B-methyl peak at $\delta -0.15$ remained intact, with its integral ratio to the sum of the *t*-butyl peaks the same as in the starting mixture.

We are exploring other routes to halomethaneboronic esters.

Experimental

Methaneboronic Anhydride-Pyridine Complex.-A solution of 2.4 moles (800 ml., 3 M) of methylmagnesium bromide in ether (Arapahoe Chemical Co.) was added under nitrogen to 300 ml. of methyl borate in 1 l. of ether which was stirred and kept below -55°. The mixture was acidified with a slight excess of 3 Mhydrochloric acid saturated with sodium chloride and then was separated and extracted with three 250-ml. portions of butanol. The organic phase was washed with 150 ml. of saturated sodium chloride, then extracted with 100 g. of sodium hydroxide in 180 ml. of water followed by two portions of 20 g. of sodium hydroxide in 36 ml. of water, and finally with 100 ml. of water. The aqueous solution of sodium methaneboronate was concentrated at 20 mm. until the pot temperature reached 60-80° and a frothy semisolid residue remained. To this was added 400 ml. of pyridine and 50 ml. of water. A solution of pyridine bisulfate was prepared by adding 90 ml. of pyridine dropwise to 110 ml. of concentrated sulfuric acid (caution: exothermic). The pyridine bisulfate was added dropwise to the stirred suspension of sodium methaneboronate and the mixture was refluxed for 2 hr. After cooling, the sodium sulfate was filtered and washed with 250 ml. of benzene. The combined organic phase was refluxed under an efficient 30-cm. packed column fitted at the head with a Dean-Stark trap until all the water was removed (\sim 140 ml.). Benzene and pyridine were distilled through the column, the methaneboronic anhydride-pyridine complex was distilled, b.p. 139-143° (700 mm.), yield 134 g. (82%), solidified on cooling. The analytical sample was sublimed under vacuum, m.p. 91.5-95.5°

Anal. Calcd. for $C_8H_{14}B_8NO_8$: C, 46.95; H, 6.90; B, 15.86; N, 6.85. Found: C, 46.74; H, 7.04; B, 15.62; N, 6.91.

Methaneboronic anhydride^{3a} was obtained in 77% yield by adding 1.67 ml. of 96% sulfuric acid to 6.36 g. of the boronic anhydride-pyridine complex cooled in an ice bath, stirring, and distilling at atmospheric pressure under nitrogen.

Chlorination of Methaneboronic Anhydride .--- Ultraviolet irradiation of 2.7 g. of methaneboronic anhydride and 6.8 g. of tbutyl hypochlorite⁶ in 20 ml. of benzene led to an exothermic reaction. Distillation at 20 mm. led to decomposition. The infrared spectrum of the distillate was that of t-butyl borate apparently contaminated with a related substance. The glassy residue crystallized on treatment with water. Attempts to distil the product at lower pressure also led to decomposition. When 0.42 g. of methaneboronic anhydride and 1.20 g. of t-butyl hypochlorite in 3 ml. of benzene were irradiated at room temperature, about 70 ml. of gas (30%) was collected over water, in which it was somewhat soluble. The same reactants without the solvent were irradiated and the gas was condensed at -70° . It was shown to be methyl chloride by infrared comparison with an authentic sample. The infrared spectrum of the nonvolatile liquid product showed the presence of only a trace of ketone. The bulk of the material was a compound related to t-butyl borate, the chief difference in the infrared spectrum being strong bands at 13.5, 13.7, and 14.0 μ and the absence of t-butyl borate band at 15

Di-t-butyl Methaneboronate.—The method described for the preparation of di-t-butyl ethyleneboronate⁷ was used. Methaneboronic anhydride-pyridine complex (31 g.), 250 ml. of t-butyl alcohol, and 120 ml. of benzene refluxed for 5 days under a 30-cm. column with removal of the water formed yielded 55 g. (70%) of di-t-butyl methaneboronate, b.p. $44-45^{\circ}$ (21 mm.), m.p. -39 to -37° . When the reaction was run on four times this scale in the same apparatus, the yield was only 63% after 27 days. Water failed to separate when a Dean-Stark trap was used. A still head with a cold-finger condenser and space for about 1 ml. of liquid to collect above the takeoff valve proved satisfactory.

