

염화알루미늄 존재하에서의 수소화붕소나트륨과 대표적 유기화합물과의 반응

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Reaction of Representative Organic Compounds with Sodium Borohydride in the Presence of Aluminum Chloride

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요약 유기화합물의 선택환원에 필요한 자료를 얻기 위하여 수소화붕소나트륨과 염화알루미늄의 3:1 혼합물의 테트라히드로푸란 용액에서의 환원성을 규명하였다. 49개의 대표적 유기화합물을 골라 이시약과 실온에서 작용하여 대략의 반응속도와 정량관계를 알아보았다.

테트라히드로푸란 용액에서 염화알루미늄 1몰에 수소화붕소나트륨 3몰을 가하면 현탁용액이 생기는데 수소화붕소나트륨 보다는 훨씬 환원성이 강하다. 알데히드와 케톤은 한시간 이내에 빨리 환원되고 아실유도체는 서서히 그러나 카르복시산은 매우 느리게 환원되었다. 에스테르, 락톤, 에폭시드는 수소화붕소나트륨이나 보란보다 훨씬 빨리 환원되었다. 삼차 아미드는 서서히 환원되었으나 일차 아미드는 수소는 발생하지만 환원은 거의 일어나지 않았다. 벤조니트릴은 30분에 환원이 완결되었으나 카프로니트릴은 느리게 환원되었다. 니트로화합물, 이황화물, 술폰등은 이 시약과 반응하지 않으나 아조, 아족시, 옥심기는 서서히 반응하고 이소시아나산페닐은 도중단계까지만 환원되었다. 올레핀은 쉽게 수소화붕소화 반응을 하였다.

Abstract. The addition of one mole of aluminum chloride to three moles of sodium borohydride in tetrahydrofuran gives a turbid solution with enormously more powerful reducing properties than those of sodium borohydride itself. The reducing properties of this reagent were tested with 49 organic compounds which have representative functional groups. Alcohols liberated hydrogen immediately but showed no sign of hydrogenolysis of alkoxy group. Aldehydes and ketones were reduced rapidly within one hr. Acyl derivatives were reduced moderately, however, carboxylic acids were reduced much more slowly, Esters, lactones and epoxides were reduced readily than sodium borohydride or borane. Tertiary amide was reduced slowly, however, primary amide consumed one hydride for hydrogen evolution but reduction was sluggish. Aromatic nitrile was reduced

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much more readily than aliphatic nitrile. Nitro compounds were inert to this reagent but azo and azoxy groups were slowly attacked. Oxime was reduced slowly but isocyanate was only partially reduced. Disulfide and sulfoxide were attacked slowly but sulfide and sulfone were inert. Olefin was hydroborated rapidly.

Introduction

The discovery of sodium borohydride¹ and lithium aluminum hydride² brought about a revolutionary change in the procedures utilized for the reduction of functional groups in organic chemistry. Of these two reagents, sodium borohydride is a relatively mild reducing agent which is practically specific for the carbonyl group in aldehydes and ketones, whereas lithium aluminum hydride is an exceedingly powerful reagent which attacks almost all reducible groups³.

Therefore the reducing capabilities of lithium tri-*t*-butoxy-aluminum hydride⁴, lithium trimethoxyaluminum hydride⁵, aluminum hydride⁶, diborane⁷, thexylborane⁸, disiamylborane⁹, and 9-borabicyclononan¹⁰ were studied, in order to decrease the reducing properties of lithium aluminum hydride and increase the reducing properties of borohydride. And these hydride were able to do many valuable selective reductions. In this line of investigation, Brown and Subba Rao have discovered that the addition of anhydrous aluminum chloride or other polyvalent metal halides, such as gallium chloride or titanium tetrachloride provides solutions of tremendously enhanced reducing capacities than sodium borohydride itself.¹¹

In this study, we used the same mixture of sodium borohydride and aluminum chloride(3 : 1) but changed the solvent, thus we chose tetrahydrofuran with small amount of triglyme, and the reducing properties of this reagent were tested with the standard list of compounds which was tested for many other hydrides⁴⁻¹⁰

in the same method, in the hope that we could compare this reagent with other hydride more effectively.

