tivity in neutral and alkaline solutions should render it a very convenient reducing agent for organic compounds.[1]

Schlesinger and co-workers[2] have described the preparation of a 1.0-ml. sample of pyridine–borane from the reaction of pyridine and diborane at room temperature. They report its melting point as 10–11° and list some vapor pressures. A very convenient method for the preparation of this compound has been developed in this Laboratory. It is similar to one developed by Schaeffer[3] for the preparation of trimethylamine–borane except that a safer solvent than ether, pyridine, is used; a cheaper and more readily available reagent than $LiBH_4$, $NaBH_4$, is used; and a simpler method for separating the reaction products is available.

The reaction for the preparation of pyridine–borane follows the equation

$$C_5H_5N{\cdot}HCl + NaBH_4 \longrightarrow C_5H_5NBH_3 + NaCl + H_2$$

Sodium chloride precipitates quantitatively from the pyridine solution of pyridine–borane and the two can be separated readily by filtration. The excess pyridine is distilled away under vacuum at 50°. Unreacted $C_5H_5N{\cdot}HCl$ is precipitated by the addition of an equal volume of ether. The ether pumped off and the treatment repeated. Two or three such treatments yield pure pyridine–borane. Alternatively, the crude pyridine–borane can be purified by shaking with water, in which it is insoluble and with which it does not react readily, to dissolve any contaminating NaCl or $C_5H_5N{\cdot}HCl$. Several preparations of pyridine–borane have been performed. They all yield 80–90% of 95–100% pure compound.

In a typical preparation 65.9 g. of $C_5H_5N{\cdot}HCl$ (0.57 mole)[4] was suspended in 150 ml. of pyridine and treated with 22.14 g. (0.585 mole) of $NaBH_4$ in 575 ml. of pyridine by the usual Grignard technique. The reaction was completed smoothly according to the general procedure outlined above. Forty-nine grams of pyridine–borane was obtained for a yield of 93%. The yield was quantitative based on the NaCl produced (33.2 g.). The crude product was treated once with ether and then extracted with water. A yield of 87% of 99.8% pure $C_5H_5NBH_3$ was obtained.

The identity of pyridine–borane was established by the following analyses: (a) hydrogen evolved during acid hydrolysis amounted to 3.20% (theor. = 3.25); (b) reducing power by the iodate procedure[5] yielded 3.18 and 3.17% H_2; (c) boron by base titration in the presence of mannitol after base hydrolysis to remove pyridine yielded 11.51 and 11.55% (theor. = 11.64); and (d) pyridine by the $CuSO_4$–KCNS technique[6] yielded 84.19 and 84.70% (theor. = 85.11%). In agreement with the findings of Schlesinger and co-workers the compound melted at 10–11°, and exhibited a vapor pressure of less than 0.1 mm. at room temperature. It is quite soluble in ether but insoluble in water. It has an index of refraction of 1.5280 at 25°. It reacts rapidly with acids with the evolution of hydrogen.

DEPARTMENT OF CHEMISTRY
HOWARD UNIVERSITY
WASHINGTON 1, D. C.

---

[1] The action of pyridine–borane on certain organic compounds is now under investigation in this Laboratory.

[2] H. C. Brown, H. I. Schlesinger and S. Z. Cardon, THIS JOURNAL, **64**, 328 (1942).

[3] G. W. Schaeffer and E. R. Anderson, *ibid.*, **71**, 2143 (1949).

[4] Pure anhydrous $C_5H_5N{\cdot}HCl$ is readily prepared by treating a solution of pyridine in ether with pure dry HCl, filtering off the excess ether and pumping dry *in vacuo*.

[5] E. Jensen, D. Lyttle and W. Struck, *Anal. Chem.*, **24**, 1843 (1952).

[6] *C. A.*, **19**, 2181 (1924).

New Preparations of Anhydrous Iodides of Groups I and II Metals

BY MODDIE D. TAYLOR AND LOUIS R. GRANT

RECEIVED OCTOBER 1, 1954

Because of the current interest in reactions in non-aqueous solvents anhydrous iodides have assumed importance since their solubility is generally appreciable in such solvents. These compounds are usually not conveniently prepared from their hydrated forms because they tend to pass over to basic iodides during the process of dehydration. Other methods of preparation include the direct reaction of the metal and iodine and the action of ammonium iodide on the metal oxide at elevated temperature. The former reaction is inconvenient because the metal is often not available and the latter, besides being inconvenient because the reaction is between solids at elevated temperature, seldom goes quantitatively to completion and nearly always is contaminated with residual ammonium iodide. Two methods for preparing anhydrous iodides have been developed in this Laboratory. They both are rapid, quantitatively complete and yield a pure iodide. The methods have been applied specifically to lithium and barium iodides but are almost certainly suitable for other metal iodides of groups I and II and may prove suitable for iodides of many other metals.