Anal. Caled. for $C_9H_{21}BO_2$: C, 62.82; H, 12.30; B, 6.29. Found: C, 62.61; H, 12.35; B, 6.19.

Bis(2-trichloromethyl-2-propyl) methaneboronate was prepared in a manner analogous to the *t*-butyl ester from 2-trichloromethyl2-propanol and the methaneboronic anhydride-pyridine complex in about 50% yield. The analytical sample was sublimed at 0.1 mm., m.p. $94-106^{\circ}$.

Anal. Calcd. for $C_{9}H_{15}BCl_{6}O_{2}$: C, 28.5; H, 3.99; B, 2.85; Cl, 56.2. Found: C, 28.32; H, 3.95; B, 2.80; Cl, 55.84.

Di-n-butyl Chloromethaneboronate.—A mixture of 43 g. (0.25 mole) of di-t-butyl methaneboronate and 30 mg. of t-butyl hypochlorite⁶ in a Pyrex flask surrounded by an ice bath was irradiated with a mercury vapor lamp. The lamp distance was adjusted so that several hours were required for the color to fade. t-Butyl alcohol was distilled in a spinning-band column at atmospheric pressure, then di-t-butyl methaneboronate (18.4 g.). n-Butyl alcohol (50 ml.) was added to the residue and distilled at 20 mm. Di-n-butyl methaneboronate recovery was 8.0 g., b.p. 28° (0.1 mm.). Two fractions of dibutyl chloromethaneboronate were collected at $41-42^{\circ}$ (0.02 mm.), 4.05 g. of 91% and 1.39 g. of 69% material by n.m.r. analysis, the remainder being butyl borate. The yield was 9% or, based on t-butyl methaneboronate and a similar amount of higher boiling residue remained. Pure dibutyl chloromethaneboronate was obtained by refractionation, b.p. $34-35^{\circ}$ (0.02 mm.).

Anal. Caled. for $C_9H_{20}BClO_2$: C, 52.35; H, 9.76; B, 5.24; Cl, 17.16. Found: C, 52.12; H, 9.53; B, 5.29; Cl, 17.35.

The Structure and Some Properties of Phenylhydrazine Borane and 1,1-Diphenylhydrazine Borane

RONALD J. BAUMGARTEN AND MALCOLM C. HENRY

U. S. Army Natick Laboratories, Natick, Massachusetts

Received May 29, 1964

The synthesis of phenylhydrazine borane (I) from phenylhydrazine hydrochloride and sodium borohydride has been reported by Lang.¹ Although the elemental analyses and structural proof of borane I were not included in Lang's patent, its melting point and solubility characteristics, as well as its instability to 50% sulfuric acid, and stability to water and acetic acid, were noted. A later patent of Fleming² reported that borane I, hydrazobenzene borane, and hydrazine borane, had a mild reducing action on vat dyes.



We have prepared borane I and the previously unreported 1,1-diphenylhydrazine borane (II) by a procedure similar to the methods previously described.^{1,2} The elemental analyses and molecular weight determinations, and the spectral and chemical properties reported in this paper for boranes I and II, lend support to the assigned structures.³ In particular, the infrared data summarized for various boron compounds in Table I, lend support for the structures as written.

Borane I is a stable, white, crystalline compound. Hydrolysis of borane I with 3 N hydrochloric acid gave phenylhydrazine hydrochloride, hydrogen, and boric

⁽⁶⁾ H. M. Teeter and E. W. Bell, Org. Syn., 32, 20 (1952).

⁽⁷⁾ D. S. Matteson, J. Org. Chem., 27, 3712 (1962).

⁽¹⁾ K. Lang, German Patent 1,068,231 (1959); Chem. Abstr., 55, 23950g (1961).

⁽²⁾ R. A. Fleming, U. S. Patent 2,992,061 (1961); Chem. Abstr., 55, 24030d (1961).

⁽³⁾ There is still some doubt in regards to which nitrogen the BH; is bonded, but considerations of the relative basicities of the two nitrogens and the method of preparation favor the structures as assigned.

