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187. Shun-ichi Yamada and Shiro Ikegami : Chemistry of Sodium Borohydride and Diborane. I. Some New-type of Amine Boranes.

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With respect to the reaction of the organic compounds with chemically reactive diborane or the organoboron compounds, many interesting studies[1,2] have been made. Especially, the hydroboration reaction, discovered and developed by Brown and his co-workers,[3a~e] has widely been available as one of the most important methods to the syntheses of organic compounds such as alcohols, ketones and amines.[4] An application of diborane to the reduction of the various functional groups has also been studied and the reducing power of diborane was also compared with that of the milder reducing agents such as sodium borohydride.[3d] Diborane, showing its specificity as an acidic reducing agent, reduces readily carboxylic acid and nitrile, which are difficult to be reduced with sodium borohydride, to give the corresponding reduced products.

Many reports for converting azomethine compounds to the corresponding amines with sodium borohydride in the hydroxylic solvents have been published,[5] but hitherto not with diborane.

Amine borane is considered to be one of the useful agents for hydroboration[6~13] and/or reduction,[14~19] but it requires more slightly drastic reaction conditions than that of diborane. Billman. *et al.*[20,21] reported the conversion of Schiff bases to the corresponding secondary amines with amine boranes, such as dimethylamine borane and trimethylamine borane, in glacial acetic acid at refluxing temperature. On the contrary, it was indicated by Kelley, *et al.*,[17] that the reduction of N-benzylideneaniline with ethylenediamine diborane in diglyme did not take place.

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1) W. Gerrard, "The Organic Chemistry of Boron," (1961), Academic Press, London and New York.
2) H. Steinberg, "Organoboron Chemistry," Vol. 1 (1964), John-Wiley & Sons, Inc., New York.
3) *a*) H. C. Brown : "Organometallic Chemistry," Ed. by H. Zeiss, p. 150 (1960), Reinfold, Publishing Corporation, New York. *b*) H. C. Brown : Tetrahedron, **12**, 117 (1961). *c*) T. Inukai : J. Soc. Org. Synth. Chem. Japan, **19**, 735 (1961). *d*) H. C. Brown : "Hydroboration," (1962), W. A. Benjamin, Inc., Publishers, New York. *e*) G. Zweifel, H. C. Brown : "Organic Reactions," Vol. XIII, p. 1 (1963), John-Wiley & Sons, Inc., New York.
4) H. C. Brown, W. R. Heydkamp, E. Breuer, W. S. Murphy : J. Am. Chem. Soc., **86**, 3566 (1964).
5) W. Schenker : Angew. Chem., **73**, 81 (1961) and related references herein cited.
6) R. Köster : *Ibid.*, **69**, 684 (1957).
7) M. F. Hawthorne : J. Org. Chem., **23**, 1788 (1958).
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9) M. G. Hawthorne : *Ibid.*, **82**, 748 (1960).
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17) H. C. Kelley, J. O. Edwards : *Ibid.*, **82**, 4842 (1960).
18) H. C. Kelley, M. B. Giusto, F. R. Marchelli : *Ibid.*, **86**, 3882 (1964).
19) R. J. Baumgarten, M. C. Henry : J. Org. Chem., **29**, 3400 (1964).
20) J. H. Billman, J. W. McDowell : *Ibid.*, **26**, 1437 (1961).
21) *Idem* : *Ibid.*, **27**, 2640 (1962).

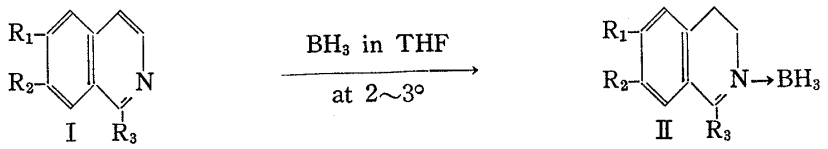
Recently, Feuer and Vincent,[23] and Ioffe, *et al.*[23] reported that the reduction of oximes with diborane in tetrahydrofuran afforded the corresponding hydroxylamines in a good yield.