Experiment

Reagent. In a 100ml flask, previously dried in an oven and cooled down to room temperature under dry nitrogen, fitted with an inlet port, rubber syringe cap and magnetic stirring bar and connected to a gas meter via a reflux condenser, there was placed 30.4 ml of dry tetrahydrofuran (THF) and 6ml of 1.66M sodium borohydride (10 mmoles) solution in triglyme and to this solution 3.6 ml of 0.92 M aluminum chloride (3.3 mmoles) solution in THF was added slowly with constant stirring, using hypodermic syringes to transfer solutions. The solution became turbid immediately and the precipitate settled down on standing. The clear solution and the whole turbid solution were analyzed for the hydride using 2 N H₂SO₄ and 2 N NaOH. And also after 3 hr at room temperature, the clear solution and the precipitate were analyzed for aluminum and chloride. (Table 1, 2)

The sodium borohydride used was 95% pure using hydride analysis, and the concentration of triglyme solution was determined by measuring the hydrogen evolution on hydrolysis. The aluminum chloride was used after sublimation under dry hydrogen chloride and the concentration of THF solution was determined by the neutralization titration with standard NaOH solution on the hydrochloric acid produced by the hydrolysis of the aluminum chloride solution in THF.

Table 1. Reaction of sodium borohydride with aluminum chloride in THF at room temperature

| Hydrolyzing solution | 1 hr | | 3 hr | | 6 hr | |
|-----------------------------------|-------------|--------------------|-------------|--------------------|-------------|--------------------|
| | Clear soln. | Whole turbid soln. | Clear soln. | Whole turbid soln. | Clear soln. | Whole turbid soln. |
| 2N H ₂ SO ₄ | — | 0.98* | 0.68 | 0.98 | 0.68 | 0.98 |
| 2N NaOH | — | 0.83 | 0.68 | 0.98 | 0.68 | 0.98 |

*μmoles of "hydride" per ml of solution.

Table 2. Analysis of the reaction mixture of sodium borohydride and aluminum chloride (3 : 1) in THF at room temperature

| | Hydride | Aluminum* | Chloride* |
|----------------|---------|-----------|-----------|
| Clear solution | 69.5% | 99.1% | 57.6% |
| Precipitate | 30.5% | 0.9% | 42.4% |

* I. M. Kolthoff, E. B. Sandell, E. J. Meehan and S. Bruckenstein, "Quantitative Chemical Analysis" 4th Ed. p. 599 and p. 720, The Macmillan Company 1969.

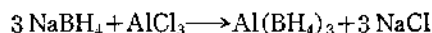
For the rate and stoichiometry studies, the above turbid solution was prepared in a large scale and used for several reactions. The hydride solution showed no appreciable concentration change in 48 hr at room temperature. The compounds used were from the same collection utilized in the earlier studies.⁴⁻¹⁰

Procedure. All reductions were carried out under a dry nitrogen atmosphere, using hypodermic syringes to transfer solutions. In a 100 ml flask, fitted with the same as described above, 26.6 ml of 1.5 M (in H⁻) the hydride solution and 3.4 ml of THF were placed, and 10 ml of 1 M solution of a compound in THF was added slowly. (The reaction mixture is 1M in H⁻ and 0.25 M in compound) The hydrogen gas evolved was measured, and the reaction mixture was kept at room temperature with constant stirring. At different time intervals, 4 ml aliquots were withdrawn and quenched in 2 N H₂SO₄ or in concentrated hydrochloric acid. (for nitrogen-containing compounds). The hydrogen evolved was measured volumetrically. The reaction was continued until two or more

analysis indicated a constant utilization of hydride or proceeded too slowly.

Results and Discussion

Reagent. The reagent was prepared by mixing sodium borohydride and anhydrous aluminum chloride in a mole ratio 3 to 1. in tetrahydrofuran mixed with small amount of triglyme. As shown in the experimental part the sodium borohydride, which is stable in 2 N NaOH, changed to other more active hydride which can be hydrolyzed with 2 N NaOH. The analysis of the reagent (see experimental part) shows that this is not a simple formation of aluminum borohydride.