Notes

TABLE I							
CHARACTERISTIC INFRARED	BANDS	OF	VARIOUS	BORON-NITROGEN	Compounds		

- I		Presently assigned	T 1 - D DT 1	Presently assigned
Compound	Lit. $B - H$, cm	$B-H, cm.^{-1}$	Lit. B-N, cm	B-N, cm.
H ₈ NBH ₈	$\gamma 2215,^{a} 2270,^{a} 2315^{a}$		$\gamma_s 776^a$	
	σ 1155, 1258 -		$\gamma_{s} 190^{\circ}$	
OU NH DH	ε /19 ^α	9200 9270 9400	γ 180 ⁰⁰	1. 74914
CH ₃ NH ₂ BH ₃		γ 2300, 2370, 2400		$(\gamma 143)^{\circ}$
(OIL) NHEH		$\sigma 1170, (1520)^{\circ}$	$ca. \gamma 105 hc$	(605) (hr m)
$(CH_3)_2$ NHDH3		γ 2270, 2220, 2000 - 1170 (1909)d	ca. $\gamma 105^{\circ\circ}$	$(\gamma 095)^{-}(01, w)$
(CII.) NPH	. 0970 * 0070*	- 9982 9982 9260	. 1955	(600)d
$(C\Pi_3)_3$ ND Π_3	$\gamma 2512, 2210$	γ 2203, 2203, 2300	$\gamma 1255$	$(\gamma 090)^{\prime\prime}$
	$\sigma 1109, 1110$	$\gamma 2370$ = 1170 (1192)d (1958)d	γ 1200	$(\gamma 0 m)^{-1}$
	$\gamma 2300, 2200$ $\sigma 1168^{f}$	σ 1170, (1123) ⁻ , (1238) ⁻	γ 007 ° °	
	~ 2350.7 22807		~ 1090/	$(\sim 710)^{d}$ (w)
NBH₃	= 1165 f < 0.001	7 1163 (1000)4	, 1000	(),120) ()
$B_{10}H_{12}(NH_3)_2$	$\gamma 2500,^{g} \sigma 1020^{g}$	0 1100, (1000)	Probably below	
			$\gamma 1000^{g}$	
$(CH_3)_3NBH_2t$ -Hex	2381, [*] 2326 [*]			
	No BH ₃ bands in σ 1170 region'			
$(CH_3)_3BNH_3$			$\gamma 1106^{\circ}$	
$H_2NNH_2BH_3$	$\gamma \ 2360,^a \ 2270,^a \ 2210^a$		γ 745,° 752,° γ_{as} 912°	
	σ 1263,ª 1180,ª 1152ª σ 1127ª			
		× 2420 2360 2200		
		7 2420, 2000, 2230		$(n, 715)^{d, j}$
		0 1100, (1210)		(7,10)
()-NNH2BH3 (II)	γ 2465, 2390, 2340, 2265 σ 1155, 1072, (1244), d (1232) d		j
\mathbf{D}^{H}	$1000, 1800^{k}$ (bridge H)			
Diboranes (various)	1900-1800 (bridge fr)			
	$\gamma 2030-2530$			
	$\epsilon 970 - 940$ - 1905 - 1140 ^k (1075 - 1010) ^{k, l}			
R.BNHNHBR.	0 1200-1140 (1010-1010)		$\sim 1500 - 1350^{m}$	
Roragina	$\sim 2504^{n} 2556^{n}$		$\sim 1465 \ n \ 1464^{n}$	
a I Couboou and E D:	olton Z anona allaam Cham 21	0 193 (1961) & Raman mastra	(P. C. Taylor and C	I Cluff Mataina
- 182. 390 (1958). 4 These	assignments are tentative becau	use of the large discrepancies which	h exist in the literature of	ver the assignment

182, 390 (1958). ^d These assignments are tentative because of the large discrepancies which exist in the literature over the assignment of these bands. ^e B. Rice, R. J. Galiano, and W. J. Lehmann, J. Phys. Chem., 61, 1222 (1957). ^f A. R. Katritzky, J. Chem. Soc., 2049 (1959). ^e J. Williams, R. L. Williams, and J. C. Wright, *ibid.*, 5816 (1963). ^h H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, pp. 178-189. ⁱ J. Goubeau and H. J. Becher, Z. anorg. allgem. Chem., 268, 9 (1952). ⁱ The monosubstituted aromatic carbon-hydrogen vibrations show up in this region, making it difficult to assign the boron-nitrogen vibration. ^{*} L. J. Bellamy, W. Gerrard, M. F. Lappert, and R. L. Williams, J. Chem. Soc., 2412 (1958). ⁱ The authors were doubtful about this assignment. ^m K. Niedenzu, Angew. Chem., 76, 168 (1964), Angew. Chem., Intern. Ed. Engl., 3, 87 (1964). ⁿ W. Gerrard, "The Organic Chemistry of Boron," Academic Press, New York, N. Y., 1961, p. 230.

acid. Borane II is a white, crystalline, water-sensitive, compound. Traces of moisture existing in solvents such as benzene, hydrolyze borane II to 1,1-diphenylhydrazine, hydrogen, and boric acid. Boranes I and II reduce silver nitrate and iodine. Borane I was recovered unchanged after treatment with lithium aluminum hydride in tetrahydrofuran, followed by hydrolysis of the reaction mixture.