Dialkylalane, having the same reducing power as that of dialkylborane, took place an addition reaction to Schiff bases with remarkable ease and the corresponding reduced products were quantitatively obtained by hydrolysis of the adducts.[24,25]

During the course of our investigation on the asymmetric hydroboration using dialkylborane, it became necessary to elucidate the reactivity of diborane to carbon-nitrogen double bond. Present paper deals with the reaction of diborane with 3,4-dihydroisoquinoline derivatives which are readily reduced with sodium borohydride in hydroxylic solvents.

First, the four 3,4-dihydroisoquinoline derivatives, that is, 3,4-dihydroisoquinoline (Ia), 6,7-dimethoxy-3,4-dihydroisoquinoline (Ic) and their 1-methyl derivatives (Ib and Id), were synthesized respectively from the corresponding amides by Bischler-Napieralski reaction, with polyphosphoric acid for the syntheses of Ia and Ib according to the method of Cannon, *et al.*[26] and with phosphoryl chloride for those of Ic[27] and Id.[28]

An equimolar amount of diborane generated from sodium borohydride and boron trifluoride etherate according to the similar procedure of Brown's method[3e] was gradually passed into a cooled solution of 3,4-dihydroisoquinoline derivative (Ia~e) dissolved in dehydrated tetrahydrofuran under nitrogen atmosphere with stirring. After the reaction mixture was stirred under cooling for one hour, the solvent was evaporated *in vacuo* to leave a white crystalline mass which could be easily recrystallized from



a : $R_1=R_2=R_3=H$ c : $R_1=R_2=OCH_3$, $R_3=H$
b : $R_1=R_2=H$, $R_3=CH_3$ d : $R_1=R_2=OCH_3$, $R_3=CH_3$

Chart 1.

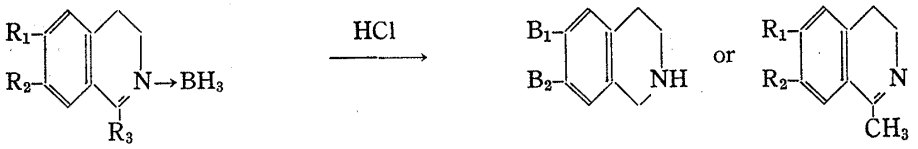


Chart 2.

dry isopropanol. Unexpectedly, the white crystals thus obtained were not the reduced product and it was found to be amine borane (II) in every experiment, whose structural proof was indicated in the following description. The melting points and analytical data of amine boranes (IIa~d) are shown in Table I. The ultraviolet absorption spectral curves of IIa~d in 90% aqueous ethanol resemble respectively to those of the starting

22) *a*) H. Feuer, B.F. Vincent, Jr.: J. Am. Chem. Soc., **84**, 3771 (1962). *b*) H. Feuer, B.F. Vincent, Jr., R.S. Bartlett: J. Org. Chem., **30**, 2877 (1965).
23) S.L. Ioffe, V.A. Tartakovski, A.A. Medvedeva, S.S. Novikov: Izv. Akad. Nauk SSSR, Ser. Khim., **1964**, 1537.
24) W.P. Neumann: Angew. Chem., **70**, 401 (1958).
25) *Idem*: Ann., **618**, 90 (1958).
26) J.G. Cannon, G.L. Webster: J. Am. Pharm. Assoc., **47**, 353 (1958).
27) W.M. Whaley, M. Meadow: J. Chem. Soc., **1953**, 1067.
28) A.M. Barbier, P. Rumpf: Bull. soc. chim. France, **1953**, 293.

materials (Ia~d) in ethanol solution containing 0.1 *N* hydrochloric acid as shown in Fig. 1 and Fig. 2. The ultraviolet spectra suggest that the chromophoric system of the products is very similar to that of the hydrochlorides of the starting materials.

