

Wet SiO_2 As a Suitable Media for Fast and Efficient Reduction of Carbonyl Compounds with NaBH_3CN under Solvent-Free and Acid-Free Conditions

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Reduction of carbonyl compounds such as aldehydes, ketones, α,β -unsaturated enals and enones, α -diketones and acyloins was carried out readily with NaBH_3CN in the presence of wet SiO_2 as a neutral media. The reactions were performed at solvent-free conditions in oil bath (70 - 80 °C) or under microwave irradiation (240 W) to give the product alcohols in high to excellent yields. Regioselective 1,2-reduction of conjugated carbonyl compounds took place in a perfect selectivity without any side product formation.

Key Words: NaBH_3CN , Wet SiO_2 , Solvent-free, Microwave irradiation, Reduction

Introduction

Reduction is one of the most important reactions in organic synthesis and a vast variety of reducing agents have been introduced for this achievement.¹ In this context, considerable attention has been devoted to modified borohydride agents for reduction of organic functional groups.^{2,3} NaBH_3CN carrying an electron withdrawing cyanide group is a remarkable stable and selective reducing agent and has been found many applications in organic synthesis.⁴ It is clear that the reducing capabilities of NaBH_3CN for the reduction of carbonyl compounds vary greatly with pH. Thus in basic or neutral media, aldehydes and ketones are practically inert toward the reagent and adequate reduction rates are only obtained under acidic conditions (pH 3 - 4).^{5,6} Although, NaBH_3CN has been used in many organic reactions, however, this reagent suffers from harsh reaction conditions (strong acidic media), limitation to use acid-sensitive functional groups and formation of side products.

Therefore, the development and introduction of convenient methods which use green and mild reaction conditions are practically concerned and still in demand. So, we wish to introduce wet SiO_2 as a suitable and neutral media for fast and efficient reduction of various carbonyl compounds with NaBH_3CN under solvent-free and acid-free conditions.

Results and Discussion

In order to overcome the disadvantages of sodium cyanoborohydride at low pH values, we decided to investigate the possibility of replacing strongly acidic conditions with a suitable solid and neutral media without losing the reducing power of NaBH_3CN . In addition, the reductions can be carried out under eco-friendly conditions.

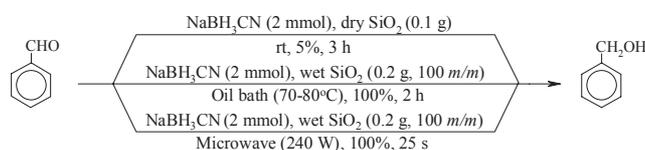
The literature review shows that wet SiO_2 as an inexpensive and readily available reagent has been widely used in organic synthesis.⁷ Therefore, in continuation of our research program toward the development of new modified borohydride agents,³ we decided to examine the reducing capability of $\text{NaBH}_3\text{CN}/\text{wet SiO}_2$ system for reduction of carbonyl compounds under sol-

vent-free and acid-free conditions. Reaction conditions were preliminary optimized by reduction of benzaldehyde (1 mmol) as a model compound with NaBH_3CN (2 mmol) in the presence or absence of SiO_2 (dry and wet) at different conditions. As seen in Table 1, NaBH_3CN exhibited the best reducing capability in the presence of wet SiO_2 under solvent-free conditions. However, 0.2 g wet SiO_2 (100 m/m, mass ratio) which is prepared by simply mixing of water (0.1 g) and SiO_2 (0.1 g) was the requirement for complete reduction of PhCHO at room temperature or oil bath conditions (entries 5, 6).

On the other hand, microwave irradiation as an unconventional energy source has been widely used to perform many kinds of chemical reactions and numerous reviews and papers demonstrated its importance.⁸ It is well known microwave dielectric heating effect uses the ability of liquids and solids to transform electromagnetic energy into heat and so drive chemical reactions effectively and quickly. Thus, we decided to incorporate microwave irradiation with $\text{NaBH}_3\text{CN}/\text{wet SiO}_2$ as a new protocol for solvent-free reduction of carbonyl compounds. The experiment showed that reduction of PhCHO (1 mmol) with NaBH_3CN (2 mmol)/wet SiO_2 (0.2 g, 100 m/m) system was dramatically accelerated under microwave irradiation and completed within 25 sec (Table 1, entry 8) (Scheme 1).