Boranes I and II are structurally analogous to the amine boranes which are known to reduce aldehydes, ketones, acid chlorides, and p-quinone to the corresponding alcohols in high yields at room temperature.⁴ In addition, olefins are hydroborated by amine boranes, but esters, carboxylic acids, the carboxylate anion, amides, aromatic nitro and azo compounds, alkyl halides, and sulfonic acids are not attacked by amine boranes under any conditions yet tried. We have found

(4) H. Nöth and H. Beyer, Ber., 93, 1078 (1960); M. F. Hawthorne, J. Org. Chem., 23, 1788 (1958); W. M. Jones, J. Am. Chem. Soc., 82, 2528 (1960); H. C. Kelly, Dissertation Abstr., 23, 2317 (1963); W. Gerrard, "The Organic Chemistry of Boron," Academic Press, New York, N. Y., 1961, pp. 155, 160; H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p. 100.

borane I to have similar, but not identical, reducing properties to these amine boranes⁵; namely, aldehydes, ketones, acid chlorides, and *p*-quinone were reduced to the corresponding alcohols by borane I in *ca*. 30-57%yields at $25-30^{\circ}$ (eq. 1), while esters, carboxylic acids, and aromatic nitro compounds were recovered unchanged after prolonged treatment with I. In addition, nitrosobenzene was reduced by borane I to a complex mixture, from which azoxybenzene was identified as a major component. We have also observed that dimethylamine borane reduced nitrosobenzene to azoxybenzene, but the crude yield of azoxybenzene was much purer with the latter reagent.⁶⁻⁸ In contrast to the

⁽⁵⁾ The amine boranes, in turn, behave similarly to sodium borohydride in their reactions with unsaturated compounds. $\!\!\!\!^4$

⁽⁶⁾ Sodium borohydride also reduces nitrosobenzene to azoxybenzene.^{1*} Lithium aluminum hydride, on the other hand, reduces nitrosobenzene to azobenzene.^{7b} In addition, it should be noted that hydrazine hydrate reduces nitrosobenzene to azoxybenzene in the absence of a catalyst, and to aniline in the presence of either palladium-charcoal or Raney nickel.⁸

 ^{(7) (}a) J. H. Boyer and S. E. Ellzey, Jr., J. Am. Chem. Soc., 82, 2528
(1960). (b) Th. Weil, B. Prijs, and H. Erlenmeyer, Helv. Chim. Acta, 36, 142 (1953).

 ⁽⁸⁾ S. Pietra, Ann. chim. (Rome), 47, 410 (1957); Chem. Abstr., 51, 14438h (1957).

hydroborations with amine boranes, however, transstilbene was recovered largely unchanged, even when heated under reflux with borane I for 10 days. Qualitative observations indicated that borane II reacts similarly to borane I (eq. 1). Also isolated were $RR'C==NNHC_6H_5 + RR'C==0$.



The reductions with borane I were carried out in a variety of solvents and in the absence of solvent.⁹ Similar results were obtained in all cases. The presence or absence of air or the presence of an excess or equimolar amount of the carbonyl compound being reduced, did not greatly effect the results. Hydrolysis of the borane intermediates with water or hydrochloric acid also had little effect on product yields. Other identified products are indicated in equation 1. Methylphenylcarbinol of negligible optical activity was produced from either the acidic or neutral workup of the intermediate resulting from the reaction of acetophenone with borane I.

The order of reactivity of borane I with various carbonyl compounds was found to be *o*-phthaldialdehyde⁹ > benzaldehyde > acetophenone > benzophenone.

