SYNTHETICALLY USEFUL REACTIONS WITH NICKEL BORIDE. A REVIEW

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INTRODUCTION

1. Background

Many transition metals and their compounds have useful catalytic properties due to their variable valency. Recently, transition metals have been used as catalysts or as additives in conjunction with complex metal hydrides to modulate the scope, regio and stereoselectivity of such reductions. Many useful synthetic methods have been developed by trying various combinations of salt and complex hydride reducing agents. The resulting systems are complex and in most cases virtually nothing is known about mechanism or reactive intermediates.

The reaction of sodium borohydride with Co(II), Ni(II) and Cu(II) salts in protic solvents affords black precipitates which contain both boron and hydrogen. These black precipitates may be borides as in case of Ni(II) and Co(II) or can be a mixture of zero valent metal and boride as in case of Cu(II). In 1951, Paul et al.[1] reported that these black precipitates catalyze hydrogenation reactions. Since borides actively catalyze the decomposition of sodium borohydride, they are commonly used as practical controlled sources of hydrogen (*Eq. 1*).

$$NaBH_4 + 2H_2O \xrightarrow{\quad M_2B \quad} NaBO_2 + 4H_2 \qquad (1)$$

The discovery of borides has opened a new area of research for chemists to unfold the applications of these catalysts and to understand them.

Our recent experience of reductions using nickel boride showed that it gives a remarkable variety of products of wide applications depending on the reaction conditions. However, the information about its use in synthetic organic chemistry is widely scattered . The object of this review is, therefore, to summarize and correlate whatever information is available about nickel boride and to stimulate practical applications.

2. Catalyst Preparation

Borides generally are prepared by heating metals with boron, reduction of metal oxides by mixtures of carbon and boron carbide, electrolysis of fused salts and by a variety of other methods. Schlesinger[2] reported a simple synthesis of nickel boride in his pioneering work on borohydrides. Combination of nickel(II) salts with aqueous sodium borohydride deposited a finely divided black precipitate of Ni_2B (*Eq. 2*).

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$$4NaBH_4 + 2NiCl_2 + 9H_2O \longrightarrow Ni_2B + 3H_3BO_3 + 4NaCl + 12.5\,H_2 \qquad (2)$$

It will be apparent that small variations in the method of preparation can dramatically affect the activity, selectivity, physical and chemical properties of the boride. For example, in aqueous media, a granular black material is formed from sodium borohydride and Ni(II) acetate.[3] This material, P-1 Ni, is at least as active as Raney Ni for double bond hydrogenations. However, in 95% ethanol, a nearly colloidal black suspension is produced, which is more sensitive to the double bond structure and is designated P-2 Ni.[4] Similarly a P-1.5 Ni catalyst is prepared using 50% ethanol-water solution as solvent. These designations are derived from Purdue University where the work on nickel boride catalyst was initiated.[3,4] However, in good donor solvents such as N,N-dimethylformamide or N,N-dimethylacetamide, soluble metal (hydride, borohydride) species are produced, which can catalyze homogeneous hydrogenations or other hydride reductions. Violent exothermic reactions can occur, generating flammable gases. Dissolving $NaBH_4$ in DMF on a large scale with inefficient cooling is hazardous. To avoid a potential violent reaction, the use of N,N-dimethylacetamide is recommended, especially in processes conducted at elevated temperatures[10b] (**Caution**: Concentrated solutions of $NaBH_4$ in DMF in the absence of reducible substrate are unsafe at elevated temperatures). This is not to say, however, that borides cannot be prepared in one solvent and then used to catalyze reactions in another.[10b]

Other versions of this synthesis have been conducted in alcoholic or ether solvents under an inert atmosphere or under hydrogen pressure.[5] Some reductions even require *in situ* preparation of the catalyst. Nickel boride catalysts have also been deposited in the presence of promoter metals (about 2%) e.g., chromium, tungsten or vanadium[2b], to increase catalytic activity. Boudart[6] has shown that this increase in activity (as measured by dehydrogenation of isopropyl alcohol to acetone) is directly proportional to an increase in catalyst surface area, presumably owing to the presence of a foreign material during catalyst precipitation.

