 2-ethylpyridine, 16.93 ± 0.10; 2-isopropylpyridine, 16.66 ± 0.14; 2-*t*-butylpyridine, 12.11 ± 0.12; 2,6-lutidine, 16.34 ± 0.16 kcal./mole. The increases in the heat of reaction of diborane with 3- and 4-picoline over pyridine are in accord with the increased base strength caused by the inductive effect of the methyl groups. The decreases in the heats of reaction of the 2-alkylpyridines are attributed to the conflicting steric requirements of the borane group and the 2-alkyl substituents. From the difference between the calculated and experimental heats, strains of 6.3 and 2.7 kcal./mole are estimated for 2-*t*-butylpyridine–borane and 2,6-lutidine–borane and for the related homomorphs, *o*-*t*-butyltoluene and hemimellitene. The borane addition compounds of pyridine and the monoalkylpyridines were prepared and characterized.

The geometry of the borane group in addition compounds should be closely related to that of the methyl group in related derivatives. Similarly, the geometry of the trimethylboron group should be closely related to that of the *t*-butyl group.[3] On this basis similar strains would be anticipated for the three compounds, I–III.



I II III

In addition, heat of formation data for the borane addition compounds of the pyridine compounds were desired for comparison with the available data on the activation energies for the reaction of methyl iodide with the same bases.[4,5]

The development of a calorimeter[3] which could be used with the usual high vacuum equipment[6] made it possible to undertake the determination of the heats of reaction of diborane with the pyridine bases.

## Results

In the original experiments dilute solutions of pyridine in nitrobenzene were treated in the calorimeter with a slight excess of diborane. Unfortunately, the resulting heats of reaction proved quite erratic. The formation of small quantities of hydrogen was noted. This was attributed to the presence of traces of water present in the calorimeter in spite of the most elaborate precautions to work under anhydrous conditions.

It proved possible to overcome these difficulties by utilizing nitrobenzene solutions containing the pyridine base in considerable excess. A small quantity of diborane was introduced into the calorimeter and permitted to react. After temperature equilibrium had been achieved, a carefully meas-

(1) Based upon a thesis submitted by Lionel Domash in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(3) H. C. Brown and D. Gintis, THIS JOURNAL, **78**, 5378 (1956).

(4) H. C. Brown and A. Cahn, *ibid.*, **77**, 1715 (1955).

(5) H. C. Brown, D. Gintis and H. Podall, *ibid.*, **78**, 5375 (1956).

(6) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

TABLE I

CALORIMETRIC HEATS OF REACTION OF DIBORANE WITH PYRIDINE, MONOALKYLPYRIDINES AND 2,6-LUTIDINE IN NITROBENZENE SOLUTION AT 25°