Table I. Properties and Analyses of Borane Complexes of 3,4-Dihydroisoquinoline Derivatives

Compound No.	Appearance	m.p. (°C)	Formula	Analysis (%) Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
IIa	white needles	71.5~72.5	$C_9H_{12}NB$	74.54	8.34	9.66	74.07	8.65	9.40
IIb	〃	68.5~69	$C_{10}H_{14}NB$	75.52	8.87	8.81	75.54	9.16	8.77
IIc	〃	144.5~145.5	$C_{11}H_{16}O_2NB$	64.39	7.86	6.83	64.60	7.81	6.87
IId	〃	156~156.5	$C_{12}H_{18}O_2NB$	65.78	8.28	6.39	66.03	8.44	6.42

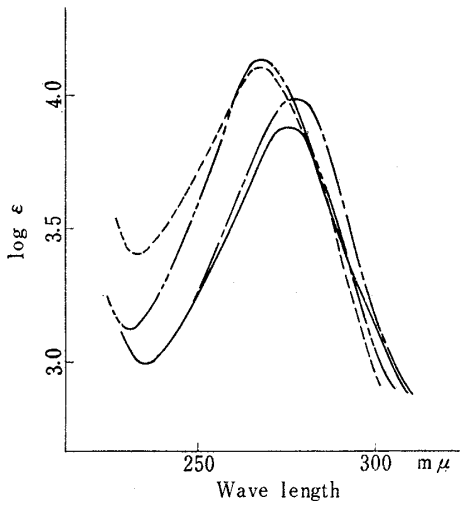


Fig. 1. Ultraviolet Spectral Curves of Ia (—·—·—) and Ib (—··—··) in 0.1*N* HCl-EtOH and IIa (————) and IIb (- - - - - -) in 90% EtOH

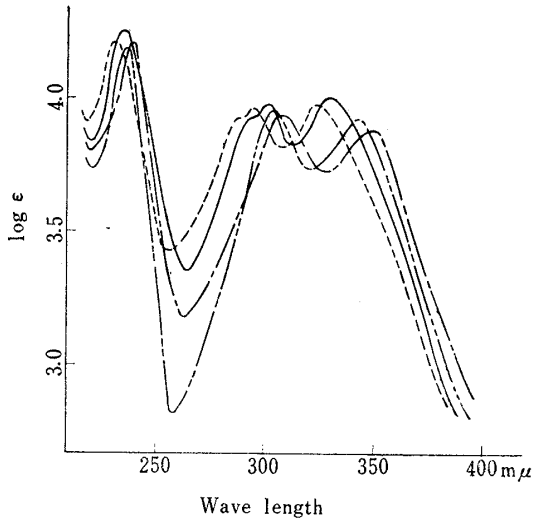


Fig. 2. Ultraviolet Spectral Curves of Ic (—·—·—) and Id (—··—··) in 0.1*N* HCl-EtOH and IIc (————) and IId (- - - - - -) in 90% EtOH

The characteristic bands of theinfrared absorption spectra of amine boranes (IIa~d) and the starting materials (Ia~d), which may be assigned to the asymmetric and symmetric BH stretching and deformation vibrations and the C=N stretching vibration, are given in Table II. These spectral modes assigned to the boron-hydrogen frequencies of IIa~d are very similar to those of the other amine borane complexes in the literatures.[19,29~35] In the case of R_3=H, amine boranes (IIa and IIc) exhibit the C=N stretching vibration at lower wave-length than that of isoquinoline derivatives (Ia and Ic). In contrast, IIb and IId have the C=N stretching vibration at a little higher wavelength than that of Ib and Id. Presumably, the differences of the spectral data would suggest

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31) M. F. Hawthorne: J. Am. Chem. Soc., **80**, 4291 (1958).
32) *Idem*: *Ibid.*, **83**, 831 (1961).
33) *Idem*: *Ibid.*, **84**, 121 (1962).
34) G. M. Wyman, K. Niedenzu, J. W. Dawson: J. Chem. Soc., **1962**, 4068.
35) L. J. Bellamy, W. Gerrard, M. F. Lappert, R. L. Williams: *Ibid.*, **1958**, 2412.

Table II. Infrared Spectral Bands of 3,4-Dihydroisoquinoline Derivatives and Their Borane Complexes

Compound No.	$\nu_{C=N}$ cm^{-1}	ν_{HB} cm^{-1}	σ_{BH} cm^{-1}
Ia[a]	1625		
IIa[b]	1643	2370, 2290, 2240	1165, 1141
Ib[a]	1628		
IIb[b]	1624	2370, 2290, 2260	1178, 1150
Ic[a]	1630		
IIc[b]	1646	2380sh, 2275, 2240	1170, 1150
Id[b]	1627		
IId[b]	1622	2370, 2285, 2250	1170, 1150

a) Measured in capillary film *b*) Measured in KBr tablet

the strain effect due to the steric repulsion between N-borane and 1-methyl group or the peri effect of 8-hydrogen and 1-methyl group.