Preparation of Lithium Iodide.—Lithium iodide is prepared by the action of lithium hydride on iodine in ether solution.

$$2LiH + I_2 \xrightarrow{\text{ether}} 2LiI + H_2$$

Lithium hydride is used in excess and is readily filtered away from the lithium iodide which is very soluble in ether. The ether is pumped away leaving pure LiI.

In a typical experiment 19.0 g. (0.075 mole) of I_2 was mixed with 1.36 g. (0.17 mole) of LiH intimately in a 500-ml. three-neck flask provided with a stirrer and a dropping funnel containing 250 ml. of ether. The ether was added in small portions initially because the reaction is quite vigorous. Hydrogen was given off during the reaction and continued to be evolved until approximately 100 ml. of ether had been added. One hundred-fifty more milliliters of ether was now added and the mixture was refluxed for one hour. The mixture was filtered and the ether distilled away leaving a white salt tinged slightly yellow. After vacuum drying for one hour at 30–35°, 19.7 g. of a pure white salt was obtained for a yield of 98%.

A gravimetric iodide analysis indicated a purity of 99.0%. An analysis for lithium by passing an aqueous solution of lithium iodide through the acid form of a cation-exchange resin and titrating the acid eluted indicated a purity of 99.23%. If not properly protected from the atmosphere, lithium iodide assumes a yellowish tint and eventually becomes a deep brown.

Preparation of Barium Iodide.—An attempt to prepare barium iodide by the method developed for lithium iodide failed. It was discovered, however, that this substance could be prepared by a method equally as convenient and effective. Barium hydride reacts spontaneously with ammonium iodide in pyridine to yield barium iodide.

$$BaH_2 + 2NH_4I \xrightarrow{C_5H_5N} BaI_3 + 2NH_3 + H_2$$

Barium hydride is used in excess and is filtered away from the BaI_2 which dissolves in the pyridine, in which it is quite soluble.

In a typical experiment 12.0 g. (0.086 mole) of BaH_2 was suspended in 500 ml. of anhydrous pyridine in a 1-liter round-bottom, three-neck flask equipped with a dropping funnel and a mercury sealed stirrer; 21.87 g. (0.151 mole) of NH_4I dissolved in 125 ml. of pyridine was introduced into the dropping funnel and slowly added to the BaH_2 suspension with stirring. The evolution of hydrogen served as a good indicator for the completion of the experiment. The resulting mixture was filtered through a medium porosity funnel and the pyridine distilled away under vacuum.

The resulting salt was dried at 80–100° in the vacuum oven and analyzed as $BaI_2 \cdot C_5H_5N$ (pyridine determined by difference). The pyridine was removed by heating the compound to 150–160° *in vacuo;* 28.6 g. of anhydrous barium iodide, a yield of 97%, was obtained. It analyzed 100.1% pure by the gravimetric iodide method. Barium iodide can be kept in a stoppered bottle for months during which time it is only slightly discolored.

The quantity of pyridine used can probably be reduced $^1/_2$ or $^1/_4$ since BaI_2 is known to be quite soluble in pyridine.

DEPARTMENT OF CHEMISTRY
HOWARD UNIVERSITY
WASHINGTON 1, D. C.

The Carbon Monoxide Quantum Yield in the Photolysis of Diisopropyl Ketone[1]

BY S. G. WHITEWAY AND C. R. MASSON

RECEIVED NOVEMBER 20, 1954

The CO quantum yield in the photolysis of diisopropyl ketone has been measured using di-*n*-propyl ketone as an internal actinometer.[2,3]

Experimental

The ketones (Eastman Kodak Co. White Label) were stored over Drierite for three months, then distilled through a 12-plate column, the middle fraction being retained. Samples were degassed at about −50° before being used.

The light source was an Hanovia S-100 mercury arc. An essentially parallel beam of light was obtained by a quartz lens and two stops. The light just filled a quartz reaction cell 20 cm. long and 2 cm. i.d., and was then focused by a second quartz lens onto an R. C. A. 935 phototube, connected through a shunt to a Leeds and Northrup type 2290 galvanometer. The reaction cell was contained in an aluminum block furnace, the temperature of which was controlled to ±0.5° with a photoelectric relay operating on the light beam from a galvanometer, the latter being actuated by a thermocouple near the reaction cell.

The absorption coefficients of both di-*n*- and diiso-propyl ketone were measured at 100°, over a pressure range of from 15 to 90 mm., using essentially 3130 Å. light. For this, filters were used consisting of 3 mm. Corning #9863 (Red-purple Corex), 5 cm. of 0.0005 *M* K_2CrO_4, 5 cm. of 0.178 *M* $NiCl_2$ and 2 mm. of Pyrex.[4] The extinction coefficients were 7.5 ± 0.3 and 9.05 ± 0.15 cm.$^{-1}$ moles^{-1} liter for the normal and isoketones, respectively.

