A full treatment of the subject, including analysis of data for a wider variety of binary systems, will be published in the near future.[5]

Acknowledgment.—Support of the United States Air Force under Contract AF 49(638)-1341 is gratefully acknowledged.

(5) A. Abe and P. J. Flory, in preparation.

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RECEIVED JUNE 8, 1964

The Reaction of Organoboranes with Chloramine and with Hydroxylamine-O-sulfonic Acid. A Convenient Synthesis of Amines from Olefins *via* Hydroboration

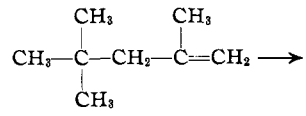
Sir:

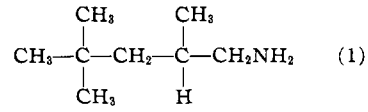
We wish to report that organoboranes, such as are produced in the hydroboration of representative olefins,[1] react readily with either chloramine or with hydroxylamine-O-sulfonic acid to form the corresponding amine. In the majority of cases examined, yields of 60% (±5%) have been realized. Consequently, this procedure permits a simple conversion of olefinic derivatives into the corresponding amine.

In the procedure the olefin in tetrahydrofuran solution is conveniently converted into the corresponding organoborane by treatment with the equivalent quantity of diborane in tetrahydrofuran solution.[2] In the chloramine route, the organoborane, with added alkali, is treated with a freshly prepared solution of chloramine[3] for 1 hr. at room temperature. In the hydroxylamine-O-sulfonic acid procedure the reagent[4] is added directly to the tetrahydrofuran solution and the reaction mixture heated under reflux for 3 hr. In both procedures the solutions are acidified with hydrochloric acid, extracted with ether to remove residual organoboron derivatives, and the amines are then isolated from the acidic aqueous solutions by standard methods.

The yields are similar in both procedures. However, the commercial availability of hydroxylamine-O-sulfonic acid avoids the synthesis and standarization of the chloramine solution. Consequently, the use of the hydroxylamine-O-sulfonic acid is preferable in cases where the reagent is available.

In this way 1-octene has been converted into *n*-octylamine, α-methylstyrene into 2-phenyl-1-aminopropane, and 2,3,3-trimethyl-1-pentene into 2,3,3-trimethyl-1-aminopentane (1). Similarly, cyclopentene and cyclohexene have been converted into the corresponding amines, and norbornene into *exo*-norbornylamine (2). The mildness of the procedure is indicated by the conversion of β-pinene into *cis*-myrtanylamine (3), without evidence of any rearrangement or alteration of the carbon skeleton.





(1)

(2)

(3)

Representative results are summarized in Table I.

TABLE I

CONVERSION OF OLEFINS INTO AMINES BY THE HYDROBORATION-ANIMATION REACTION

Olefin	Amine	Yield, % Hydroxylamine-O-sulfonic acid	Yield, % Chloramine
1-Octene	*n*-Octylamine	64	
1-Decene	*n*-Decylamine		51
2-Methyl-1-pentene	2-Methyl-1-aminopentane	59	29
2,4,4-Trimethyl-1-pentene	2,4,4-Trimethyl-1-aminopentane	58	28
α-Methylstyrene	2-Phenyl-1-aminopropane	58	58
1,1-Diphenylethylene	β,β-Diphenylethylamine	27	
Cyclopentene	Cyclopentylamine	59	50
Cyclohexene	Cyclohexylamine	55	49
1-Methylcyclohexene	*trans*-2-Methylcyclohexylamine		8.5
Norbornene	*exo*-Norbornylamine	52	51
β-Pinene	*cis*-Myrtanylamine	55	48
Ethyl undecenoate	11-Aminoundecanoic acid	30	30