| Base | Borane,[a] mmoles | $\Delta T$, °C. | Molar heat of reacn. $(-\Delta H)$[b] $\frac{1}{2}(BH_3)_2(g.)$[c] | Molar heat of reacn. $(-\Delta H)$[b] $\frac{1}{2}(BH_3)_2$ (soln.)[d] |
|---|---|---|---|---|
| Pyridine | 1.942 | 1.595 | 17.72 | 14.4 |
| | 0.500 | 0.413 | 17.82 | 14.5 |
| | 1.940 | 1.619 | 17.99 | 14.7 |
| | | Mean[e] | 17.91 ± 0.24 | 14.6 |
| 4-Picoline | 1.401 | 1.182 | 18.19 | 14.9 |
| | 0.615 | 0.534 | 18.72 | 15.4 |
| | 1.303 | 1.115 | 18.45 | 15.2 |
| | | Mean | 18.45 ± 0.18 | 15.2 |
| 3-Picoline | 1.858 | 1.566 | 18.17 | 14.9 |
| | 1.598 | 1.366 | 18.44 | 15.1 |
| | 1.431 | 1.199 | 18.08 | 14.8 |
| | | Mean[e] | 18.16 ± 0.16 | 14.9 |
| 2-Picoline | 1.441 | 1.153 | 17.25 | 14.0 |
| | 1.686 | 1.334 | 17.05 | 13.8 |
| | 1.468 | 1.167 | 17.14 | 13.8 |
| | | Mean[e] | 17.16 ± 0.11 | 13.9 |
| 2-Ethylpyridine | 1.335 | 1.040 | 16.79 | 13.5 |
| | 1.415 | 1.119 | 17.06 | 13.8 |
| | 1.121 | 0.881 | 16.95 | 13.7 |
| | | Mean | 16.93 ± 0.10 | 13.6 |
| 2-Isopropylpyridine | 1.292 | 1.001 | 16.70 | 13.4 |
| | 0.578 | 0.451 | 16.82 | 13.5 |
| | 1.273 | .971 | 16.45 | 13.2 |
| | | Mean | 16.66 ± 0.14 | 13.4 |
| 2-*t*-Butylpyridine | 0.688 | .384 | 12.03 | 8.7 |
| | 1.471 | .829 | 12.15 | 8.9 |
| | 0.973 | .537 | 11.90 | 8.6 |
| | | Mean[e] | 12.11 ± 0.12 | 8.8 |
| 2,6-Lutidine[f] | 1.272 | .970 | 16.45 | 13.2 |
| | 1.145 | .875 | 16.48 | 13.2 |
| | 1.006 | .751 | 16.10 | 12.8 |
| | | Mean | 16.34 ± 0.16 | 13.0 |

[a] Mmoles $B_2H_6/2$. [b] Kcal./mole. [c] $-\Delta H$ for reaction: $\frac{1}{2}B_2H_6(g) + Py(soln.) = Py:BH_3(soln.)$. [d] $-\Delta H$ for reaction: $\frac{1}{2}B_2H_6(soln.) + Py(soln.) = Py:BH_3(soln.)$. [e] Mean value based upon additional measurements not included in table. [f] Measurements by D. Gintis.

ured quantity of diborane was added and the temperature rise noted. The heat of reaction was then calculated on the basis of the diborane introduced. In many cases a second and a third measurement could be carried out on the same solution.

The experimental data are summarized in Table I.

Because of the low solubility of diborane in nitrobenzene, it proved impossible to determine the heat of solution by direct measurement in the calorimeter. Accordingly, the heat of solution was estimated to be 3.3 kcal./mole from the change in solubility of diborane with temperature. The heats of reaction for all components in solution (Table I) are based on this value for the heat of solution.

Diborane was shown to react with each of the pyridine bases in the ratio $^1/_2$ $B_2H_6$:Py. The borane addition compounds were examined for melting points and vapor pressures. The data are summarized in Table II.

TABLE II

PHYSICAL PROPERTIES OF THE PYRIDINE–BORANES

| Compound | M.p., °C. | Vapor pressures, mm. (°C.) | | |
|---|---|---|---|---|
| Pyridine–borane | 10–11 | 2.5(104) | 5.4(120) | |
| 4-Picoline–borane | 72–74 | 1.2(105) | 2.8(115) | 6.3(126) |
| 3-Picoline–borane | 9.5–10.5 | 1.1(100) | 2.1(110) | 3.6(120) |
| 2-Picoline–borane | 50–51 | 1.7(100) | 3.5(110) | 5.5(119) |
| 2-Ethylpyridine–borane | 48–50 | 2.5( 80) | 5.3( 90) | 8.6(100) |
| 2-Isopropylpyridine–borane | 18–19 | 2.0( 60) | 4.6( 70) | 8.0( 80) |
| 2-*t*-Butylpyridine–borane | 24–25 | 7.0( 35) | 14( 45) | 22( 50) |
| 2,6-Lutidine–borane | 110–111 | 1.1( 85) | 2.3( 95) | 4.9(105) |