A crystalline compound, $C_{11}H_{16}N_3BBrO$ (VIII), insoluble in most organic solvents and sensitive to acids, bases, and water, was obtained from the reaction of Nbromosuccinimide with borane I and pyridine in methylene chloride solution. Hydrolysis of VIII with hydrochloric acid gave phenylhydrazine hydrochloride and pyridinium hydrochloride as the major products.¹⁰

Identification of the various reaction products was established by means of melting and mixture melting points, thin layer chromatography, infrared spectra, and gas phase chromatography.

Experimental

Materials and General Identification Procedures.—Molecular weights were taken on a Mechrolab, Inc., osmometer, Model 301A. The Thomas-Hoover capillary melting point apparatus was used for melting point determinations. Infrared spectra were taken on the Beckman IR 9 infrared spectrophotometer. The ultraviolet spectrum was taken on the Perkin-Elmer Model 20L ultraviolet-visible spectrophotometer. The ETL-NPL automatic polarimeter type 143A was used for the optical rotation measurements. Micro, thin layer chromatography was performed as described by Peifer.¹¹ The gas phase chromatography

(10) The products from the hydrolysis of VIII, as well as the infrared spectrum and elemental analyses of VIII, indicate that compound VIII consists of units of phenylhydrazine, pyridine, B-H, Br, and water. A possible structure for VIII follows.



(11) J. J. Peifer, Mikrochim. Acta, 529 (1962).

In addition to the identifying procedures described in each preparation, the products were, as a rule, confirmed with the aid of thin layer chromatography, infrared spectroscopy, and mixture melting points, where applicable.

Phenylhydrazine Borane (I).—Borane I, m.p. 117-119° dec. (lit.¹ m.p. 115°), was prepared in 60-80% yields by the method of Lang.¹

Anal. Caled. for $C_6H_{11}BN_2$: C, 59.08; H, 9.09; N, 22.97; mol. wt., 122. Found: C, 59.20, 59.08; H, 9.10, 9.15; N, 22.86; mol. wt., 121, 120, 122 (osmometer, benzene).

Borane I is soluble in methylene chloride, tetrahydrofuran, benzene, toluene, and ethanol, slightly soluble in chloroform, and sparingly soluble in carbon tetrachloride. Borane I crystallized in long white needles from methylene chloride-hexane. Borane I can be stored for long periods of time in an amber bottle at room temperature.

Infrared spectrum (KBr): 3223 (s), 3238 (s), 3185 (m), 3628 (s), 2419 (s), 2360 (s), 2289 (m), 1941 (w), 1855 (w), 1721 (w), 1602 (m), 1580 (s). 1509 (mw), 1498 (s), 1483 (w), 1446 (m), 1348 (m), 1333 (m), 1297 (s), 1238 (w), 1210 (m), 1163 (s), 1112 (mw), 1092 (w), 1064 (mw), 1037 (m), 1029 (m), 997 (w), 937 (mw), 892 (m), 846 (m), 764 (s), 715 (mw), 690 (s), 615 (w), 580 (m), 501 (s), and 415 (w) cm.⁻¹ principal peaks.

580 (m), 501 (s), and 415 (w) cm. ⁻¹ principal peaks. Ultraviolet spectrum: λ_{max}^{EtoH} 233 m μ (ϵ 1.1 × 10⁴), 282 m μ (ϵ 2.8 × 10³).

1,1-Diphenylhydrazine Borane (II).¹²—Borane II, m.p. 82-84° dec., was prepared in 50% yield by the method used to obtain borane 1.¹ Anhydrous conditions were more critical in this case, as borane II decomposed with hydrogen evolution in moist solvents. Recrystallization from dry toluene-hexane gave white needles, m.p. 87-89° dec. Borane II is soluble in the same solvents as borane I, but the degree of solubility is significantly greater in ether, benzene, methylene chloride, toluene, tetra-hydrofuran, and chloroform.

Anal. Caled. for $C_{12}H_{15}BN_2$: C, 73.44; H, 7.45; N, 13.79. Found: C, 72.64, 72.73; H, 7.67, 7.78; N, 14.05.

Infrared spectrum (KBr): 3248 (mw), 3195 (s), 3160 (s), 3100 (m), 2465 (mw), 2390 (ssh), 2340 (s), 2265 (m), 1588 (s), 1491 (s), 1453 (mw), 1449 (mw), 1364 (mw), 1345 (mw), 1311 (mw), 1298 (mw), 1244 (m), 1232 (m), 1188 (w), 1155 (s), 1072, (m), 1038 (m), 1022 (m), 1017 (msh), 992 (w), 969 (w), 918 (w), 879 (w), 868 (mw), 782 (m), 750 (s), 698 (s), 686 (s), 601 (w), 559 (m), 528 (mw), and 460 (w) cm.⁻¹ principal peaks.