Catalyst activity and selectivity can be improved by support on an inert solid surface such as charcoal.[7a] A novel approach is to prepare the catalyst consisting of very small particles of the nickel boride uniformly dispersed in a small non-porous polymer gel (e.g. cross-linked 2-hydroxyethyl methacrylate).[7b] Nakao *et al.*[8a] reported that a solution of colloidal nickel boride protected by polyvinylpyrrolidone (CNB-PVP) exhibited more than 10 times the catalytic activity for olefin hydrogenation compared to Ni_2B precipitated without using polymers. A supported catalyst, which is formed by immobilizing the initially formed nickel boride on the surface of insoluble $Mg(OH)_2$ present in solution, shows even better activity.[8b]

3. Catalyst Composition and Properties

Nickel boride is nonmagnetic and nonpyrophoric.[3] It can be filtered and stored moist without problems. However when dry, it becomes pyrophoric and ferromagnetic. It is very soluble in

dilute mineral acids such as hydrochloric, sulfuric and nitric acids but is insoluble in alkali. However, the choice of acid used depends on specific reactions. It has also been observed that preformed nickel boride is inactive in catalyzing certain desulfurization and deselenization reactions.

The actual composition of borides prepared from inorganic salts depends to a great extent on the specific mode of preparation. Maybury, Mitchell and Hawthorne[9] analyzed nickel boride prepared in ethanol under nitrogen atmosphere using a three-fold excess of $NaBH_4$ and concluded that Ni_2B inadequately represents its composition. Besides containing solvent and adsorbed H_2, which was released upon heating, the solids were contaminated with tightly trapped NaCl. On the basis of the metal:boron ratio and the amounts of H_2 evolved, the formula $(Ni_2B)_2H_3$ was suggested. X-ray diffraction analysis revealed the structure of nickel boride to be amorphous. Certain preparations of Ni_2B, however, become crystalline when heated to 250° or higher. These crystalline materials have been identified as mixtures of Ni and Ni_2B or Ni_3B. The loss of boron from original products on heating is possibly due to oxidation of the material by adsorbed water but the reduction of boron by clathered hydrogen causing evolution of diborane cannot be ruled out. While loss of boron with concomitant crystallization of the structure has been confirmed by several groups[10a], it remains to be seen whether these more ordered borides retain their former activity.

Recently, Okamoto et al.[11] have used X-ray photoelectron spectroscopy (XPS) to examine the surface structure of amorphous nickel boride. These studies revealed that surface nickel existed in three forms-nickel(0), nickel oxide (NiO) and boron bound nickel. Two forms of boron were detected regardless of the solvent or metal salt used, namely, nickel bound boron (designated B-I boron) and BO_2 (designated B-II boron). It is known that $NaBO_2$ may be produced as a side product in the reduction of a nickel salt with sodium borohydride to produce nickel boride (nickel boride catalyzes the decomposition of $NaBH_4$).

$$NaBH_4 + 2H_2O \longrightarrow NaBO_2 + 4H_2 \qquad (3)$$

Quantitative treatment of XPS data[12] allowed one to estimate that the $NaBO_2$ overlayer was approximately 36A° thick for the P-2 Ni catalyst (oxide/boride ratio ~ 10 on the catalyst surface). For a P-1 boride prepared in aqueous solution, the boride is dominant on the surface (oxide/boride ratio ~ 0.25). It was demonstrated that the oxidized form of boron (BO_2^-) could be washed off with water.

The question arises as to why does catalyst activity vary so markedly with the method of boride preparation? In the first place, surface contamination by spectator ions such as Na^+ and Cl^- can dramatically reduce activity. The lower the ion's solubility in boride forming solvent, the higher the concentration as surface contaminants. The following evidence suggests that maximizing boron bound nickel is the key to prepare active catalysts[11a:](i) catalytic activity (in hydrogenation reactions) decreases with increasing nickel oxide content which in turn depends strongly on the starting nickel salt. For example, boride made from nickel chloride contains 17% nickel oxide and is a good catalyst whereas that from nickel formate contains 85% nickel oxide and is very weakly active in alkene hydrogenations. (ii) The surface concentration of B-I boron (nickel bound boron) is heavily dependent

on the choice of solvent and metal salt. While the boron binding energy for B-I boron in each catalyst remains constant (independent of the precursor salt, reaction temperature and amounts of $NaBH_4$), the specific activity of catalyst increases linearly with B-I boron content. This correlation best explains, for example, why P-1 Ni is a more active hydrogenation catalyst than P-2 Ni, which is more selective, since the former contains 40% higher levels of B-I boron than the latter. It has been proposed that nickel bound boron (B-I boron) donates electrons to the nickel resulting in electron rich sites on the catalyst surface. *Table* 1 summarizes the surface features of different nickel borides prepared by reducing different metal salts in water.[11a]