The successful results either in oil bath or under microwave irradiation explored the suitability of wet SiO_2 (0.2 g, 100 m/m) for fast and efficient reduction of benzaldehyde with NaBH_3CN in a neutral media, and therefore they were selected as the optimum reaction conditions.

The synthetic utility of $\text{NaBH}_3\text{CN}/\text{wet SiO}_2$ system was further studied by the reduction of various aliphatic and aromatic aldehydes at the optimized conditions. The results showed that



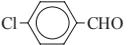
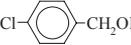
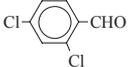
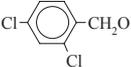
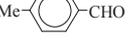
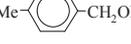
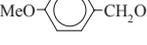
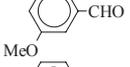
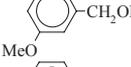
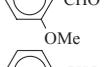
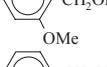
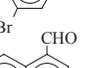
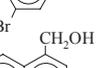
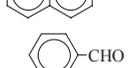
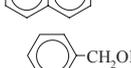
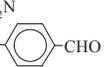
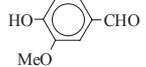
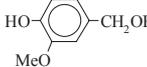
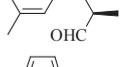
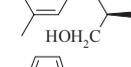
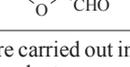
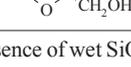
Scheme 1

Table 1. Solvent-free reduction of benzaldehyde and acetophenone with NaBH₃CN in the presence or absence of SiO₂ under different condition^a

Entry	Reaction components Molar ratio	Media	Condition ^b	Time	Conversion (%)
1	PhCHO/NaBH ₃ CN (1:2)	H ₂ O (2 mL)	Reflux	3 h	5
2	PhCHO/NaBH ₃ CN (1:2)	Solvent-free	Oil bath	3 h	35
3	PhCHO/NaBH ₃ CN (1:2)	Dry SiO ₂ (0.1 g)	rt	3 h	5
4	PhCHO/NaBH ₃ CN (1:2)	Wet SiO ₂ (0.16 g, 60% <i>m/m</i>)	rt	5 h	80
5	PhCHO/NaBH ₃ CN (1:2)	Wet SiO ₂ (0.2 g, 100% <i>m/m</i>)	rt	3.5 h	100
6	PhCHO/NaBH ₃ CN (1:2)	Wet SiO ₂ (0.2 g, 100% <i>m/m</i>)	Oil bath	2 h	100
7	PhCHO/NaBH ₃ CN (1:2)	Wet SiO ₂ (0.16 g, 60% <i>m/m</i>)	Microwave	2 min	100
8	PhCHO/NaBH ₃ CN (1:2)	Wet SiO ₂ (0.2 g, 100% <i>m/m</i>)	Microwave	25 sec	100
9	PhCOCH ₃ /NaBH ₃ CN (1:3)	Dry SiO ₂ (0.1 g)	Oil bath	12 h	0
10	PhCOCH ₃ /NaBH ₃ CN (1:3)	Wet SiO ₂ (0.2 g, 100% <i>m/m</i>)	Oil bath	2.3 h	100
11	PhCOCH ₃ /NaBH ₃ CN (1:3)	Wet SiO ₂ (0.13 g, 30% <i>m/m</i>)	Microwave	20 min	70
12	PhCOCH ₃ /NaBH ₃ CN (1:3)	Wet SiO ₂ (0.16 g, 60% <i>m/m</i>)	Microwave	3 min	95
13	PhCOCH ₃ /NaBH ₃ CN (1:3)	Wet SiO ₂ (0.2 g, 100% <i>m/m</i>)	Microwave	60 sec	100

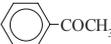
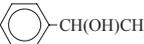
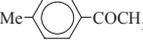
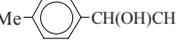
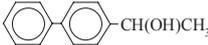
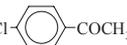
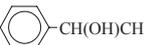
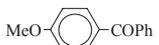
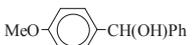
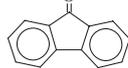
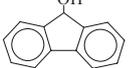
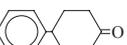
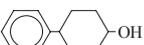
^aReduction of benzaldehyde and acetophenone was carried out in 1 mmol scale. ^bTemperature of oil bath was 70 - 80 °C and the irradiation of microwaves was carried out at 240 W.

