

The flask was flushed with nitrogen and 33.3 ml. of a 1.0 *M* solution of borane in tetrahydrofuran<sup>2,5</sup> 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).<sup>6</sup> 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.,  $n_D^{20}$  1.5240.

In a 100-ml. flask was placed 6.8 g. (50 mmoles) of  $\alpha$ -pinene,  $[\alpha]_D^{26}$   $-20.4^\circ$ , 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.,  $n_D^{20}$  1.4898,  $d_4^{22}$  0.9150,  $[\alpha]_D^{26}$   $-27.85^\circ$ .

*Anal.* Calcd. for C<sub>10</sub>H<sub>19</sub>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<sub>17</sub>H<sub>23</sub>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 by the 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.

R. B. WETHERILL LABORATORY  
PURDUE UNIVERSITY  
LAFAYETTE, INDIANA

HERBERT C. BROWN  
WOLFGANG R. HEYDKAMP  
ELI BREUER  
WILLIAM S. MURPHY

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 aluminum hydride.<sup>1</sup> 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.<sup>2</sup> 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%.<sup>3,4</sup> Moreover, cleavage of the carbon-nitrogen bond to yield the alcohol can become an important side reaction.<sup>1</sup> 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%.<sup>5</sup>

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. <sup>a</sup>	Isolated
Hexanoic <sup>d</sup>	<i>n</i> -Hexylamine	87	
N-Methylhexanoic <sup>c</sup>	Methyl- <i>n</i> -hexylamine	98	
N,N-Dimethylhexanoic <sup>b</sup>	Dimethyl- <i>n</i> -hexylamine	95	
Pivalic <sup>d</sup>	Neopentylamine	83	
N-Methylpivalic <sup>c</sup>	Methylneopentylamine	83	
N,N-Dimethylpivalic <sup>b</sup>	Dimethylneopentylamine	92	79
Benzoic <sup>c</sup>	Benzylamine	87	
N,N-Dimethylbenzoic <sup>b</sup>	Dimethylbenzylamine	98	
N,N-Dimethyl- <i>p</i> -nitrobenzoic <sup>b</sup>	Dimethyl- <i>p</i> -nitrobenzylamine	97	84
N,N-Diethylpivalic <sup>b</sup>	Diethylneopentylamine	94	81
N,N-Diisopropylbenzoic	Diisopropylbenzylamine	98	

<sup>a</sup> Determined by gas chromatographic analysis, isolation as the picrate, or by titration. <sup>b</sup> One and two-thirds moles of BH<sub>3</sub> per mole of amide, heated under reflux in tetrahydrofuran for 1 hr. <sup>c</sup> Two moles of BH<sub>3</sub> per mole of amide, heated under reflux for 1 hr. <sup>d</sup> Two and one-third moles of BH<sub>3</sub> per mole of amide, heated under reflux for 2 hr. <sup>e</sup> Two and one-third moles of BH<sub>3</sub> per mole of amide, heated under reflux for 8 hr.

(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. Ufer 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.

To a solution of 200 ml. of 1.67 *M* borane in tetrahydrofuran<sup>6,7</sup> in a 500-ml. flask (nitrogen atmosphere) was added 25.8 g. (200 mmoles) of *N,N*-dimethylpivalamide in 100 ml. of tetrahydrofuran over 15 min. The temperature was maintained at approximately 0° during the addition. The colorless solution was then refluxed for 1 hr. The flask was permitted to cool to room temperature and 50 ml. of 6 *M* hydrochloric acid was added. The tetrahydrofuran was removed by distillation at atmospheric pressure as hydrogen was evolved (15.5 l., 0.60 mole) from the hydrolysis of excess reagent. Sodium hydroxide pellets were added to saturate the aqueous phase, and the latter was extracted three times with a total of 100 ml. of ether. After drying over sodium sulfate, distillation yielded 18.2 g. (79% yield) of dimethylneopentylamine, b.p. 95–96°,  $n_D^{20}$  1.3982.

In extending this procedure to primary and secondary amides, the amount of borane used was increased by 1 equiv. for each equivalent of "active" hydrogen present in the amide. The reduction of primary amides appears to be considerably slower than that of secondary and tertiary. Consequently, it was found desirable to increase the reaction time to 2 hr. for primary aliphatic amides and to 8 hr. for primary aromatic amides (Table I).

**Acknowledgment.**—This investigation was made possible by Grant GM 10937 from the National Institutes of Health.

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

(7) One molar solution of borane in tetrahydrofuran is now commercially available from Metal Hydrides Incorporated, Beverly, Mass.

R. B. WETHERILL LABORATORY  
PURDUE UNIVERSITY  
LAFAYETTE, INDIANA

HERBERT C. BROWN  
PETER HEIM

RECEIVED JULY 15, 1964

## Phase Transitions and the Radiative Neutron Capture in Solid Organic Media

Sir:

During recent studies in this laboratory of the radiative neutron capture (Szilard–Chalmers effect<sup>1</sup>) in solid organic halides, it was found that the organic yield of <sup>80</sup>Br presents a marked dependence on the phase transitions of the corresponding solid organic media.