Table 1. Surface Characterization of Nickel Boride (P-1 Ni)

Precursor	Metal %	B/M ratio	% of B-I	% of B-II	B-M/M
$Ni(OAc)_2$	61	0.54	51	49	0.45
$NiSO_4$	86	0.55	58	42	0.37
$NiCl_2$	83	0.47	56	44	0.32
$NiBr_2$	77	0.38	56	44	0.27

Maybury et al.[12] correlated the activity of various nickel boride catalysts to the surface areas of undispersed catalyst. Normalization of the activity to surface area ($\bar{a}_{60/SA}$) gives an indication of the dependence of activity on surface area. As can be seen, the normalized activities of all the nickel boride catalysts are relatively constant and show a standard deviation of $\pm 18\%$ from the mean value (*Table* 2).

Table 2. Surface Area and Catalytic Activities of the Ni_2B[a]

Catalyst	$\bar{a}_{60}$[b]	SA[c]	$\bar{a}_{60/SA}$
P-1	2.14	24.1	0.089
P-1.5	4.60	40.8	0.112
P-1.75	4.40	39.5	0.111
P-2	4.40	58.0	0.076
		Mean 0.097(+18%)	

a) Conditions:Substrate = acrylonitrile; pressure = 6 atm; temp. 70°; substrate/catalyst ratio=1000. b) The average activity is defined as the number of mmol of product per mmol of catalyst per min. The average activity during the first sixty min is known as the catalyst's "average initial activity" ($\bar{a}_{60}$). c) SA = Surface area (m ^{2}/g).

It has been observed that the ethanol content of the catalyst significantly affects the surface chemistry. Although the initial activities of P-1.50, P-1.75 and P-2 catalysts are essentially identical (*Table* 2), P-1.75 Ni and P-2 Ni contain a thick overlayer of oxidized boron (B-II boron) whereas P-1.5 catalyst has a thinner borate overlayer. This borate overlayer was shown to interfere in the hydrogenation of acrylonitrile. In addition, if surface areas are considered to be 40.8 and 24.1 m²/g as discussed above, the P-1.5 catalyst is approximately 100% more active than P-1 Ni catalyst. It is to be

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noted that for the same substrate/catalyst ratio (K), the lifetime of the P-1.5 catalyst is nearly three times the value for P-2 catalyst (*Table* 3).

Table 3. Comparison of Activities and Life Time of P-2 and P-1.5 Ni Catalyst in the Reduction of Carbon-Carbon Multiple Bonds in Acrylonitrile

Catalyst	K^a	$\bar{a}_{60}$	$\bar{a}_t$	UZ_t^b	% reaction	t, min
P-2	1000	4.10	1.94	350	35	180
P-1.5	1000	4.60	2.13	970	97	455

a) K = Substrate/catalyst ratio. b) UZ_t = Turnover number, defined as the number of mmol of product per mmol of catalyst at time t. It is taken as the quantitative measure of the catalyst's life time.

I. REDUCTIONS WITH NICKEL BORIDE

1. Hydrogenation of Alkenes and Alkynes

The use of nickel boride prepared from $NiX_2/NaBH_4$ as heterogeneous hydrogenation catalyst was first reported by Paul *et al.*[1] This catalyst was about as active as Raney Ni in the hydrogenation of saffrole, furfural and benzonitrile, but exhibited superior catalyst life. Koritala and Dutton[13] prepared Ni_2B by reducing nickel acetate with aqueous $NaBH_4$ under nitrogen atmosphere to produc commercially useful catalysts. In the selective hydrogenation of soyabean oil, this boride produced little or no stearate and 80-90% of mono- or diunsaturated esters.