Hydrolysis of Boranes I and II.—Borane I (1.00 g., 8.20 mmoles) was added slowly to an excess of 3 N hydrochloric acid while the solution was being stirred. Vigorous hydrogen evolution was noted during the early stages of the reaction. The hydrolysis was allowed to proceed for 5 hr., after which time 2 ml. of 12 N hydrochloric acid was added. The acid-insoluble product was filtered, washed with 3 N hydrochloric acid, and dried to give 1.02 g. (7.05 mmoles, 86.0%) of phenylhydrazine hydrochloride (III), m.p. 247–249° dec. (lit.¹³ m.p. of III 243–246° dec.). Evaporation of the filtrate gave 540 mg. of crude boric acid. Recrystallization of the crude boric acid from water gave 250 mg. (4.05 mmoles, 49.4%) of boric acid (m.p. and m.m.p. 178–180° dec.).

Borane II was similarly hydrolyzed to give 87.2% of 1,1-diphenylhydrazine hydrochloride (m.p. and m.m.p. 160–165° dec.) and 43.5% of boric acid (m.p. and m.m.p. 178–180° dec.). When borane II was dissolved in wet benzene, 1,1-diphenylhydrazine was identified as a hydrolysis product.

Reductions. A. Acetophenone (IV).—Phenylhydrazine borane (I) (1.67 g., 13.7 mmoles) was added to 20 ml. of dry methylene chloride contained in a three-neck round bottom flask equipped with a pressure equalizing dropping funnel, and a magnetic stirrer. Acetophenone (3.05 g., 25.4 mmoles) dissolved in 5 ml. of methylene chloride was added dropwise at 25° while the solution was being stirred. The reaction mixture was stirred for 24 hr., after which 15 ml. of 4 N hydrochloric acid was added. The reaction mixture was stirred again for 12 hr., after which the product of hydrolysis was suction filtered to give 2.1 g., of crude

⁽⁹⁾ The reaction with o-phthaldialdehyde occurs explosively after an induction period of about 30 sec.; in dilute methylene chloride, the reaction occurs at a moderate rate to give a complex mixture of products. Dimethylamine borane behaves similarly with o-phthaldialdehyde; a small amount of o-xylene α, α' -diol was isolated from the run in methylene chloride solution.

⁽¹²⁾ We wish to thank Mr. Robert E. Sacher, for his aid in the preparation of this compound.

^{(13) &}quot;The Merck Index," 7th Ed., Merck & Co., Inc., Rahway, N. J., 1960, p. 803.

phenylhydrazine hydrochloride. The filtrate was extracted with three 20-ml. portions of methylene chloride. After the combined methylene chloride extracts were washed with water, sodium carbonate solution, and water again, the methylene chloride solution was dried over sodium sulfate. Removal of the methylene chloride in vacuo gave 3.0 g., of a cloudy oil which was largely a mixture of IV, methylphenylcarbinol (V), and the phenyl-hydrazone of IV (VI). Extraction of this oil with ethanol, left behind 120 mg. of crude VI. Recrystallization of VI from etherethanol gave 62 mg. (0.30 mmole, 1.2%) of white crystals melting at 104-106° (lit.14 m.p. 105°). Molecular distillation of the ethanol-soluble material gave 2.2 g. of a clear oil and 270 mg. of tarry residue. Gas phase chromatography (retention time for authentic material and product IV, 5 min. 10 sec.; authentic and product alcohol V, 8 min. 20 sec.; both at 158° and under the column conditions described under Materials) indicated that the ratio of IV to alcohol V to unknown volatiles was 1.5:1.4:0.13. The yields were, therefore, 1.1 g. (9.2 mmoles, 36%) of IV; 1.0 g. (8.2 mmoles, 32%) of alcohol V, $[\alpha]^{25}D + 1.8^{\circ}$ (c 1.1, ethanol), lit.¹⁵ $[\alpha]D + 43.4^{\circ}$, collected from gas phase chromatography; and ca. 4% of unidentified volatiles.