The addition compounds appeared to be stable to air and water, but react vigorously with acid to evolve hydrogen. The compounds are quite unstable to heat. Thus when an attempt was made to measure the vapor pressure of pyridine–borane at 120°, rapid decomposition with evolution of hydrogen was observed. At the same time the product changed from a colorless liquid to a red solid of negligible volatility. Similar changes were noted with the other derivatives. At lower temperatures the reaction is slower, but occurs at a rate sufficiently fast so as to render vapor pressure measurements difficult. In order to avoid these secondary reactions, the vapor pressure measurements were taken as rapidly as possible with minimum exposure to high temperatures. For these reasons the pressures reported are subject to relatively large uncertainties and are of interest primarily in indicating the marked increase in the vapor pressure with increasing steric requirements of the 2-alkyl group.

## Discussion

For convenience in following the discussion the experimental results are summarized in Table III.

It is apparent that just as in the case of the corresponding reactions with trimethylboron[3] and boron trifluoride[7] there is observed an increase in the heat of reaction over pyridine of 0.3 kcal. for 3-picoline and 0.5 kcal. for 4-picoline. Such increases can be correlated with the observed increases in base strengths for the three bases: pyridine, $pK_a$ 5.17; 3-picoline, 5.68; 4-picoline, 6.02.

(7) H. C. Brown and R. H. Horowitz, THIS JOURNAL, **77**, 1733 (1955).

TABLE III

MOLAR HEATS OF REACTION OF DIBORANE WITH PYRIDINE, THE MONOALKYLPYRIDINES AND 2,6-LUTIDINE IN NITROBENZENE SOLUTION AT 25°

| Base | Heat of reaction, kcal./mole, $-\Delta H$ $^1/_2B_2H_6$ (g) | $-\Delta H$ $^1/_2B_2H_6$ (soln.) | $\Delta H_{Py} - \Delta H_{B,}$[a] kcal./mole | $\Delta H_{4\text{-Pic}} - \Delta H_{B,}$[a] kcal./mole |
|---|---|---|---|---|
| Pyridine | 17.9 | 14.6 | 0 | |
| 4-Picoline | 18.5 | 15.2 | 0.5 | |
| 3-Picoline | 18.2 | 14.9 | .3 | |
| 2-Picoline | 17.2 | 13.9 | | −1.3 |
| 2-Ethylpyridine | 16.9 | 13.6 | | −1.5 |
| 2-Isopropylpyridine | 16.7 | 13.4 | | −1.8 |
| 2-*t*-Butylpyridine | 12.1 | 8.8 | | −6.3 |
| 2,6-Lutidine | 16.3 | 13.0 | | (−2.7)[b] |

[a] Calculated from the original data (Table I). [b] Calculated using $-\Delta H_{4\text{-Pic}} + 0.5$ for the value in absence of steric effects.

In the case of the 4-alkylpyridines, no significant change in the $pK_a$ values was observed as the alkyl group was varied from methyl, to ethyl, to isopropyl, to *t*-butyl.[8] Similarly, no significant change was observed in the heats of reaction with boron trifluoride.[7] Consequently, it is reasonable to assume that the heats of reaction of diborane with the 4-alkylpyridines should not differ significantly from that observed for 4-picoline. In view of the similarity in base strengths of the 4-alkylpyridines with those of the 2-derivatives, the value of 18.5 kcal./mole may be taken as an estimate of the heat of reaction of diborane with the 2-alkylpyridines in the absence of steric effects.

The deficiencies (in kcal./mole) of 1.3 for 2-methyl-, 1.5 for 2-ethyl-, 1.8 for 2-isopropyl- and 6.3 for 2-*t*-butylpyridine may be taken as a measure of the steric strains resulting from the interaction of the borane group with the corresponding alkyl groups in the 2-position.