In the systematic study of olefin heterogeneous hydrogenation using nickel boride, Brown *et al.*[3,4,14,15] observed that P-1 Ni (under H_2 in ethanol, r.t., 1 atm) was considerably more reactive than commercial Raney Ni towards less reactive alkenes like cyclopentene, cyclohexene and cyclooctene. The P-1 boride does not isomerize reactive alkenes and permitted the selective hydrogenation of conjugated alkenes.[3] Thus 2-methyl-1,5-hexadiene gave pure 2-methyl-1-hexene in 93% yield whil 4-vinylcyclohexene afforded ethyl cyclohex-3-ene in 99% yield if the reaction was stopped after uptake of 1.0 eq. of H_2. When nickel acetate was reduced with $NaBH_4$ in ethanol, the activity of resulting P-2 Ni proved very sensitive to steric hindrance and olefinic substitution pattern (*Table* 4).

Slight increases in hindrance were strongly reflected in the relative rates of hydrogenation using P-2 Ni: e.g., 1-octene, 1.00; 3-methyl-1-butene 0.23; 3,3-dimethyl-1-butene, 0.07. Substitution of the olefinic moiety more markedly affected the reduction rate: 1-octene, 1.0; 2-methyl-1-pentene 0.004; 2-methyl-2-pentene, 0.001 and 2,3-dimethyl-2-butene, 0 (no hydrogenation). This extreme sensitivity to substitution is in marked contrast to Pt, Pt/C and P-1 Ni, which reduce even tetrasubstituted alkenes without difficulty. Another important observation was that while strained double bonds were readily reduced, cyclohexene was unexpectedly inert towards P-2 Ni. No hydrogenolysis of benzylic, allylic or propargyllic groups in ethers or alcohols was observed and partial reduction of dienes and terminal alkynes to monoenes was easily achieved (*Table* 5).[14] Moreover, when P-2 Ni was used in conjunction with ethylenediamine, a catalyst modifier, it selectively reduced disubstituted alkynes to *cis*-alkenes (*Table* 6).[15] Borohydride exchange resin (BER)-nickel acetate has also been used recently for the reduction of alkenes[16a] and *cis*-selective semi-hydrogenation of acetylenes.[16b]

Table 4. Hydrogenation of Alkenes over Nickel Boride[a]

	Compound	$T_{50\%}$ (min)[b]	
		P-1	P-2
1.	1-Octene	6	4.3
2.	3-Methyl -1-butene	10	10
3.	3,3-Dimethyl-1-butene	8.5	48
4.	2 Methyl-1-butene	13	720
5.	2-Methyl-2-butene	130	>24 hrs
6.	2,3-Dimethyl-2-butene	360	∞
7.	Cyclooctene	12	40
8.	Cyclopentene	8	8
9.	Cyclohexene	16	>8hrs
10.	Norbornene	6.0	4.0
11.	Safrole[c]	6.0	2.5
12.	styrene[c]	7.5	5.5
13.	α-Methylstyrene[c]	9.5	120
14.	Allylbenzene[c]	6.5	4.1

a) 40 mmol of substrate, 5 mmol of Ni_2B, 95% ethanol at 25° and 730 mm pressure. b) Time in min for the uptake of 20 mmol of hydrogen. c) Reduction of side chain only, no reduction of aromatic ring.

Recently, reductions of α,β-unsaturated five membered lactones and lactams to saturated lactones and lactams[17a,b] (*Eq.* 4), as well as chalcones to dihydrochalcones, have been reported[17c] (*Eq.* 5).

$$\text{(4)}$$

$$\text{(5)}$$
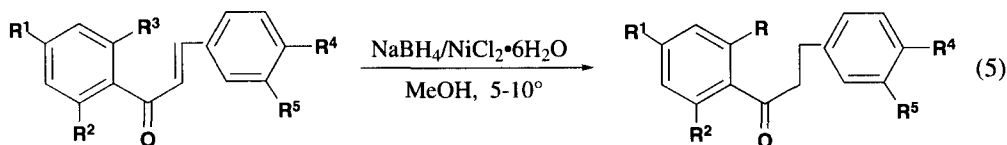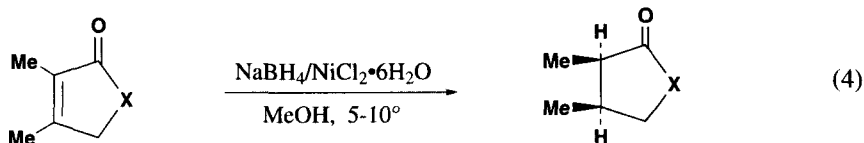
Belisle *et al.*[17d] recently used *ex situ* generated nickel boride (SC-1, Ni_2B) for selective 1,4-hydrogenation of α,β-unsaturated ketones and aldehydes at one atmosphere pressure. They prepared nickel boride by refluxing nickel chloride and sodium borohydride in methanol to destroy any residual $NaBH_4$, which usually gives side products by reduction of the carbonyl group (*Eq.* 6). Recently 1,5-dihydro-2H-imidazoles have been reported to undergo double bond migration to give 4,5-dihydro-1H-imidazoles in high yields (*Eq.* 7).[18]