One possible outcome of this analysis is that the products are aluminum hydride and sodium monochloroborohydride the latter being partially soluble in this solvent mixture.



57.6% in soln.

42.4% in ppt.

According to this scheme, the calculated hydride in solution would be 68% which is good agreement with the experimental

$$\left(3 + 9 \times \frac{57.6}{100}\right) / 12 \times 100 = 68(\%)$$

result 69.5%. Since our main interest was to explore the easily obtainable hydride system

for the sake of selective reductions, we did not examine the reagent further. Therefore we tested the reducing capabilities of this reagent with 49 representative compounds in the same manner as already studied for other hydrides.⁴⁻¹⁰

Rate and Stoichiometry Studies

Alcohols, Phenols, Amines and Thiols.

Alcohols, phenol and benzenethiol evolved one equivalent of hydrogen immediately whereas 0.18 equivalent from amine and 0.56 equivalent from hexanethiol. If aluminum chloride a strong

Lewis acid, were present as it is, one would expect the hydrogenolysis¹² of alkoxy function of benzyl alcohol but we did not observe any hydride consumption for reduction the results are summarized in Table 3.

Aldehydes and Ketones. The aldehydes and ketones examined all consumed one hydride indicating reduction to the corresponding alcohols. Again there was no sign of hydrogenolysis of alkoxy function even in the case of benzophenone. Cinnamaldehyde consumed a total of 2.38 hydrides, presumably one for the double bond, one for the carbonyl group and

Table 3. Reaction of representative "active hydrogen" compounds with sodium borohydride-aluminum chloride in tetrahydrofuran at room temperature.

| Compound ^(a) | Time, hr | Hydrogen evolved ^(b) | Hydride used ^(b) | Hydride used for reduction ^(b) |
|-------------------------|----------|---------------------------------|-----------------------------|---|
| 1-Hexanol | 0.5 | 1.00 | 1.00 | 0.00 |
| | 1.0 | 1.00 | 1.00 | 0.00 |
| | 3.0 | 1.00 | 1.00 | 0.00 |
| | 6.0 | 1.00 | 1.00 | 0.00 |
| Benzyl alcohol | 0.5 | 1.00 | 1.00 | 0.00 |
| | 1.0 | 1.00 | 1.00 | 0.00 |
| | 3.0 | 1.00 | 1.00 | 0.00 |
| 3-Hexanol | 0.5 | 1.08 | 1.08 | 0.00 |
| | 1.0 | 1.08 | 1.08 | 0.00 |
| | 3.0 | 1.08 | 1.08 | 0.00 |
| 3-Ethyl-3-pentanol | 0.5 | 0.98 | 0.98 | 0.00 |
| | 1.0 | 1.08 | 1.08 | 0.00 |
| | 3.0 | 1.08 | 1.08 | 0.00 |
| Phenol | 0.5 | 1.09 | 1.09 | 0.00 |
| | 1.0 | 1.09 | 1.09 | 0.00 |
| | 3.0 | 1.09 | 1.09 | 0.00 |
| <i>n</i> -Hexylamine | 0.5 | 0.18 | 0.18 | 0.00 |
| | 1.0 | 0.18 | 0.18 | 0.00 |
| 1-Hexanethiol | 0.5 | 0.49 | 0.49 | 0.00 |
| | 1.0 | 0.56 | 0.56 | 0.00 |
| | 3.0 | 0.56 | 0.56 | 0.00 |
| Benzenethiol | 0.5 | 1.06 | 1.06 | 0.00 |
| | 1.0 | 1.06 | 1.06 | 0.00 |
| | 3.0 | 1.06 | 1.06 | 0.00 |

a) 10.0 mmoles of compound, except were otherwise indicated, to 40.0 mmoles of hydride.

b) Moles/mole of compound.