It was pointed out previously that 2-picoline–trimethylboron (I) is homomorphic with 2-*t*-butylpyridine–borane (III). The strain of 6.3 kcal./mole, estimated for the latter compound, agrees with the value 5.9 kcal./mole, estimated from the trimethylboron data,[3] within the limits of experimental uncertainty in each value (±0.2 kcal./mole).

The heats of combustion of *o*-, *m*- and *p*-*t*-butyltoluene have been measured recently by Dr. E. J. Prosen and his associates at the National Bureau of Standards. They calculate the standard heats of formation (gas, 25°) to be (kcal./mole): *p*-*t*-butyltoluene, −13.6 ± 0.4; *m*-*t*-butyltoluene, −13.0 ± 0.4; *o*-*t*-butyltoluene, −8.0 ± 0.4.[9] From these data the strain in *o*-*t*-butyltoluene (II) may be estimated to be 5.6 kcal./mole.

From these three values it appears reasonable to assign a relatively constant strain of 6.0 kcal./mole to the homomorphs of *o*-*t*-butyltoluene.

From the observation that a 4-methyl group increases the heat of reaction of pyridine with diborane by 0.5 kcal./mole, the heat of reaction of 2,6-lutidine with diborane is estimated as 19.0 kcal./mole in the absence of steric effects. The experimental heat, 16.3 kcal./mole, leads to an estimate

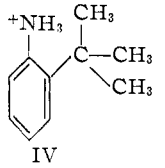
(8) H. C. Brown and X. R. Mihm, *ibid.*, **77**, 1723 (1955).

(9) Private communication from Dr. E. J. Prosen.

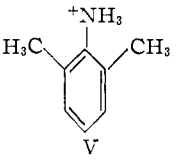
of 2.7 kcal./mole strain in homomorphs of 1,2,3-trimethylbenzene (hemimellitene).

The difference in the heats of formation of 1,3,5-trimethylbenzene and 1,2,3-trimethylbenzene is 1.6 kcal./mole for the gases at 25°.[10] The discrepancy between the 1.6 kcal./mole value, based on heat of combustion data, and the 2.7 kcal./mole value, based on the calorimetric data reported in the present paper, is relatively large. However, the agreement is probably as good as can be expected in view of the fact that the 1.6 kcal./mole value is based on a small difference between two very large quantities. We shall therefore adopt 2.7 kcal./mole as our estimate for the strain in homomorphs of hemimellitene.

Some time ago the unexpected weakness of *o-t*-butylaniline and 2,6-dimethylaniline was attributed to strain in the corresponding anilinium ions (IV, V), leading to an increased tendency to transfer the proton to the solvent.[11]




IV




V

The strains estimated in the present study for homomorphs of *o-t*-butyltoluene and hemimellitene support this interpretation.

It should be pointed out that the transfer of a proton to the solvent is postulated to reduce, but not to eliminate, the strain. Consequently, the change in strain accompanying ionization must be much less than that accompanying the formation of the homomorphic borane derivatives. The situation is further complicated by the question of the importance of steric hindrance to solvation of the anilinium ion and amine in the ionization equilibrium.[12]

The data on the heats of reaction of diborane with the pyridine bases permit a direct comparison of the strains in these addition compounds with the strains in the related transition states for the reaction of methyl iodide with these bases. Discussion of these phenomena will be deferred to the final paper of this group to permit a systematic examination of the relationship between the steric requirements of the acid component and the strains in the addition compounds and transition states.

## Experimental Part

**Materials.**—The nitrobenzene and pyridine bases have been described in previous papers of this series.

Diborane was prepared by the reaction of lithium aluminum hydride with boron trifluoride etherate.[13] The diborane was purified by fractional distillation in the vacuum line from traps maintained at −140°. Since diborane tends to undergo some decomposition on standing at room temperature, the gas was purified at frequent intervals. As a further test, the purity of the gas was tested just before each calorimetric measurement by combining the theoretical amount of the gas with a slight excess of the pyridine base. The small amount of free gas after the reaction was carefully measured and applied as a correction in calculating the amount of gas introduced into the calorimeter.