Table 2. Solvent-free reduction of aldehydes with NaBH₃CN/wet SiO₂ system^a

Entry	Substrate	Product	Molar ratio Subs./NaBH ₃ CN	Oil bath		Microwave	
				Time (h)	Yield (%) ^b	Time (sec)	Yield (%) ^b
1			1:2	2	95	25	96
2			1:2	3	98	40	98
3			1:2	3.1	98	45	98
4			1:2	4.3	98	60	99
5			1:2	3.8	96	35	98
6			1:2	3.2	94	40	96
7			1:2	4	95	40	95
8			1:2	2.3	96	45	96
9			1:2	4	98	90	97
10			1:2	2	94	35	95
11			1:2	2	99	20	99
12			1:2	3.2	92	45	93
13			1:2	2.3	91	50	92
14			1:2	1.5	89	45	91

^aAll reactions were carried out in the presence of wet SiO₂ (0.2 g, 100% *m/m*) in oil bath (70 - 80 °C) or under microwave irradiation (240 W). ^bYields refer to isolated pure products.

Table 3. Solvent-free reduction of ketones with NaBH₃CN/wet SiO₂ system^a

Entry	Substrate	Product	Molar ratio Subs./NaBH ₃ CN	Oil bath		Microwave	
				Time (h)	Yield (%) ^b	Time (sec)	Yield (%) ^b
1			1:3	2.3	97	60	97
2			1:3	3	96	80	98
3			1:3	2.8	96	80	96
4			1:3	4.5	99	200	99
5			1:3	2.5	95	70	97
6			1:4	3.8	97	120	96
7			1:3	4.5	99	180	99
8			1:3	3.7	96	120	96
9			1:5	4.2	97	180	98
10			1:5	3	96	100	96
11			1:3	1.5	92	25	91
12			1:3	2	95	30	96

^aAll reactions were carried out in the presence of wet SiO₂ (0.2 g, 100% *m/m*) in oil bath (70 - 80 °C) or under microwave irradiation (240 W). ^bYields refer to isolated pure products.

Table 4. Comparison of reduction of aldehydes and ketones with NaBH₃CN in wet SiO₂ and acidic MeOH

Entry	Substrate	Product	Molar Ratio, ^a Time (h) and Yield (%)		
			Wet SiO ₂ /oil bath ^b	Wet SiO ₂ /microwave ^b	Acidic MeOH ^{c,5}
1	PhCHO	PhCH ₂ OH	(1:2)(2)(95)	(1:2)(25 sec)(96)	(1:1)(2)(87)
2	PhCOCH ₃	PhCH(OH)CH ₃	(1:3)(2.3)(97)	(1:3)(60 sec)(97)	(1:1.07)(1)(93)
3	Ph ₂ CO	Ph ₂ CHOH	(1:3)(4.5)(99)	(1:3)(180 sec)(99)	(1:1)(14)(70)
4	Cyclohexanone	Cyclohexanol	(1:3)(1.5)(92)	(1:3)(25 sec)(91)	(1:0.5)(1)(88)
5	Furfural	Furfuryl alcohol	(1:2)(1.5)(89)	(1:2)(45 sec)(91)	(1:1)(1)(0) ^d

^aMolar ratio as Subs./NaBH₃CN; ^bThe present work; ^cApproximate pH 3 - 4; ^dReduction of furfural with NaBH₃CN in acidic MeOH (2 N, HCl) produced polymeric tar material.

all types of aldehydes were reduced efficiently with NaBH₃CN (2 mmol)/wet SiO₂ (0.2 g, 100 *m/m*) in oil bath (within 2 - 4.3 h) or under microwave irradiation (within 20 - 90 sec) to give the corresponding primary alcohols in high to excellent yields (Table 2).

Next, we turned our attention to the reduction of ketones with NaBH₃CN/wet SiO₂ system. The experiments for reduction of acetophenone exhibited due to less reactivity of ketones relative to aldehydes, the reduction required higher quantity of NaBH₃CN (3 mmol) in the presence of wet SiO₂ (0.2 g, 100 *m/m*). The reaction was carried out efficiently in oil bath or under microwave irradiation within 2.3 h and 60 sec, respectively

(Table 1, entries 10, 13). The capability of NaBH₃CN/wet SiO₂ system was studied more with the reduction of structurally different aliphatic and aromatic ketones by 3 - 5 molar equivalents of NaBH₃CN in the presence of wet SiO₂ (0.2 g, 100 *m/m*). Table 3 shows that all ketone compounds were reduced efficiently under solvent-free conditions to give the corresponding secondary alcohols in high to excellent yields.