Table 4. Reaction of representative aldehydes and ketones with sodium borohydride-aluminum chloride in tetrahydrofuran at room temperature.

| Compound ^(a) | Time hr | Hydrogen evolved ^(b) | Hydride used ^(a) | Hydride used for reduction ^(b) |
|-------------------------------|---------|---------------------------------|-----------------------------|---|
| Caproaldehyde | 0.5 | 0.18 | 1.03 | 0.85 |
| | 1.0 | | 1.10 | 0.93 |
| | 3.0 | | 1.26 | 1.08 |
| | 6.0 | | 1.26 | 1.08 |
| Benzaldehyde | 0.5 | 0.12 | 1.17 | 1.05 |
| | 1.0 | | 1.17 | 1.05 |
| | 3.0 | | 1.17 | 1.05 |
| 2-Heptanone | 0.5 | 0.09 | 1.12 | 1.03 |
| | 1.0 | | 1.12 | 1.03 |
| | 3.0 | | 1.12 | 1.03 |
| Norcamphor | 0.5 | 0.08 | 1.09 | 1.01 |
| | 1.0 | | 1.09 | 1.01 |
| | 3.0 | | 1.09 | 1.01 |
| Acetophenone | 0.5 | 0.09 | 1.12 | 1.03 |
| | 1.0 | | 1.12 | 1.03 |
| | 3.0 | | 1.12 | 1.03 |
| Benzophenone | 0.5 | 0.02 | 1.02 | 1.00 |
| | 1.0 | | 1.02 | 1.00 |
| | 3.0 | | 1.02 | 1.00 |
| Cinnamaldehyde ^(c) | 0.5 | 0.03 | 1.44 | 1.41 |
| | 1.0 | | 2.12 | 2.09 |
| | 3.0 | | 2.16 | 2.13 |
| | 6.0 | | 2.21 | 2.18 |
| | 10.0 | | 2.40 | 2.38 |
| | 24.0 | | 2.40 | 2.38 |

a~b, See corresponding footnotes in Table 3.

c, Hydride: Compound, 5 : 1

Table 5. Reaction of representative quinones with sodium borohydride-aluminum chloride in tetrahydrofuran at room temperature.

| compound ^(a) | Time hr | Hydrogen evolved ^(b) | Hydride used ^(a) | Hydride used for reduction ^(b) |
|------------------------------|---------|---------------------------------|-----------------------------|---|
| <i>p</i> -Benzoquinone | 0.5 | 0.89 | 2.47 | 1.58 |
| | 1.0 | 0.80 | 2.40 | 1.60 |
| | 3.0 | 0.89 | 2.47 | 1.58 |
| Anthraquinone ^(c) | 0.5 | 0.17 | 1.66 | 1.49 |
| | 1.0 | 0.17 | 2.00 | 1.83 |
| | 3.0 | 0.23 | 2.14 | 1.89 |
| | 6.0 | 0.20 | 2.17 | 1.97 |

a~b, See corresponding footnote in Table 3.

c, Reverse addition, yellowgreen precipitate.

0.38 for rehydrobaration after elimination⁷. The results are summerized in *Table 4*.

Quinones. One hydride consumption for reduction and one for hydrogen evolution is expected for *p*-benzoquinone to be reduced to hydroquinone.⁷ Therefore the higher hydride consumption suggest that some of the 1,4-dihydroxy hexadiene produced may be hydroborated further. The reduction of anthraquinone is similar with aluminium hydride⁶ but slower. The results are summerized in *Table 5*.

Carboxylic Acids and Derivatives. It is surprizing that this reagent, which is capable to hydroborate, react very slowly with carboxylic acids. Caproic acid was reduced to alcohol in 0.5 hr with BH_3 ⁷, and in 3 hr with AlH_3 ⁶ both at 0°C. Yet with this reagent, caproic acid consumed only one hydride for reduction in 10 hr and remain constant until 24 hr. We are going to explore further the possibility of partial reduction of acid to aldehyde. Anhydrides and benzoyl chloride were reduced moder-

Table 6. Reaction of representative acids and acyl derivatives with sodium borohydride-aluminum chloride in tetrahydrofuran at room temperature.