**Calorimeter.**—The calorimeter was constructed according to the design previously reported.[3] The heat capacity of the calorimeter was established by measuring the heat of solution of hydrogen chloride in water. Three successive determinations gave a mean value of 4.65 ± 0.12 cal./deg. The value 0.355 cal./g. was used for the heat capacity of nitrobenzene. The calorimeter thermometer was calibrated against a Leeds and Northrup platinum resistance thermometer and Mueller bridge.

**Heat of Reaction of Diborane with the Pyridine Bases.**—Because of the difficulty of preparing and keeping diborane of high purity, we originally undertook to measure the heats of reaction by using the pyridine base in slight deficiency. In these experiments solutions of 2.5 mmoles of the pyridine base in 40.00 ml. of nitrobenzene were introduced into the calorimeter with careful attention to protection from oxygen and moisture. To this solution was added a slight excess of diborane, 2.6–2.7 mmoles. The results proved to be erratic. The formation of hydrogen was noted and it was concluded that the reaction of diborane with residual traces of moisture was the cause of the experimental difficulty.

The procedure was thereupon modified to use relatively concentrated solutions of the pyridine base (10 mmoles in 40.00 ml. of nitrobenzene) and the diborane in deficiency. The solution was introduced into the calorimeter and treated with a small amount of diborane (0.2–0.5 mmole) to remove residual traces of moisture and other reactive impurities. A sample of diborane was treated with a measured amount of pyridine base and the residual gas measured (0.5–2.0%). A carefully measured sample of diborane (0.5–1.0 mmole), corrected for the presence of this impurity, was introduced into the calorimeter and permitted to react with the base. After the temperature rise had been noted and the calorimeter had returned to the initial temperature, a second and then a third measurement was made on the same solution. Consistent results in a series of three such measurements were considered to indicate the substantial removal or absence of reactive impurities.

The results are summarized in Table I.

**The Heat of Solution of Diborane in Nitrobenzene.**—Because of the low solubility of diborane in nitrobenzene, the heat of solution could not be determined in the calorimeter. The solubility of diborane in nitrobenzene was determined at 6, 14.2 and 24.0°. From the Henry's law constants (mm./mmole), 2242, 2634 and 3231 at the three temperatures, the heat of solution was calculated to be 3.3 kcal./mole. The solubility of diborane was quite low and no great accuracy can be claimed for this value.

**Addition Compounds of Diborane with the Pyridine Bases.** A weighed sample of the pyridine base was introduced into a small tensimeter containing a mercury manometer which could be completely immersed. A slight deficiency of diborane was permitted to react. The residual gas was transferred back to a calibrated volume and measured. This correction was applied to the calorimetric run which was carried out soon afterward. The material in the tensimeter was then treated with a second portion of diborane, so that a considerable excess of diborane was present. The excess gas was recovered and measured. In each case the ratio of the reactants was $1.00Py:0.50B_2H_6$, corresponding to the formation of a simple borine derivative, $Py:BH_3$.

The products were either colorless liquids, melting slightly below room temperatures, or white crystalline solids. On heating, they showed a tendency to undergo decomposition with the formation of orange to red colored solids. The tensimeter was immersed in an oil-bath and the pressures measured at several temperatures (Table II). Because of the secondary decomposition mentioned above, the pressure readings were made rapidly to minimize the effect of these changes.

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(10) F. D. Rossini, ed., "Selected Values of Properties of Hydrocarbons," National Bureau of Standards, Washington, D. C., 1951.

(11) H. C. Brown and A. Cahn, THIS JOURNAL, **72**, 2939 (1950).

(12) P. D. Bartlett, M. Roha and R. M. Stiles, *ibid.*, **76**, 2349 (1954).

(13) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *ibid.*, **69**, 1199 (1947); I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik and G. B. L. Smith, *ibid.*, **74**, 901 (1952).