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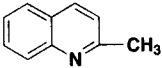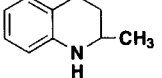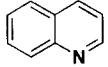**Table 5.** Selective Hydrogenations over P-2 Ni
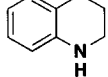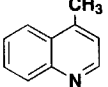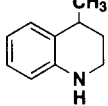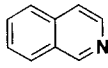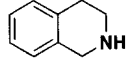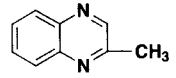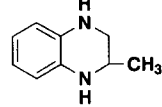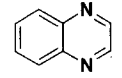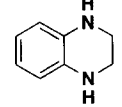
Substrate	Product	%Yield(GC)
1-Hexyne	*n*-hexane	16
	1-hexene	68
	1-hexyne	16
3-Hexyne	*n*-hexane	1
	cis-3-hexene	96
	trans-3-hexene	3
1-Octene + 2-methyl-	1-octene	96
1-pentene	*n*-octane	4
	2-methylpentane	6
	2-methyl-1-pentene	94
1-Octene + cyclohexene	*n*-octane	94
	1-octene	6
	Cyclohexane	4
	Cyclohexene	96
Norbornene + cyclopentene	norbornane	47
	norbornene	3
	cyclopentane	2
	cyclopentene	48
4-Vinylcyclohexene	ethylcyclohexane	2
	4-ethylcyclohexene	97
	vinylcyclohexane	1
2-Methyl-1, 5-hexadiene	2-methylhexane	2
	2-methyl-1-hexene	96
	other methylhexenes	2
5-Methylenenorbornene	methylnorbornanes	1
	methylnorbornenes	2
	2-methylenenorbornane	96
	5-methylenenorbornene	2
Isoprene	2-methylbutene	4
	isoprene	5
	methylbutene	91
1, 8-Cyclohexadiene	cyclohexane	2
	cyclohexene	89
	benzene	9
1-Penten-3-ol	3-pentanol	>99
1-Vinylcyclohexanol	1-ethylcyclohexanol	>99
3-Methyl-1-pentyn-3-ol	3-methyl-3-pentanol	>99
1-Ethynylcyclohexanol	1-ethylcyclohexanol	>99

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$$PhCH=CHCHO \xrightarrow[\text{MeOH, } 25°, \text{ 24 hrs}]{\text{SC-1, Ni}_2\text{B, H}_2} PhCH_2CH_2CHO \qquad (6)$$

$$X = S, O$$

Y = H when X = S
Y = p-MeO when X = O

$$(7)$$
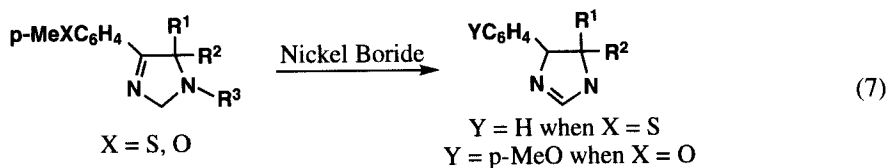
Table 6. Stereospecific Reduction of Alkynes by P-2 Ni[a]

Substrate (mmol)	P-2 Ni (mmol)	% Olefin	*cis*:trans	Total Yield, %
hex-3-yne (40)	5.0	98	97:1	95
hex-3-yne (200)	10.0	97	200:1	95
1-phenylpropyne (100)	5.0	96	200:1	95
hex-3-yn-1-ol (40)	5.0	98	100:1	94

a) Molar ratio of catalyst to ethylenediamine was 3:1.