| Compound acid ^(a) | Time, hr | Hydrogen evolved ^(b) | Hydride used ^(b) | Hydride used for reduction ^(b) |
|-----------------------------------|----------|---------------------------------|-----------------------------|---|
| Caproic ^(c) | 0.5 | 1.12 | 1.44 | 0.32 |
| | 1.0 | | 1.54 | 0.42 |
| | 3.0 | | 1.82 | 0.70 |
| | 6.0 | | 1.94 | 0.94 |
| | 10.0 | | 2.12 | 1.00 |
| | 24.0 | | 2.12 | 1.00 |
| Benzoic acid ^(c) | 0.5 | 1.05 | 1.44 | 0.39 |
| | 1.0 | | 1.54 | 0.49 |
| | 3.0 | | 1.82 | 0.77 |
| | 6.0 | | 1.87 | 0.82 |
| | 12.0 | | 2.11 | 1.06 |
| | 24.0 | | 2.30 | 1.25 |
| | 41.0 | | 2.64 | 1.59 |
| Acetic anhydride ^(d) | 1.0 | 0.05 | 2.66 | 2.61 |
| | 3.0 | | 2.86 | 2.81 |
| | 6.0 | | 3.02 | 2.97 |
| | 24.0 | | 3.23 | 3.18 |
| | 48.0 | | 3.62 | 3.57 |
| Succinic anhydride ^(e) | 1.0 | 0.00 | 2.27 | 2.27 |
| | 3.0 | | 2.74 | 2.74 |
| | 6.0 | | 3.04 | 3.04 |
| | 24.0 | | 3.33 | 3.33 |
| Benzoyl chloride | 0.5 | 0.05 | 0.87 | 0.82 |
| | 1.0 | | 1.42 | 1.37 |
| | 3.0 | | 1.81 | 1.76 |
| | 6.0 | | 2.12 | 2.07 |
| | 12.0 | | 2.12 | 2.07 |

a~b, See corresponding footnote in *Table 3*.

e, White precipitate.

c, Hydride : Compound, 5 : 1. *d~e*, Hydride : Compound, 6.66 : 1

ately, the latter completing the reduction in 6 hr. The results are summarized in Table 6.

Esters and Lactones. All the esters and lactones consumed two hydrides in 3 to 6 hr, completing the reduction to alcohol stage. In the case of isopropenyl acetate, the two hydrides were consumed rapidly and the third hydride was consumed in 24 hr. Presumably hydroboration, elimination, and rehydroboration would be responsible to the rapid two hydride

uptake, the reduction of acetate being the slow hydride consumption. The results are summarized in Table 7.

Epoxides. All the three epoxides tested were reduced rapidly with this reagent. This is a remarkable contrast to sodium borohydride or borane, and comparable to the reaction of borane-borohydride mixture¹³. The results are summarized in Table 8.

Amides and Nitriles. The primary amide,

Table 7. Reaction of representative esters and lactones with sodium borohydride-aluminum chloride in tetrahydrofuran at room temperature.

| Compound ^(c) | Time, hr | Hydrogen evolved ^(b) | Hydride used ^(b) | Hydride used for reduction ^(b) |
|--|----------|---------------------------------|-----------------------------|---|
| Ethyl caproate | 0.5 | 0.04 | 1.64 | 1.60 |
| | 1.0 | | 1.87 | 1.83 |
| | 3.0 | | 2.09 | 2.06 |
| | 6.0 | | 2.09 | 2.06 |
| Ethyl benzoate | 0.5 | 0.03 | 0.86 | 0.83 |
| | 1.0 | | 1.44 | 1.41 |
| | 3.0 | | 1.91 | 1.88 |
| | 6.0 | | 2.01 | 1.98 |
| | 12.0 | | 2.19 | 2.16 |
| Phenyl acetate | 24.0 | 0.27 | 2.19 | 2.16 |
| | 0.5 | | 1.11 | 0.84 |
| | 1.0 | | 1.57 | 1.30 |
| | 3.0 | | 2.05 | 1.78 |
| | 6.0 | | 2.23 | 1.96 |
| | 12.0 | | 2.23 | 1.96 |
| γ -Butyrolactone ^(c) | 24.0 | 0.03 | 2.46 | 2.08 |
| | 0.5 | | 2.06 | 2.03 |
| | 1.0 | | 2.06 | 2.03 |
| Phthalide | 3.0 | 0.05 | 2.06 | 2.03 |
| | 0.5 | | 1.20 | 1.15 |
| | 1.0 | | 1.46 | 1.41 |
| | 3.0 | | 1.92 | 1.87 |
| Isopropenyl acetate ^(d) | 12.0 | 0.00 | 2.15 | 2.09 |
| | 23.0 | | 2.15 | 2.09 |
| | 1.0 | | 2.45 | 2.45 |
| | 3.0 | | 2.70 | 2.70 |
| | 6.0 | | 2.77 | 2.77 |
| | 24.0 | 3.07 | 3.07 | |