When equimolar portions of borane I and acetophenone were similarly mixed, but worked up under neutral conditions (*i.e.*, water hydrolysis and Florisil chromatography), 21% of alcohol V, $[\alpha]^{25}D - 1.9^{\circ}$ (c 1.8, ethanol), and 6.9% of acetophenone were isolated.

An infrared spectrum of the solid labile intermediate (m.p. 77– 84° dec.) before hydrolysis indicated no carbonyl peak.

Boric acid was also identified as a product in the aqueous solutions of these runs.

B. Benzophenone.—Borane I (553 mg., 4.53 mmoles) was stirred for 2 days with benzophenone (1.43 g., 7.85 mmoles) in 30 ml. of methylene chloride at 25–30°, as described for the reduction of acetophenone. After hydrolysis, 1.71 g. (m.p. 40–55°) of methylene chloride soluble product was isolated. Treatment of this oily solid product with ethanol, and filtration of the ethanol-insoluble crystals, gave 212 mg. (0.78 mmoles, 10%) of the phenylhydrazone of benzophenone (VII) (m.p. 133–136°). Recrystallization of the crude VII from ethanol gave 113 mg. (0.42 mmoles, 5.4%) of white needles, m.p. 136–138° (lit.¹⁴ m.p. 137–138°). Fractional crystallization from hexane of the ethanol-soluble material, gave 806 mg. (4.4 mmoles, 56%) of white needles of benzhydrol, m.p. 66-68° (lit.¹⁶ m.p. 67.5–68°).

When a 2.8-fold molar excess of benzophenone was similarly treated with borane I and worked up as in the acetophenone runs (either acidic or neutral hydrolysis may be used), with the exception that silica gel chromatography was used for the separation of the methylene chloride-soluble products, 12% of phenylhydrazone VII, and 35% of benzhydrol were isolated.

The reaction of a 1:1 molar ratio of benzophenone with borane I in the absence of solvent, gave similar results. Essentially similar products also were obtained under argon or air atmospheres.

C. p-Quinone.—Borane I (1.00 g., 8.20 mmoles) dissolved in 20 ml. of methylene chloride was treated with 1.78 g., 16.5 mmoles, of p-quinone dissolved in 20 ml. of methylene chloride as described for the reduction of acetophenone. The reaction was almost complete after 2 hr. After 1 day at 25–30°, the solution was hydrolyzed and worked up in the manner described for benzophenone to give 995 mg. (9.05 mmoles) of crude hydroquinone, m.p. 159–163°. Recrystallization from ether-hexane gave 275 mg. (2.50 mmoles) of hydroquinone, m.p. 172° (lit.¹⁷ m.p. 172°).

D. Benzaldehyde, a twofold molar excess, dissolved in tetrahydrofuran was treated for 1 day at 25° with borane I, hydrolyzed and worked up as described for acetophenone to give benzyl alcohol (43%) and the phenylhydrazone of benzaldehyde (10%) m.p. $153-155^{\circ}$ (lit.¹⁶ m.p. $154.5-155.5^{\circ}$). The gas phase chromatography retention time of product and authentic benzyl alcohol was 4 min. 30 sec. at 103° , under the column conditions described under Materials.

E. Cinnamaldehyde (437 mg., 3.31 mmoles) dissolved in 5 ml. of ether, was added to borane I (411 mg., 3.37 mmoles) dissolved in 15 ml. of ether at 25°. The solution was stirred for 3 hr., after which hydrolysis and work-up as described for aceto-

phenone gave 57% of cinnamyl alcohol, m.p. $32-33^{\circ}$ (lit.¹⁹ m.p. 33°), and 15% of the phenylhydrazone of cinnamaldehyde.

F. Benzoyl chloride and equimolar portions of borane I were stirred in dry ether at 25° for 3 days. After hydrolysis and work-up, 10% of benzyl alcohol was isolated. Other products were unreacted benzoyl chloride, benzoic acid, and 2-benzoyl-phenylhydrazine, m.p. $166-168^{\circ}$ (lit.²⁰ m.p. 168°).