Table 7. Reduction of Heterocycles with $NiCl_2$/$NaBH_4$ in MeOH at RT[a]

Compound	NiCl$_2$ (mmol)	NaBH$_4$ (mmol)	Product	Yield (%)
	1.4	32		94
	4	32		83
	8	80		83
	8	96		87
	8	96		96
	16	160		54

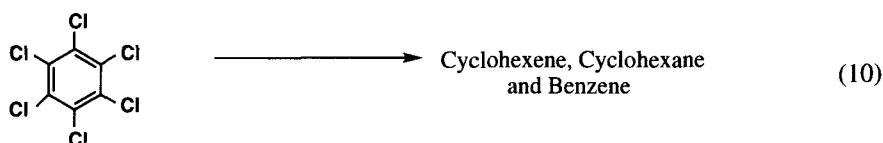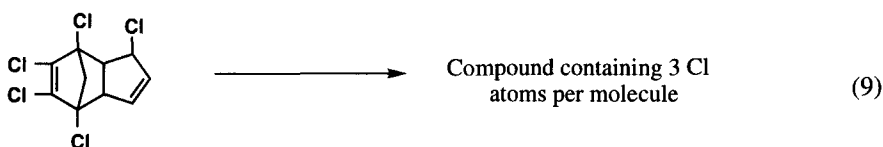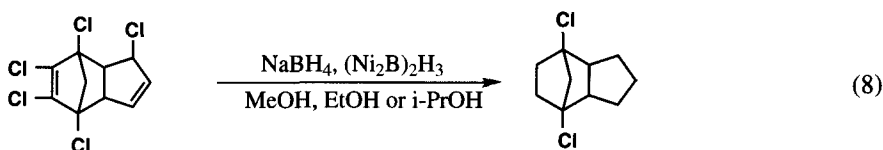a) 8 mmol of substrate was used in all the reactions.

2. Reduction of Heteroarenes

Reduction of heterocyclic compounds using $NiCl_2$ and excess $NaBH_4$ in methanol at room temperature has been described by Nose and Kudo.[19] Conversion of several quinolines, isoquinolines and quinoxalines to the corresponding tetrahydro derivatives are summarized in *Table 7*.

It was observed that (i) the reductions are catalytic in $NiCl_2$, (ii) in all reductions exothermic formation of the characteristic boride was accompanied with vigorous H_2 evolution, (iii) quinaldine was not reduced by catalytic hydrogenation over Ni_2B and (iv) tetrahydroquinaldine was produced (31%) by using preformed Ni_2B and excess $NaBH_4$. The yield of desired product was somewhat low probably because working with preformed boride avoided the uncontrolled temperature rise during exothermic boride formation.
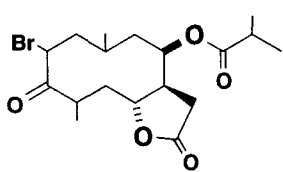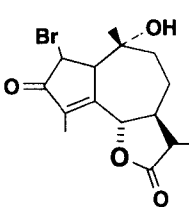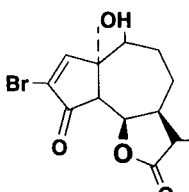
3. Reduction of Halides

Ordinary sodium borohydride will not reduce unactivated alkyl halides execpt in polar aprotic solvents[20a] or under phase transfer conditions.[20b] However, Dennis and Copper[20c] reported the reductive dechlorination of toxic polychlorinated hydrocarbon pesticides using a combination of Ni_2B and $NaBH_4$ in alcohol (*Eqs.* 8-10). Because of the difficulty of disposal of organochlorine pesticides, this procedure and variations thereof may have considerable applications. Both DDT and 2,4-DB[4-(2,4-dichlorophenoxy)butanoic acid] were also extensively dechlorinated. Nickel boride prepared in anhydrous CH_3OH liberated more free chlorine than in ethanol or 2-propanol. The presence of water retarded the reduction and reductive dehalogenation was less effective using $CoCl_2$, $MnSO_4$ or $FeSO_4$. This method has also found applications in the detoxification of polychlorinated biphenyls .

$$\xrightarrow[\text{MeOH, EtOH or i-PrOH}]{\text{NaBH}_4, \text{(Ni}_2\text{B)}_2\text{H}_3} \qquad (8)$$