a~b, See corresponding footnote in Table 3.

c, Gelatinous white precipitate

d, Hydride : Compound, 5 : 1

Table 8. Reaction of representative epoxides with sodium borohydride-aluminum chloride in tetrahydrofuran at room temperature.

| Compound ^(a) | Time, hr | Hydrogen evolved ^(b) | Hydride used ^(b) | Hydride used for reduction ^(b) |
|-------------------------|----------|---------------------------------|-----------------------------|---|
| 1,2-Butylene oxide | 0.5 | 0.02 | 1.02 | 1.00 |
| | 1.0 | | 1.02 | 1.00 |
| | 3.0 | | 1.02 | 1.00 |
| Styrene oxide | 0.5 | 0.07 | 0.91 | 0.84 |
| | 1.0 | | 0.96 | 0.89 |
| | 3.0 | | 1.11 | 1.04 |
| | 6.0 | | 1.11 | 1.04 |
| Cyclohexene oxide | 0.5 | 0.08 | 1.03 | 0.95 |
| | 1.0 | | 1.11 | 1.03 |
| | 3.0 | | 1.11 | 1.03 |

a~b, See corresponding footnote in Table 3.

Table 9. Reaction of representative amides and nitriles with sodium borohydride-aluminum chloride in tetrahydrofuran at room temperature.

| Compound ^(a) | Time, hr | Hydrogen evolved ^(b) | Hydride used ^(b) | Hydride used for reduction ^(b) |
|-------------------------|----------|---------------------------------|-----------------------------|---|
| Benzamide | 1.0 | 0.88 | 1.09 | 0.21 |
| | 3.0 | 0.91 | 1.23 | 0.32 |
| | 6.0 | 0.91 | 1.32 | 0.41 |
| | 24.0 | 0.92 | 1.61 | 0.69 |
| N,N-Dimethylcaptoamide | 0.5 | 0.00 | 1.54 | 1.54 |
| | 1.0 | | 1.59 | 1.59 |
| | 3.0 | | 1.92 | 1.92 |
| | 12.0 | | 2.08 | 2.08 |
| Capronitrile | 0.5 | 0.07 | 1.10 | 1.03 |
| | 1.0 | | 1.37 | 1.30 |
| | 3.0 | | 1.80 | 1.73 |
| | 6.0 | | 1.92 | 1.85 |
| | 24.0 | | 2.04 | 1.97 |
| Benzonitrile | 0.5 | 0.03 | 2.04 | 2.01 |
| | 1.0 | | 2.04 | 2.01 |
| | 3.0 | | 2.04 | 2.01 |

a~b, See corresponding footnote in Table 3.

benzamide, evolved about one hydrogen, but the reduction is very slow, whereas the tertiary amide, N,N-dimethylcaproamide was easily reduced, This is very similar to borane⁷. The two nitriles tested were reduced to the amine stage, however, the reduction of benzonitrile was very fast, completing two hydride uptake

in 0.5 hr, whereas capronitrile required 24 hr. The results are summarized in Table 9.