Moreover, it might be considered that amine boranes (IIa~b) were of the dimer structure. However, the dimer structure was excluded because of the method of the preparation[36] and of having no characteristic bands which were ascribed to BH_2B stretching vibration[3d] in the infrared spectra of the complexes.

Borane complexes (IIa~d) of isoquinoline derivatives thus obtained were fairly stable except 3,4-dihydroisoquinoline borane (IIa) which was partly reduced to 1,2,3,4-tetrahydroisoquinoline by the recrystallization from isopropanol. It seems to be very interesting to know that the reduction of the easily reducible carbon-nitrogen double bond did not occur and that a new type of amine borane complex was formed even in the least hindered 3,4-dihydroisoquinoline (Ia).

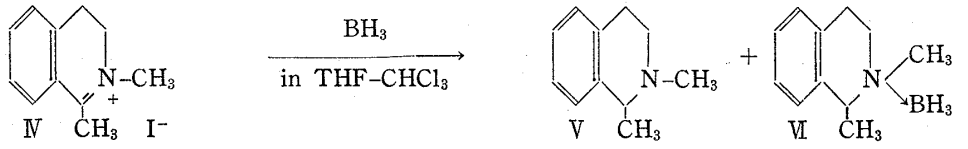
On the other hand, when the complexes (IIa~d) were treated with 5% HCl-aq. ethanol, both IIa and IIc were reduced to give the tetrahydroisoquinoline derivatives isolated as their hydrochloride, but in the case of IIb and IId, the cleavage of nitrogen-boron bond merely occurred and no reduced products were obtained with a recovery of the starting materials (Ib and Id) in nearly a quantitative yield. It seems to be difficult to explain the reason why the reduction did not occur by treatment of amine boranes (IIb and IId) with ethanolic hydrochloric acid.

The reaction of 1,2-dimethyl-3,4-dihydroisoquinolinium iodide (IV) with an equimolar amount of diborane in tetrahydrofuran or in a mixture of tetrahydrofuran and chloroform was carried out and a viscous oil left by removal of the solvent was chromatographed over alumina to obtain the reduced products, 1,2-dimethyl-1,2,3,4-tetrahydroisoquinoline (V) and its borane complex (VI). The structure of V was demonstrated by an admixture of the picrate of V with the authentic sample prepared from the corresponding amine obtained by the reduction of IV with sodium borohydride in methanol and by comparison of the infrared spectra of both compounds. The infrared spectrum of amine borane (VI) was superimposable with that of the authentic borane complex prepared from amine (V) with diborane in tetrahydrofuran and besides the picrate of the base obtained from hydrolysis of VI with hydrochloric acid in aqueous ethanol was found to be identical with the authentic picrate of V prepared by the method described above by admixture. It was found that in the case of quaternary amine (IV), the reduction with diborane occurred easily even though IV has methyl group at the position 1.

36) It has been shown that diborane dissociates to form the monomeric borane in tetrahydrofuran. *a*) J. R. Elliott, W. L. Roth, G. F. Roedel, E. M. Boldebuck: J. Am. Chem. Soc., **74**, 5211 (1952). *b*) B. Rice, J. A. Livasy, G. W. Schaeffer: *Ibid.*, **77**, 2750 (1955).

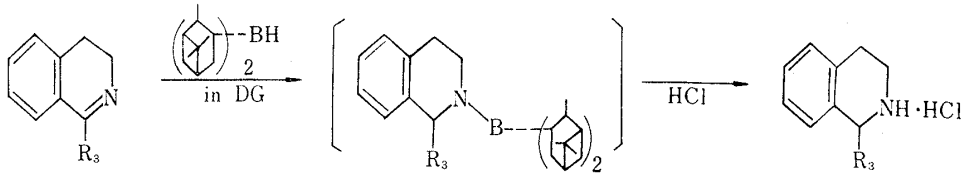
Furthermore, to clarify the influence of lone pair electrons of nitrogen atom, the reaction of Ib with a large excess of diborane in tetrahydrofuran was carried out. However, the reduction did not occur and only the amine borane (IIb) was obtained, moreover the similar reaction on IIb was tried using fivefold excess of the reagent, but it resulted in a quantitative recovery of amine borane IIb. It should be noted that amine borane IIb was not reduced with excess diborane, although quaternary ammonium salt IV was reduced easily.