Compound containing 3 Cl
atoms per molecule $\qquad (9)$

Cyclohexene, Cyclohexane
and Benzene $\qquad (10)$

In contrast with an earlier report,[10b] mixing $NiCl_2$ with $NaBH_4$ (1.5 mol equiv) in DMF with no special precautions to exclude air generated a black precipitate of nickel boride which stoichiometrically reduced α-haloketones (*Table* 8).[21] Reactions of vicinal -dibromides (**I-III**) using the same procedure afforded alkenes in 80-90% yield. Alkyl chlorides were inert to this boride while bromides and iodides were reduced in only poor yield.[21] Reduction of aryl halides[22a] and alkyl halides[22b] has

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also been reported with borohydride exchange resin (BER)-nickel acetate.

R = OH, Cl

I　　　　　　　**II**　　　　　　　**III**
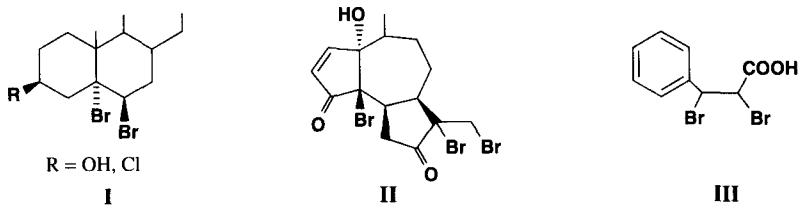
Entry	α–Haloketone reduced	% Yield of parent ketone
1.	2-Chlorocyclohexanone	75
2.	2-Bromocyclohexanone	90
3.	2α -Bromocholestan-3-one	95
4.	p-Bromophenancyl bromide	98
5.	Phenacyl bromide	98
6.	α-Bromocamphor	NR
7.	2α-Chlorocholest-4-en-3-one	70[b]
8.	3β-Acetoxy-7α-bromocholestan-6-one	95
9.		85
10.		95
11.		50[b,c]

a) Substrate: $NiCl_2$: $NaBH_4$ = 0.5:1.25:2.0 mmol. b) The rest of the material in case of entry 7 and 11 was unreacted starting α-haloketone. c) Exo-methylene group, conjugated with the lactone moiety or isolated, is not reduced.
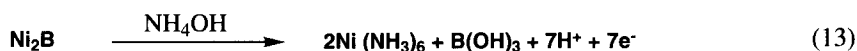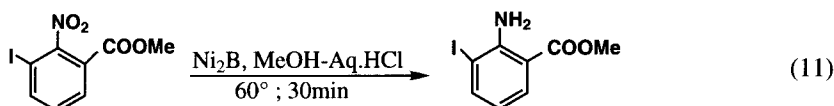
4. Reduction of Nitrocompounds

a). Nitroarenes

The reduction of aromatic nitro compounds to amines is an important synthetic reaction, especially in large scale pharmaceutical and industrial chemical processes. Nickel boride supported on charcoal converted p-nitrophenyl glycosides to p-aminophenylglycosides.[23] $NiCl_2$ has been used with $NaBH_4$ in methanol to reduce nitroarenes to anilines in good yield (*Table* 9).[24a] Kudo and Nose[24] have also found that Ni_2B can reduce aromatic nitro compound in excellent yield when the reduction is carried out in strongly acidic or basic medium (*Table* 10). Even selective reduction of nitro groups in the presence of iodo and o-carbalkoxy groups has been reported (*Eq.* 11).[25] It is presumed that 1 mol of Ni_2B produces 7 electron equivalents in HCl or NH_4OH (*Eqs.* 12,13).

Table 9. Reduction of Nitroarenes with $NaBH_4$-$NiCl_2$[a]

$RC_6H_4NO_2$ (R)	Substrate:$NiCl_2$: $NaBH_4$ Yield (%)	Product ($RC_6H_4NH_2$)
H	1:2:8	76
p-CH_3	1:2:4	95
m-CH_3	1:2:4	95
o-CH_3	1:2:4	81
p-CH_3O	1:2:4	89
p-Cl	1:2:4	89
p-OH	1:2:4	88
p-COOH	1:2:4	78
o-COOH	1:2:4	86
C_4H_3[b]	1:2:4	86

a) The reaction was carried out with 8 mmol of nitroarene at 20° for 30 min in methanol; b) 1-Nitronaphthalene.