G. trans-Stilbene (1.33 g., 7.39 mmoles) in 25 ml. of tetrahydrofuran was heated under reflux with 905 mg. (7.42 mmoles) of borane I for 2 weeks. After oxidation with 20% basic hydrogen peroxide, the reaction mixture was worked up by the procedure of Hawthorne.⁴ Isolated were 682 mg. (3.79 mmoles, 51.3%) of trans-stilbene, m.p. 123-124° (lit.²¹ m.p. 125°) and 421 mg. (2.3 mmoles, 31%) of crude trans-stilbene (m.p. 118-121°). Also isolated was 108 mg. of a brown oil which did not contain 1,2diphenylethanol, as indicated by thin layer chromatography.

Ethyl benzoate and borane I (equimolar portions) were stirred in ether at 25° for 1 day. Ethyl benzoate, whose infrared spectra was identical with starting ethyl benzoate, was recovered in 95%yield.

Benzoic acid and **nitrobenzene** likewise were recovered virtually unchanged when heated under reflux for 5 days with borane I in tetrahydrofuran.

Reaction of N-Bromosuccinimide with Borane I.—N-Bromosuccinimide (765 mg., 4.31 mmoles) dissolved in 15 ml. of methylene chloride, was added dropwise to 581 mg. (4.76 mmoles) of borane I dissolved in 20 ml. of methylene chloride containing 1 ml. of pyridine, over a 30 min. period at 0°, while the solution was being stirred. Gas evolution was noted during the reaction period. After 1 hr., the white, crystalline precipitate (VIII) was filtered and washed with dry methylene chloride. The dried VIII (m.p. 179–181° dec.) weighed 379 mg. (1.3 mmoles, 30%). Crystals of VIII decomposed in aqueous or basic solution with the liberation of pyridine and a gas. The product VIII was soluble in ethanol and insoluble in ether, hexane, methylene chloride, and acetone.

Anal. Calcd. for $C_{11}H_{16}BBrN_3O$: C, 44.49; H, 5.43; Br, 26.91; N, 14.15. Found: C, 44.47; H, 4.97; Br, 26.84; N, 14.02.

Infrared spectrum (KBr): 3430 (mbr), 3205 (m), 3000 (s), 2940 (sbr), 2730 (w), 2715 (w), 2680 (w), 2635 (w), 2465 (m), 2425 (m), 2380 (w), 1638 (m), 1602 (m), 1498 (m), 1461 (s), 1450 (w), 1374 (m), 1347 (w), 1319 (m), 1243 (w), 1218 (w), 1174 (m), 1164 (s), 1121 (m), 1060 (w), 1025 (w), 1012 (w), 952 (w), 929 (w), 893 (w), 813 (w), 772 (m), 760 (m), 695 (m), 593 (w), and 502 (mw) cm.⁻¹ principal peaks.

Hydrolysis of VIII with an excess of 3 N hydrochloric acid, gave pyridinium hydrochloride and phenylhydrazine hydrochloride.

Acknowledgment.—We wish to thank Mr. John A. Sousa for his help and useful advice in the spectral work. We also thank Dr. George Thomas, Dr. Joseph Bornstein, and Dr. M. K. Wilson for their helpful suggestions. Analyses were done by Mr. Carmine DiPietro, molecular weight determinations by Dr. Wenzel E. Davidson, and the gas chromatographic analyses was done with the help of Dr. Warren V. Sherman.

(19) F. Toel, ibid., 70, 3 (1849).

(20) E. Fisher, ibid., 190, 126 (1877).

(21) W. Schlenk and E. Bergmann, *ibid.*, 463, 116 (1928).

The Preparation of 2-Arylimidazo[4,5-b]pyridines

D. L. GARMAISE AND J. KOMLOSSY

Research Department, Abbott Laboratories Limited, Montreal, Quebec

Received May 26, 1964

Some 2-arylimidazo [4,5-b] pyridines have been mentioned in the literature,¹ but it would appear from the

⁽¹⁴⁾ E. Fisher, Ber., 17, 576 (1884).

⁽¹⁵⁾ A. McKenzie and G. W. Clough, J. Chem. Soc., 103, 689 (1913).

⁽¹⁶⁾ E. Linnemann, Ann., 133, 8 (1865).

⁽¹⁷⁾ R. Kempf, J. prakt. Chem., [2] 78, 256 (1908).

⁽¹⁸⁾ H. Biltz, Ann., 305, 171 (1899).

⁽¹⁾ T. Takahashi and S. Yajima, J. Pharm. Soc. Japan, 66, 31 (1946); Chem. Abstr., 45, 8533c (1951).