Figure 1 shows the organic yield as a function of irradiation temperature in solid CH<sub>2</sub>BrCH<sub>2</sub>Br. There appears to be an abrupt change of the yield at 10° (melting point) and at –24° (transition point). The same figure shows the dependence of the heat capacity on temperature as determined by Pitzer.<sup>2</sup> The discontinuity of the heat capacity curve at the transition point is characteristic for a 2I-type transition<sup>3</sup> and was interpreted to mean that the dibromoethane molecules undergo hindered rotation around their symmetry axis in the temperature range between 10 and –24°.<sup>2</sup>

Figure 2 shows the organic yield of <sup>80</sup>Br in CCl<sub>3</sub>Br as a function of the irradiation temperature (some of the data was taken from ref. 4). This halide is known to

(1) L. Szilard and Chalmers, *Nature*, **134**, 462 (1934).

(2) K. S. Pitzer, *J. Am. Chem. Soc.*, **62**, 331 (1940).

(3) E. F. Westrum, Jr., and J. P. McCullough in "Physics and Chemistry of the Organic Solid State," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1963, p. 80.

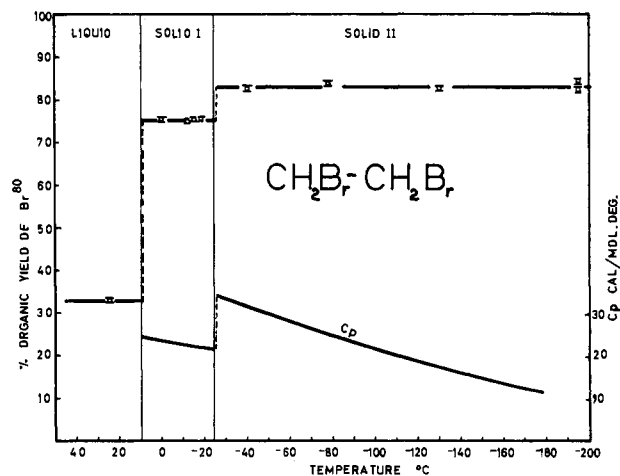


Fig. 1.—CH<sub>2</sub>BrCH<sub>2</sub>Br: upper curve, the organic yield of the ( $n, \gamma$ ) reaction as a function of temperature; lower curve, the heat capacity as a function of temperature (taken from ref. 2).

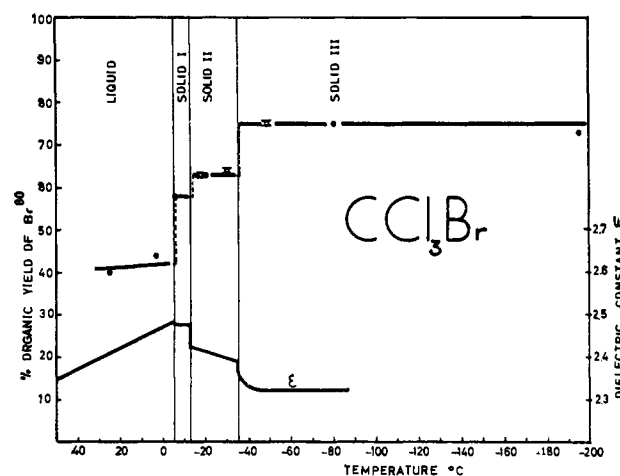


Fig. 2.—CCl<sub>3</sub>Br: upper curve, the organic yield of the ( $n, \gamma$ ) reaction as a function of temperature (●, points taken from ref. 4; ○ this work); lower curve, the dielectric constant as a function of temperature (taken from ref. 6).

have two phase transitions which appear to affect in a drastic way the chemical effect of the neutron capture.<sup>5</sup> The data obtained from the neutron irradiation is compared in the same figure with the variation of the measured dielectric constant as given by Miller and Smyth.<sup>6</sup> These authors interpreted their findings as meaning that in the solid state the CCl<sub>3</sub>Br molecules undergo "rotation around at least one axis, presumably the C–Br... with decrease of freedom at the higher transition point and disappearance below the lower."

The connection between phase transition and the Szilard–Chalmers effect might give a rationale for the apparently erratic variations of the organic yield with temperature in the organic solid state.<sup>7</sup>

Further studies are on the way to test the generality of this effect and to find a phenomenological explanation of the latter.

(4) S. Goldhaber, R. S. Chiang, and J. E. Willard, *J. Am. Chem. Soc.*, **73**, 2271 (1951).

(5) It is interesting to note at this point that the  $C(Br_2)$  value from the  $\gamma$ -ray decomposition of CCl<sub>3</sub>Br showed no such dependence on solid-phase transition; see R. F. Firestone and J. E. Willard, *ibid.*, **83**, 3551 (1961).

(6) R. C. Miller and C. P. Smyth, *ibid.*, **79**, 20 (1957).

(7) For a review of the problem and references see: T. I. Jones, R. H. Luebke, Jr., J. R. Wilson, and J. E. Willard, *J. Phys. Chem.*, **62**, 9 (1958).