Dialkylboranes such as disiamylborane and diisopinocampheylborane have also been available in achieving the hydroboration of the unhindered olefins.[3] In order to examine the reactivity of dialkylborane to the carbon-nitrogen double bond, the reaction of 3,4-dihydroisoquinoline derivatives (Ia and Ib) with diisopinocampheylborane prepared from α-pinene and diborane in diglyme or tetrahydrofuran according to the method of Brown, *et al.*[36] was examined. In the case of 3,4-dihydroisoquinoline (Ia), diisopinocampheylborane added readily under cooling to the carbon-nitrogen double bond, and



IV V VI

Chart 3.



Ia, b
Ib, quantitative recovery of the starting material

IIIa

Chart 4.

1,2,3,4-tetrahydroisoquinoline hydrochloride was obtained in a yield of 80.9% by treatment with dry hydrogen chloride for the cleavage of nitrogen-boron bond. The hydroboration of 1-methyl-3,4-dihydroisoquinoline (Ib) with diisopinocampheylborane did not proceed even on warming at 60~70° and the starting material was recovered quantitatively.

It was pointed out by Brown, *et al.*[3] that the final stage of the reaction of the trisubstituted olefins with diisopinocampheylborane is very sluggish and the slowness of the last stage is presumably due to the large steric requirements of both. As mentioned above, the failure of the hydroboration of Ib with diisopinocampheylborane would be presumably due to the same reason as Brown's prediction and this observation reveals that a nitrogen atom of carbon-nitrogen double bond has not shown any effects on the reaction of the trisubstituted azomethine with diisopinocampheylborane. Likewise, the similar hydroboration of N-(α-methylbenzylidene)benzylamine was attempted and it readily proceeded at near room temperature to afford the corresponding amine in a good yield.[37]

The reason why the cyclic trisubstituted carbon-nitrogen double bond which is less sterically hindered was not reduced by diisopinocampheylborane and open chain tisubstituted carbon-nitrogen double bond was easily reduced, has not been cleared yet. However, it might be supposed that the structure of 1-methyl-3,4-dihydroisoquinoline (Ib) was fairly fixed, whereas N-(α-methylbenzylidene)benzylamine is flexible and

37) S. Yamada, M. Tsunoda, S. Ikegami : Unpublished studies.

facilitated to be added with the bulky diisopinocampheylborane group to the carbon-nitrogen double bond from the stereochemical point of view.

Anyhow, the carbon-nitrogen double bonds of 3,4-dihydroisoquinoline derivatives (Ia~d) which would have much stronger basicity than that of Schiff bases were not reduced with diborane in tetrahydrofuran but gave the new-type of amine borane complexes (IIa~d).

Some of the details in the reaction of carbon-nitrogen double dond with diborane will be discussed in a successive paper.

Experimental*2

Materials——Tetrahydrofuran (THF) and diglyme (DG) were freshly distilled with sodium metal and stocked with sodium metal ribbons. Boron trifluoride etherate was purified by distillation under reduced pressure. Sodium borohydride from Merck, Co., was used without further purification.

Generation of Diborane——Diborane gas was generated by adding a solution of sodium borohydride in diglyme to a slight excess of boron trifluoride in diglyme according to the procedure of Brown, *et al.*,[3e] who reported that the yields of diborane by this method, using ordinary apparatus, were in the range of $90\pm5\%$.[38] In our experiments, therefore, most reactions were carried out on the basis in a 90% yield of diborane.