The observation that the yields in so many cases were in the range of 55 to 60% suggested the possibility that only two of the three alkyl groups on the organoborane were undergoing reaction. This was confirmed by the isolation of the monoalkylboronic acid from the reaction mixture and the demonstration that the reaction of such boronic acids with the reagents is very slow. The hydroboration of hindered olefins proceeds readily only to the mono- or dialkylborane stage.[1] Consequently, the yields are much lower for such derivatives. In spite of the low yield realized in applying the reaction to 1-methylcyclohexene, it is of considerable theoretical interest that the product produced was pure *trans*-2-methylcyclohexylamine, corresponding to replacement of the boron by the amino group stereospecifically with retention of configuration. Similarly, the isolation of pure *exo*-norbornylamine supports the conclusion that the reaction course is stereochemically similar to that proposed for the oxidation of the organoborane by alkaline hydrogen peroxide.[1]

The following procedures are representative

In a 500-ml. flask was placed 11.8 g. (100 mmoles) of α-methylstyrene and 30 ml. of tetrahydrofuran.

(1) For a recent summary, see H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(2) One molar solutions of borane in tetrahydrofuran are now commercially available from Metal Hydrides Incorporated, Beverly, Mass.

(3) The chloramine solution is prepared by treating dilute aqueous ammonia with sodium hypochlorite at 0°. F. Raschig, *Ber.*, **40**, 4586 (1907).

(4) Hydroxylamine-O-sulfonic acid is now commercially available from Allied Chemical Co., Marcus Hook, Pa.

The flask was flushed with nitrogen and 33.3 ml. of a 1.0 *M* solution of borane in tetrahydrofuran[2,5] was injected with a hypodermic syringe (exothermic reaction). After 1 hr., 3 ml. of water was added to destroy residual hydride, followed by 50 ml. of 3 *M* aqueous sodium hydroxide. The amination was accomplished by adding 215 ml. of 0.31 *M* freshly prepared chloramine solution (66.7 mmoles).[6] After 1 hr. at room temperature, the reaction mixture was acidified with hydrochloric acid and the acidified solution extracted with ether. The solution was made strongly alkaline with sodium hydroxide and the amine extracted with ether. There was obtained 6.94 g. (51.5% yield) of 2-phenyl-1-aminopropane, b.p. 114–116° at 35 mm., $n^{20}D$ 1.5240.

In a 100-ml. flask was placed 6.8 g. (50 mmoles) of α-pinene, $[\alpha]^{26}D$ −20.4°, in 8 ml. of tetrahydrofuran. After flushing with nitrogen, the hydroboration was accomplished by injecting 9.2 ml. of a 1.8 *M* solution of borane in tetrahydrofuran. To the solution was added 4.16 g. (36 mmoles) of solid hydroxylamine-O-sulfonic acid and the reaction mixture was heated under reflux for 3 hr. The solution was acidified with dilute hydrochloric acid and worked up as in the chloramine procedure. There was obtained 4.05 g. (53% yield) of *cis*-myrtanylamine, b.p. 60–61° at 2 mm., $n^{20}D$ 1.4898, d^{22} 0.9150, $[\alpha]^{26}D$ −27.85°.

Anal. Calcd. for $C_{10}H_{19}N$: C, 78.4; H, 12.42; N, 9.14. Found: C, 78.8; H, 12.33; N, 9.19.

The N-benzoyl derivative exhibited m.p. 105–106° (from petroleum ether).

Anal. Calcd. for $C_{17}H_{23}NO$: C, 79.3; H, 8.94; N, 5.45. Found: C, 79.4; H, 8.82; N, 5.92.

Acknowledgment.—This study was assisted by Research Award 585-C provided by the Petroleum Research Fund of the American Chemical Society, Project AT (11-1)-70 supported bythe Atomic Energy Commission, and Grant GM10937 from the National Institute of Health.

(5) G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963).

(6) Since experiment revealed that the third alkyl group does not react under these conditions, there is no point to adding the full 100 mmoles of reagent.