Nitro Compounds and Their Derivatives. Nitropropane and nitrobenzene are not affected by this reagent. Therefore one would reduce aldehyde, ketone, ester, epoxide and nitrile function in the presence of nitro group without

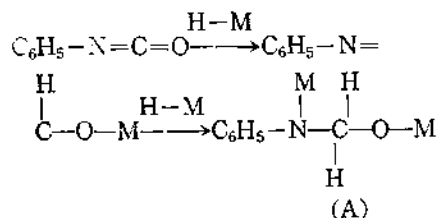
Table 10. Reaction of representative nitro compounds and their derivatives with sodium borohydride-aluminum chloride in tetrahydrofuran at room temperature.

| Compound ^(a) | Time, hr | Hydrogen evolved ^(b) | Hydride used ^(b) | Hydride used for reduction ^(b) |
|-------------------------|----------|---------------------------------|-----------------------------|---|
| 1-Nitropropane | 0.5 | 0.06 | 0.07 | 0.01 |
| | 1.0 | | 0.07 | 0.01 |
| | 3.0 | | 0.07 | 0.01 |
| | 24.0 | | 0.12 | 0.04 |
| Nitrobenzene | 0.5 | 0.19 | 0.20 | 0.01 |
| | 1.0 | | 0.20 | 0.01 |
| | 6.0 | | 0.24 | 0.05 |
| | 24.0 | | 0.24 | 0.05 |
| Azobenzene | 0.5 | 0.33 | 0.95 | 0.62 |
| | 1.0 | | 1.02 | 0.66 |
| | 3.0 | | 1.18 | 0.82 |
| | 6.0 | | 1.26 | 0.89 |
| | 24.0 | | 1.36 | 0.92 |
| | 48.0 | | 1.37 | 0.93 |
| Azoxybenzene | 0.5 | 0.00 | 0.00 | 0.00 |
| | 1.0 | | 0.00 | 0.00 |
| | 3.0 | | 0.08 | 0.08 |
| | 6.0 | | 0.47 | 0.47 |
| | 24.0 | | 0.44 | 1.31 |
| | 48.0 | | 1.60 | 1.47 |

a~b, See corresponding footnote in Table 3.

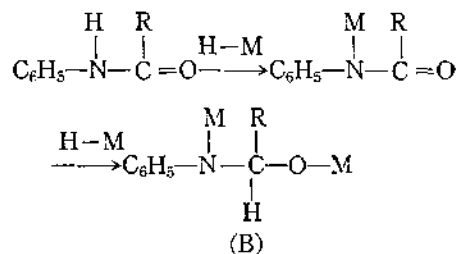
attacking the latter. Azobenzene and azoxybenzene were reduced slowly. The results are summarized in Table 10.

Other Nitrogen Compounds. Cyclohexanone oxime was reduced slowly to the amine stage, whereas phenylisocyanate was only partially reduced, similar to the reaction of borane⁷. It is quite plausible that the reduction has stopped at (A).



Since the intermediate (A) would be hydrolyzed to aldehyde and aniline, this suggest a possi-

bility of general aldehyde synthesis from N-phenylamide.



(A) and (B) is very similar, only difference is R in (B) instead of H in (A). We are going to explore further this possibility. The results are summarized in Table 11.

Sulfur Compounds and Olefin. Di-n-butyl disulfide and dimethyl sulfoxide reacted slowly with this reagent, however, methyl *p*-tolylsulfide, diphenyl sulfone, and methanesulfonic

Table 11. Reaction of representative other nitrogen compounds with sodium borohydride-aluminum chloride in tetrahydrofuran at room temperature.