General Procedures——Except the case of IIc, the reaction of isoquinoline derivatives with diborane was examined according to the following description. Diborane thus generated was passed under cooling (at 2.5~3.5°) for ca. 20 min. through a glass tube into a solution containing an equimolar amount (based on BH_3) of 3,4-dihydroisoquinoline derivative (Ia~d) in THF with stirring. After passing diborane, the reaction mixture was stirred at 2.0~2.5° for further 1 hr. and then, under N_2 atmosphere, the solvent was evaporated *in vacuo* below 40° to leave a white crystalline mass, which was recrystallized from dehyd. iso-PrOH to give white needles. The physical constants of the crystals are shown in Tables I and II.

a) 3,4-Dihydroisoquinoline borane (IIa). Amino borane (IIa : 1.0 g.) was obtained from Ia (1.31 g., 10 mmole) by the method described in general procedures. Yield, 69.0%. Further recrystallization from iso-PrOH gave white needles of m.p. 71.5~72.5°. UV $\lambda_{max}^{90\%\ EtOH}$ mμ (log ε) : 277 (3.87).

b) 1-Methyl-3,4-dihydroisoquinoline borane (IIb). Amine borane (IIb : 1.24 g.) was obtained from Ib (1.46 g., 10 mmole) by the method described above. Yield, 78.0%. Further recrystallization from iso-PrOH gave white needles of m.p. 68.5~69.0°. UV $\lambda_{max}^{90\%\ EtOH}$ mμ (log ε) : 272 (4.10).

c) 6,7-Dimethoxy-3,4-dihydroisoquinoline borane (IIc). To a solution of Ic (380 mg., 2 mmole) in dehyd. THF (10 ml.) 40 ml. of the BH_3-THF solution (an equimolar amount based on BH_3) was added dropwise under cooling with stirring and then the reaction mixture was stirred at ca. 3° for 1 hr. Evaporation of the solvent afforded a white crystalline solid, which was recrystallized from iso-PrOH to give white needles of m.p. 143~144.5°. Yield, 310 mg. or 75.6%. Further recrystallization gave white needles, m.p. 144.5~145.5° UV $\lambda_{max}^{90\%\ EtOH}$ mμ (log ε) : 242 (4.31), 290 sh. (3.91), 299 (3.98), 332 (4.01).

d) 1-Methyl-6,7-dimethoxy-3,4-dihydroisoquinoline borane (IId). Amine borane (IId : 450 mg.) was obtained from Id (510 mg., 2.5 mmole) by the method described above. Yield, 82.2%. White needles (from iso-PrOH), m.p. 156~156.5°. UV $\lambda_{max}^{90\%\ EtOH}$ mμ (log ε) : 238 (4.27), 284 sh. (3.93), 292.5 (3.97), 325 (3.98).

Decomposition of Amine Borane (IIa~d) in HCl-aq. EtOH : General Procedure——To a solution of amine borane (IIa~d) dissolved or suspended in EtOH (4.5 ml.), was added conc. aq. HCl (0.5 ml.) dropwise under cooling with stirring and sluggish evolution of gas was observed. The reaction mixture was stirred under cooling for 30 min. and refluxed gently for 30 min. in order to complete the decomposition of amine borane. Removal of the solvent gave a white crystalline solid, which was purified either by recrystallization, or preparation of picrate.

a) Decomposition IIa. Hydrochloride of amine (370 mg.) was obtained from IIa (400 mg.) after recrystallization of the crude product from iso-PrOH according to the method described in general procedure. Yield, 78.0%. White plates, m.p. 198~199°. The hydrochloride was found to be identical with the authentic sample, 1,2,3,4-tetrahydroisoquinoline hydrochloride, by a mixed melting point and the comparison of infrared absorption spectra.

b) Decomposition of IIb. Picrate of amine (170 mg.) which was recrystallized from EtOH-acetone, was obtained from IIb (100 mg.) by the method described above. Yield, 71.6%. Yellow needles, m.p. 192~193° (decomp.). A mixed melting point with 1-methyl-3,4-dihydroisoquinoline picrate was undepressed, and the infrared spectra of the two samples were superimposable. IR spectra of both compounds showed C=N stretching vibration at 1655 cm^{-1}.

*2 All melting points and boiling points are uncorrected.