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RECEIVED JULY 15, 1964

Diborane as a Mild Reducing Agent for the Conversion of Primary, Secondary, and Tertiary Amides into the Corresponding Amines

Sir:

Diborane is a mild reducing agent with characteristics which are frequently very different from those of sodium borohydride or lithium aluminium hydride.[1] In the course of an extensive study of the rates of reaction of diborane in tetrahydrofuran solution with compounds containing representative functional groups, we have observed that the reduction of primary, secondary, and, especially, tertiary amides proceeds rapidly under relatively mild conditions and provides the basis for a procedure of considerable generality for converting such amides into the corresponding amines in yields approaching 100%.

Lithium aluminum hydride has also been applied to such reductions.[2] However, it is reported that such reductions of tertiary amides are relatively slow, requiring approximately 20 hr. for the reduction stage and providing yields of tertiary amines in the neighborhood of 50%.[3,4] Moreover, cleavage of the carbon–nitrogen bond to yield the alcohol can become an important side reaction.[1] Finally, the exceedingly powerful reducing action of lithium aluminum hydride greatly limits the possibility for achieving the reduction with other reducible groups present.

In contrast, the present procedure has permitted the reduction of N,N-diethylpivalamide to N,N-diethylneopentylamine in 94% yield, and N,N-diisopropylbenzamide to N,N-diisopropylbenzylamine in 98% yield. A reaction time of only 1 hr. (refluxing tetrahydrofuran) was adequate for the reduction. Moreover, in no case have we observed any tendency for a competitive rupture of the carbon–nitrogen bond. Finally, the mildness of the reagent makes possible the presence of other substituents less susceptible to the reducing action of the reagent. Thus, N,N-dimethylnitrobenzamide was successfully converted into N,N-dimethyl-*p*-nitrobenzylamine in a yield of 97%.[5]

The experimental results are summarized in Table I.

TABLE I

REDUCTION OF REPRESENTATIVE AMIDES TO AMINES BY DIBORANE IN TETRAHYDROFURAN

Acid amide	Product	Yield, % Anal.[a]	Isolated
Hexanoic[d]	*n*-Hexylamine	87	
N-Methylhexanoic[c]	Methyl-*n*-hexylamine	98	
N,N-Dimethylhexanoic[b]	Dimethyl-*n*-hexylamine	95	
Pivalic[d]	Neopentylamine	83	
N-Methylpivalic[c]	Methylneopentylamine	83	
N,N-Dimethylpivalic[b]	Dimethylneopentylamine	92	79
Benzoic[e]	Benzylamine	87	
N,N-Dimethylbenzoic[b]	Dimethylbenzylamine	98	
N,N-Dimethyl-*p*-nitrobenzoic[b]	Dimethyl-*p*-nitrobenzylamine	97	84
N,N-Diethylpivalic[b]	Diethylneopentylamine	94	81
N,N-Diisopropylbenzoic	Diisopropylbenzylamine	98	

[a] Determined by gas chromatographic analysis, isolation as the picrate, or by titration. [b] One and two-thirds moles of BH_3 per mole of amide, heated under reflux in tetrahydrofuran for 1 hr. [c] Two moles of BH_3 per mole of amide, heated under reflux for 1 hr. [d] Two and one-third moles of BH_3 per mole of amide, heated under reflux for 2 hr. [e] Two and one-third moles of BH_3 per mole of amide, heated under reflux for 8 hr.

(1) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **82**, 681 (1960).

(2) For a summary of the literature see N. C. Gaylord, "Reductions with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, pp. 544–592.

(3) H. Uffer and E. Schlittler, *Helv. Chim. Acta*, **31**, 1397 (1948).

(4) H. C. Brown and W. H. Bonner, *J. Am. Chem. Soc.*, **75**, 14 (1953).

(5) Z. B. Papanastassiou and R. J. Bruni have reported that they have successfully utilized diborane for the reduction of N-substituted fluoroacetamide derivatives to the corresponding fluoroethylamines in cases where lithium aluminum hydride and lithium aluminum hydride–aluminum chloride cause hydrogenolysis of the fluorine–carbon bond; private communication.