The suitability of NaBH₃CN/wet SiO₂ system in reduction of aldehydes and ketones was highlighted by comparison of our results with those of reported for NaBH₃CN/acidic MeOH (2 N, HCl).⁵ Case study in Table 4 shows that the reducing potential of NaBH₃CN in wet SiO₂ is more efficient than acidic

Table 5. Solvent-free reduction of α,β -unsaturated carbonyl compounds with $\text{NaBH}_3\text{CN}/\text{wet SiO}_2$ system^a

Entry	Substrate	Product	Molar ratio Subs./ NaBH_3CN	Oil bath		Microwave	
				Time (h)	Yield (%) ^b	Time (sec)	Yield (%) ^b
1			1:2	2.8	95	30	96
2			1:3	4.2	99	90	99
3			1:3	4.2	99	75	99
4			1:3	4	97	85	98
5			1:3	4.8	95	95	96
6			1:3	5	98	110	98
7			1:2	3	92	50	92
8			1:3	4	97	90	98

^aAll reactions were carried out in the presence of wet SiO_2 (0.2 g, 100% *m/m*) in oil bath (70 - 80 °C) or under microwave irradiation (240 W). ^bYields refer to isolated pure products.

MeOH. In addition, reduction of furfural as an acid-sensitive aldehyde with $\text{NaBH}_3\text{CN}/\text{wet SiO}_2$ was carried out effectively to give furfuryl alcohol as a sole product (Table 2, entry 14), whereas using NaBH_3CN in acidic MeOH gave polymeric tar material as the major product (Table 4, entry 5).

The preparation of allyl alcohols from regioselective 1,2-reduction of α,β -unsaturated aldehydes and ketones is a widely utilized method in organic synthesis.^{1,2} Considerable attentions have been paid to the development of various borohydride agents for this purpose.³ The literature review shows that reduction

Table 6. Comparison of reduction of conjugated carbonyl compounds with NaBH_3CN in wet SiO_2 or acidic media

Entry	Substrate	Condition	Molar Ratio ^a	Time (h)	Products, Yield (%)			
					Allylic alcohols	Allylic hydrocarbons	Allylic ether	Satrtng material
1	PhCH=CHCHO	Wet SiO_2 /oil bath ^b	1:2	2.8	95	-	-	-
2		Wet SiO_2 /microwave ^b	1:2	30 sec	96	-	-	-
3		Acidic MeOH ^{c,5}	1:2	1.5	80	-	8	-
4		Acidic HMPT ^{d,6}	-	-	-	-	-	-
5	PhCH=CHCOCH ₃	Wet SiO_2 /oil bath ^b	1:3	4.2	99	-	-	-
6		Wet SiO_2 /microwave ^b	1:3	90 sec	99	-	-	-
7		Acidic MeOH ^{c,6}	1:2	1.5	77	-	11	-
8		Acidic HMPT ^{d,6}	1:4	1	58	-	-	-
9	PhCH=CHCOPh	Wet SiO_2 /oil bath ^b	1:3	4.2	99	-	-	-
10		Wet SiO_2 /microwave ^b	1:3	75 sec	99	-	-	-
11		Acidic MeOH ^{c,5}	1:3	2.5	-	4.8	26	12
12		Acidic HMPT ^{e,6}	1:4	1	-	53	-	16
13		Wet SiO_2 /oil bath ^b	1:2	3	92	-	-	-
14		Wet SiO_2 /microwave ^b	1:2	50 sec	92	-	-	-
15		Acidic MeOH ^{c,5}	1:2	2	69	-	12	-
16		Acidic HMPT ^{d,6}	1:4	1.5	79	-	-	-
17		Wet SiO_2 /oil bath ^b	1:3	4	97	-	-	-
18		Wet SiO_2 /microwave ^b	1:3	90 sec	98	-	-	-
19		Acidic MeOH ^{c,5}	1:2	2	88	-	-	-
20		Acidic HMPT ^{d,6}	1:4	1.5	60	-	-	-

^aMolar ratio as Subs./ NaBH_3CN ; ^bThe present work; ^cpH 3; ^dAcidity: 1.9 M; ^eAcidity: 0.75 M; ^f(*n*-Bu)₄ NaBH_3CN was used as a reducing agent.