| Compound ^(a) | Time, hr | Hydrogen evolved ^(b) | Hydride used ^(b) | Hydride used for reduction ^(b) | |
|---|----------|---------------------------------|-----------------------------|---|------|
| Cyclohexanone oxime ^(c) | 1.0 | 0.93 | 2.09 | 1.16 | |
| | 3.0 | | 2.30 | 1.37 | |
| | 6.0 | | 2.55 | 1.62 | |
| | 24.0 | | 2.93 | 2.00 | |
| Phenyl isocyanate ^(d) | 0.5 | 0.00 | 0.95 | 0.95 | |
| | 1.0 | | 1.39 | 1.39 | |
| | 3.0 | | 1.58 | 1.58 | |
| | 6.0 | | 1.92 | 1.92 | |
| | 10.0 | | 2.09 | 2.09 | |
| | 24.0 | | 2.09 | 2.09 | |
| Pyridine | 0.5 | 0.14 | 0.63 | 0.49 | |
| | 1.0 | | 0.64 | 0.50 | |
| | 3.0 | | 0.67 | 0.53 | |
| | 6.0 | | 0.67 | 0.53 | |
| | 24.0 | | 0.16 | 0.72 | 0.56 |
| | 48.0 | | 0.16 | 0.67 | 0.53 |
| Pyridine <i>N</i> -oxide ^(e) | 1.0 | 0.24 | 2.32 | 2.08 | |
| | 3.0 | | 2.61 | 2.37 | |
| | 6.0 | | 2.87 | 2.63 | |
| | 24.0 | | 3.22 | 2.96 | |

a~*b*; See corresponding footnote in Table 3.

d; Hydride : Compound, 5 : 1

e; Hydride : Compound, 6.66 : 1

Table 12. Reaction of representative sulfur derivatives and olefin with sodium borohydride-aluminum chloride in tetrahydrofuran at room temperature.

| Compound ^(a) | Time, hr | Hydrogen evolved ^(b) | Hydride used ^(b) | Hydride used for reduction ^(b) |
|-------------------------------|----------|---------------------------------|-----------------------------|---|
| Di- <i>n</i> -butyl disulfide | 0.5 | 0.15 | 0.23 | 0.08 |
| | 1.0 | 0.17 | 0.46 | 0.29 |
| | 3.0 | 0.20 | 0.54 | 0.34 |
| | 6.0 | 0.22 | 0.65 | 0.43 |
| | 24.0 | 0.26 | 1.04 | 0.78 |
| | 48.0 | 0.33 | 1.41 | 1.08 |
| | 72.0 | 0.38 | 1.58 | 1.20 |
| | | | | |
| Methyl <i>p</i> -tolylsulfide | 0.5 | 0.00 | 0.00 | 0.00 |
| | 1.0 | 0.00 | 0.00 | 0.00 |
| | 3.0 | 0.00 | 0.00 | 0.00 |
| Dimethylsulfoxide | 0.5 | 0.09 | 0.28 | 0.19 |
| | 1.0 | 0.13 | 0.42 | 0.29 |
| | 3.0 | 0.16 | 0.66 | 0.50 |
| | 6.0 | 0.16 | 0.91 | 0.75 |
| | 24.0 | 0.18 | 1.23 | 1.05 |

| | | | | |
|----------------------|-----|------|------|------|
| Diphenyl sulfone | 0.5 | 0.03 | 0.03 | 0.00 |
| | 1.0 | | 0.03 | 0.00 |
| | 3.0 | | 0.03 | 0.00 |
| Methanesulfonic acid | 0.5 | 1.02 | 1.02 | 0.00 |
| | 1.0 | | 1.02 | 0.00 |
| | 3.0 | | 1.02 | 0.00 |
| Cyclohexene | 1.0 | 0.02 | 0.94 | 0.92 |
| | 3.0 | | 1.02 | 1.00 |
| | 6.0 | | 1.02 | 1.00 |

a~b, See corresponding footnote in *Table 3*.

acid were inert. Finally cyclohexene was tested as an representative olefin. As was expected from the reaction of cinnamaldehyde, and isopropenyl acetate, cyclohexene was rapidly hydroborate. The results are summerized in *Table 12*.

Conclusion

The reducing properties of 3 to 1 mixture of sodium borohydride and aluminum chloride in THF are characterized. Further study should be necessary to clarify the exact nature of reducing species, yet this reagent behave as it were a mixture of aluminum hydride and borane. We believe this study together with those of other hydrides,⁴⁻¹⁰ will serve for selective reduction.

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