Inclusion of the K_2CrO_4 filter gave light intensities so low that photochemical runs to determine CO yields would have been prohibitively long. The absorption experiments were repeated without the K_2CrO_4 filter, from which it was concluded that the ketones exhibited the same relative absorptions with λλ 3130, 3342 Å. as with λ 3130 Å. alone. It was therefore considered that the use of the polychromatic light was justified in subsequent CO yield determinations.

The CO was measured in a gas buret by pumping off at −210°. When other products[2] were measured, C_2H_4 was pumped off from a Ward–LeRoy[5] still at −175°, the C_3 fraction at −135°, *n*-hexane and biisopropyl at −95°. The C_3 fraction was further separated into C_3H_6 and C_3H_8 by analysis in a Blacet–Leighton[6] apparatus, using the hydroxymercurial method.[7] In the diisopropyl ketone photolysis, no C_2 fraction was found, and the fraction pumped off at −210° was found to be entirely CO by combustion in a CuO furnace.

Results

The carbon monoxide data are shown in Table I.

TABLE I

QUANTUM YIELDS

Run[a]	Temp., °C.	Pressure, mm.	Absorption,[b] %	$R_{CO} \times 10^{-11}$, molecules cc.$^{-1}$ sec.$^{-1}$	$\left(\frac{CO_{iso}}{CO_n}\right)^c$	Φ_n	Φ_{iso}
1	50	34.73	41.8	20.30	3.70	0.25[d]	0.93
2		19.88	24.6	3.25			
3	75	43.20	46.0	24.10	3.45	.29[d]	1.00
4		52.50	46.0	6.97			
5	100	18.35	24.0	14.23	2.95	.31[e]	0.92
6		22.38	24.0	4.83			
7	100	18.23	23.9	13.05	3.22	.31	1.00
8		22.23	23.9	4.05			
9	125	48.11	45.0	26.80	3.16	.31	0.98
10		58.06	45.0	8.50			
11	125	19.00	23.6	14.0	3.18	.31	0.99
12		23.00	23.3	4.35			
13	150	50.40	44.7	25.40	3.30	.31	1.03
14		61.47	45.0	7.76			

[a] Odd numbered runs are the iso compound, even numbered are the normal. [b] From absorption data for polychromatic light. [c] Calculated after reducing to the same % absorption for both compounds. [d] Calculated from temperature dependence found by Bamford and Norrish[3] and value found by Masson[2] at 113°. [e] Data of Masson.[2]

The CO quantum yield for the iso compound is thus seen to be essentially unity in the temperature range 50–150°. This indicates that the isobutyryl radical is unstable at the lowest temperature.

The following are more comprehensive analyses for the photolysis products of the two ketones at 100°, using a d.c. operated General Electric AH-6 arc[8] and Pyrex filter. This represents about a two hundred-fold increase in light intensity over that available from the S-100 arc. Ketone pressures were 16.0 mm. Rates are expressed in molecules cc.$^{-1}$ sec.$^{-1}$ × 10^{-13}.

TABLE II

Ketone	R_{CO}	$R_{C_2H_4}$	$\Delta R_{C_3H_8}$	$R_{C_3H_6}$	$R_{C_6H_{14}}$
Normal	6.42	6.25	0.42	0.723	5.46
Iso	24.2	. .	.78	7.75	27.1

The column $\Delta R_{C_3H_8}$ refers to the difference $R_{C_3H_8} - R_{C_3H_6}$. On the basis of similar free-radical mechanisms for the two ketones, this represents the C_3H_8 formed by abstraction of H from the ketone by the propyl or isopropyl radical. Comparison of the ratios C_3H_6/C_6H_{14} shows that disproportionation of radicals plays a greater role, compared to recombination, with the iso compound than with the normal. This is in agreement with the results of Blacet and Calvert[9] for the photolysis of *n*- and isobutyraldehydes.

Of especial interest is the fact that here the absence of a Norrish type II split[10] is accompanied by a CO quantum yield of unity. The absence of such a primary process in this ketone is expected, and is in accordance with the generally accepted idea that a 3-carbon chain adjacent to the carbonyl group is

---

[1] Issued as N.R.C. No. 3519.

[2] C. R. Masson, THIS JOURNAL, **74**, 4731 (1952).

[3] C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1544 (1938).

[4] R. E. Hunt and W. Davis, Jr., THIS JOURNAL, **69**, 1415 (1947).

[5] D. J. LeRoy, *Can. J. Research*, **B28**, 492 (1950).

[6] F. E. Blacet and P. A. Leighton, *Ind. Eng. Chem., Anal. Ed.*, **3**, 266 (1931).

[7] R. Pyke, A. Kahn and D. J. LeRoy, *Anal. Chem.*, **19**, 65 (1947).

[8] S. G. Whiteway and C. R. Masson, *Can. J. Chem.*, **32**, 1154 (1954).

[9] F. E. Blacet and J. G. Calvert, THIS JOURNAL, **73**, 661 (1951).

[10] C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1504 (1935).