Table 7. Solvent-free reduction of α -diketones and acyloins with NaBH₃CN/wet SiO₂ system^a

Entry	Substrate	Product	Molar ratio Subs./NaBH ₃ CN	Oil bath		Microwave	
				Time (h)	Yield (%) ^b	Time (sec)	Yield (%) ^b
1			1:4	3	93	55	93
2			1:3	2.1	94	45	94
3			1:4	4.2	95	105	96
4			1:3	3.8	95	95	96
5			1:4	3.5	96	65	97

^aAll reactions were carried out in the presence of wet SiO₂ (0.2 g, 100% *m/m*) in oil bath (70 - 80 °C) or under microwave irradiation (240 W). ^bYields refer to isolated pure products without assumption of their diastereoselectivities.

of conjugated carbonyl compounds with NaBH₃CN in acidic MeOH often afforded the corresponding allylic methyl ethers accompanied with allyl alcohols.⁶ It was also reported that doing of the reductions in acidic HMPT produces allylic hydrocarbons accompanied with allyl alcohols.⁶ Thus, reduction of conjugated carbonyl compounds with NaBH₃CN in acidic protic and aprotic solvents is not regioselective and it suffers from harsh reaction conditions (strongly acidic media) accompanied with side product formation.

In this context, the regioselectivity of NaBH₃CN/wet SiO₂ system in reduction of α,β -unsaturated aldehydes and ketones was examined by solvent-free reduction of cinnamaldehyde with 2 molar equivalents of NaBH₃CN in the presence of wet SiO₂ (0.2 g, 100 *m/m*). The reaction was carried out efficiently and exclusively in 1,2-reduction manner in oil bath or under microwave irradiation (Table 5, entry 1). This achievement encouraged us to explore the synthetic utility of NaBH₃CN/wet SiO₂ system for reduction of some conjugated enals and enones under solvent-free conditions. Reduction of benzalacetone, substituted benzalacetophenones, citral and β -ionone was examined with NaBH₃CN (2 - 3 mmol)/wet SiO₂ (0.2 g, 100 *m/m*) system and the corresponding allylic alcohols were obtained absolutely in high to excellent yields (Table 5).

In order to show the suitability and regioselectivity of NaBH₃CN/wet SiO₂ system in reduction of conjugated carbonyl compounds, we compared our results with those of reported for NaBH₃CN in acidic MeOH or HMPT⁶ (Table 6). A comparison shows that in view points of efficiency, regioselectivity and neutral reaction conditions, NaBH₃CN in wet SiO₂ is more efficient than acidic MeOH or HMPT.

Synthetic utilities of vicinal diols are well known and their preparations from reduction of α -diketones and acyloins have attracted a great deal of attention.³ In this line, we examined solvent-free reduction of α -diketones and acyloins with NaBH₃CN/wet SiO₂ system in oil bath or under microwave irradiation. Reduction of α -diketones to their vicinal diols took place by 4 molar equivalents of NaBH₃CN in the presence of wet SiO₂

(0.2 g, 100 *m/m*) (Table 7). The product 1,2-diols were obtained in excellent yields and all attempts to reduce α -diketones into acyloins were unsatisfactory by this reducing system. Reduction of acyloins to vicinal diols was also achieved successfully by NaBH₃CN in wet SiO₂. Using 2 molar equivalents of NaBH₃CN and 0.2 g wet SiO₂ (100 *m/m*) were the requirements for the formation of 1,2-diols in high yields (Table 7).

The influence of wet SiO₂ for fast and efficient reduction of carbonyl compounds by NaBH₃CN is not clear, however, we think that the following factors maybe play a role in the observed promotion: i) The adsorbed water on the surface of SiO₂ can solubilize sodium cyanoborohydride and therefore it lead to fine dispersion of reducing agent on the surface of silica gel to do more interaction with the substrate. ii) SiO₂ in the presence of water with showing a Lewis acidity character and then more interaction with the carbonyl group, make this functional group susceptible for the hydride attack. iii) The borate intermediate which is produced by reduction of a carbonyl group by NaBH₃CN can be hydrolyzed with the adsorbed water on the surface of silica gel and subsequently shows acceleration on the rate of reduction.