38) H. C. Brown, B. C. Subba Rao : J. Am. Chem. Soc., **81**, 6428 (1959).

c) Decomposition of IIc. IIIc (100 mg.) was obtained from IIc (100 mg.) according to the several procedures. Yield, 87.4%. Colorless prisms (from iso-PrOH), m.p. 256~257 : No depression of the mixed melting point of the product and 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline hydrochloride was observed and infrared absorption spectra of both were superimposable.

d) Decomposition of IId. A picrate of Id (170 mg.) was obtained from IId (100 mg.) according to the general method described above. Yellowish orange needles (from EtOH-acetone), m.p. 211~212°(decomp.). The melting point of the picrate was identical with that of 1-methyl-6,7-dimethoxy-3,4-dihydroisoquinoline picrate, and a mixing melting point was undepressed. The infrared absorption spectra of both were superimposable and showed C=N stretching vibration at 1650 cm^{-1}.

Reaction of 1,2-Dimethyl-3,4-dihydroisoquinolinium Iodide (IV) with Diborane——Diborane (15 mmole in BH_3) was passed at 2 ~ 4° for 15 min. into a solution prepared by adding dehyd. THF (100 mg.) to a solution of IV (4.33 mg., 15 mmole) dissolved in $CHCl_3$ (50 ml.) (EtOH free) with stirring. When diborane was passed through completely, the reaction mixture became colorless and then it was stirred further for 30 min. After evaporation of the solvents below 40° under N_2 atmosphere *in vacuo*, a colorless viscous oil was chromatographed over alumina (130 g.). Borane complex VI (1.56 g.) was obtained from the fraction eluted with C_6H_6, and also amine V (600 mg.) from that eluted with C_6H_6-$CHCl_3$ in 1 : 1 ratio.

VI : colorless viscous oil, b.p.$_{0.05}$ 118~123°. ν_{max}^{Cap} cm^{-1} : 2380 broad, 2270 (BH), 1175 broad (δ_{BH}). IR spectrum of VI was superimposable with that of 1,2-dimethyl-1,2,3,4-tetrahydroisoquinoline borane synthesized from the free amine with diborane in THF.

V : picrate, yellow needles, m.p. 154~155°. This picrate was found to be identical with the authentic picrate, 1,2-dimethyl-1,2,3,4-tetrahydroisoquinoline picrate, by admixture.

Moreover, a mixed melting point of the picrate obtained from hydrolysis of the amine borane VI with 5% HCl-aq. EtOH and the that of V was undepressed.

Reaction of 3,4-Dihydroisoquinoline with Diisopinocampheylborane——α-Pinene (6.8 g., 50 mmole) was dissolved in a solution of $NaBH_4$ (0.73 g., 19 mmole) in diglyme (25 ml.) and the mixture cooled to 0°, was treated with BF_3-ether (3.6 g., 25 mmole) to form diisopinocampheylborane. To this solution was added a solution Ia (3.3 g., 25 mmole) of 3,4-dihydroisoquinoline in diglyme (5 ml.) at 3~5° for 40 min. and the reaction mixture was maintained at 2~3° for further 3 hrs. In order to decompose the excess reagent, EtOH (3 ml.) was added and the solvent was removed *in vacuo*. A viscous oil thus obtained was dissolved in ether (30 ml.) and the ether solution was washed with H_2O twice and dried over $MgSO_4$. Evaporation of the solvent left a pale yellow viscous oil, which was dissolved again in dehyd. ether (20 ml.). Into the ether solution, dry HCl was passed carefully under cooling for 10 min. and then by filtration white needles, m.p. 196~197°, were obtained in a yield of 3.45 g. or 80.9%. This hydrochloride was found to be identical with the authentic sample 1,2,3,4-tetrahydroisoquinoline hydrochloride, by admixture and comparison of IR spectra of both.

The authors are gratefull to the members of the Central Analysis Room of this Faculty for microanalytical, infrared and ultraviolet spectral data.

Summary

The reduction of 3,4-dihydroisoquinoline derivatives with diborane in tetrahydrofuran was carried out, but the hydroboration to the carbon-nitrogen double bond did not occur and the isolated product was the fairly stable amine borane complex II which could be easily recrystallized from isopropanol. Also, the reductions of 1,2-dimethyl-3,4-dihydroisoquinolinium iodide with diborane and 3,4-dihydroisoquinoline and its 1-methyl derivative with diisopinocampheylborane were carried out and the results were discussed.

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