Conclusion

In this study, we have shown the suitability of wet SiO₂ (0.2 g, 100 *m/m*) as a neutral media to carry out reduction of carbonyl compounds with NaBH₃CN instead of strongly acidic conditions. All reactions took place at solvent-free conditions in oil bath or under microwave irradiation. Reduction of conjugated carbonyl compounds with NaBH₃CN/wet SiO₂ system was performed in exclusive 1,2-reduction manner and the corresponding allylic alcohols were obtained in high to excellent yields. Reduction of α -diketones and acyloins was investigated successfully with NaBH₃CN/wet SiO₂ system. Solvent-free conditions, high efficiency and regioselectivity and neutral reaction media are the advantages of NaBH₃CN/wet SiO₂ system which could be made this protocol a synthetically useful addition to the present methodologies.

Experimental Section

General. All reagents and substrates were purchased from commercial sources with the best quality and were used without further purification. SiO₂ was used in the form of silica gel 60 (70 - 230 mesh ASTM) and was purchased from Merck company. IR and ¹H/¹³C NMR spectra were recorded on Thermo Nicolet Nexus 670 FT-IR and Bruker Avance 300 MHz spectrometers, respectively. The products were characterized by a comparison with authentic samples (melting or boiling points) and their spectroscopic data. All microwave assisted reactions were carried out in a Yusch household microwave oven at 24% power amplitude (240 W). Temperature of oil bath was 70 - 80 °C. All yields refer to isolated pure products. TLC was applied for the purity determination of substrates, products and reaction monitoring over silica gel 60 F254 aluminum sheet.

A typical procedure for solvent-free reduction of carbonyl compounds with NaBH₃CN/wet SiO₂ under oil bath conditions. To a round-bottomed flask (5 mL), SiO₂ (0.1 g) and H₂O (0.1 g) were added and the mixture was stirred with a magnetic stirrer for 2 min to yield wet SiO₂ (0.2 g, 100% m/m). PhCHO (0.106 g, 1 mmol) was then added to the flask and the resulting mixture was stirred for an additional 5 min. By addition of NaBH₃CN (0.125 g, 2 mmol) and running the reaction mixture under oil bath (70 - 80 °C) conditions, the reaction was completed in 2 h. The progress of the reaction was monitored by TLC (eluent; *n*-hexane/Et₂O: 5/2). After all, MeOH (2 mL) was added and the mixture was stirred for 15 min at room temperature. Methanolic solution was filtered and then dried over anhydrous Na₂SO₄. Evaporation of all volatile materials after a short column chromatography of the resulting crude product over silica gel (eluent; *n*-hexane/Et₂O: 5/2) gave the pure colorless liquid benzyl alcohol (0.103 g, 95%, Table 2).

Caution: Due to evolution of few amount of HCN gas from the reaction mixture (tested by a Litmus strip), it is strongly recommended to perform all reduction reactions under a good fuming hood or conducting the gas to a KOH solution via a sealed system.

A typical procedure for solvent-free reduction of carbonyl compounds with NaBH₃CN/wet SiO₂ under microwave irradiation. In a round-bottomed flask (5 mL) charged with wet SiO₂ (0.2 g, 100 m/m), acetophenone (0.12 g, 1 mmol) was added and the reaction mixture was stirred for 5 min. After addition of NaBH₃CN (0.188 g, 3 mmol), the mixture was irradiated in a household microwave oven (240 W) for 60 sec. The progress of the reaction was monitored by TLC (eluent; *n*-hexane/Et₂O: 5/2). MeOH (2 mL) was then added and the reaction mixture was continued to stirring for 15 min. Methanolic solution was filtered and then dried over anhydrous Na₂SO₄. Evaporation of all volatile materials after a short column chromatography of the resulting crude product over silica gel (eluent; *n*-hexane/Et₂O: 5/2) gave the pure colorless liquid 1-phenylethanol (0.118 g, 97%, Table 3).

Caution: It's strongly recommended to perform all microwave-assisted reductions under a good fuming hood.

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