$$\text{(11)}$$

$$Ni_2B \xrightarrow{\text{HCl, } H_2O} NiCl_2 + B(OH)_3 + 7H^+ + 7e^- \qquad (12)$$

$$Ni_2B \xrightarrow{\text{NH}_4OH} 2Ni\,(NH_3)_6 + B(OH)_3 + 7H^+ + 7e^- \qquad (13)$$

The reduction of a nitro compound requires 1 molar equivalent of Ni_2B since 6 electron equivalents are necessary for the reduction of a nitro group. It is noteworthy that nitro compounds can be selectively reduced with Ni_2B in dil HCl or conc NH_4OH to the corresponding amines under mild conditions in good yield (*Table* 11).[24c]

Table 10. Reduction of Nitroarenes with Ni_2B in Acidic and Basic solutions

$R(R-NO_2)$	Ni_2B(Molar equiv)	Medium	% Yield (RNH_2)
p-$CH_3C_6H_4$	1	3N HCl	94
o-$CH_3C_6H_4$	1	3N HCl	84
p-ClC_6H_4	1	3N HCl	96
o-ClC_6H_4	1	3N HCl	80
p-$CH_3OC_6H_4$	1	3N HCl	88
1- Naphthyl	1	3N HCl	80
p-$CH_3C_6H_4$	1	15N NH_4OH	96
o-$CH_3C_6H_4$	1	15N NH_4OH	93
p-ClC_6H_4	1	15N NH_4OH	87
o-ClC_6H_4	1	15N NH_4OH	85
p-$CH_3OC_6H_4$	1	15N NH_4OH	80
1-Naphthyl	1	15N NH_4OH	83

a) Reaction conditions: 40°C for 30 min

Table 11. Selective reduction of Nitro Group with Ni_2B[a]

Compound	Ni_2B(eq.)	Medium	Product	Yield(%)
6-Nitroquinoline	1	15N NH_4OH	6-Aminoquinoline	87
p-$O_2NC_6H_4COOCH_3$	2	3N HCl	p-$H_2NC_6H_4COOCH_3$	97
o-$O_2NC_6H_4CONH_2$	2	15N NH_4OH	o-$H_2NC_6H_4CONH_2$	70
p-$O_2NC_6H_4CN$	2	3N HCl	p-$H_2NC_6H_4CN$	60
p-$O_2NC_6H_4CN$	2	15N NH_4OH	p-$H_2NC_6H_4CN$	81
p-$O_2NC_6H_4COCH_3$	2	3N HCl	p-$H_2NC_6H_4COCH_3$	89

a) Reaction conditions: 40° for 30 min.

b) Nitroalkanes

Nitroaliphatic compounds have traditionally been reduced to amines by high pressure hydrogenation, $LiAlH_4$ or aluminum amalgam. In 1985, Osby and Ganem[26] reported that $NiCl_2/NaBH_4/CH_3OH$ rapidly reduced a variety of primary, secondary and tertiary ni amines at room temperature (*Table* 12). Nickel boride, prepared *in situ*, was the active catalyst, requiring dissolved $NaBH_4$ (and not H_2) as the reducing agent. The reagent selectively reduced nitrocyclohexane in the presence of hexanenitrile. Borohydride exchange resin (BER)-nickel acetate has also been reported to reduce nitroarenes and nitroalkanes quantitatively to the corresponding amines.[27] Recently reductive elimination of α-chloronitro derivatives to corresponding olefins has been reported with nickel boride generated *in situ*. (*Eq.* 14).[28]

14

$$R_1R_2C\overset{|}{\underset{Cl}{\rule{0pt}{0pt}}}\!\!-\!\!\overset{|}{\underset{NO_2}{\rule{0pt}{0pt}}}CR_3R_4 \xrightarrow[\text{DMF, r.t.}]{\text{Nickel Boride}} R_1R_2C=CR_3R_4 \qquad (14)$$
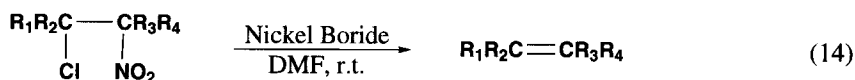
Table 12. Ni_2B Reductions of Nitroaliphatic Compounds[a]

Reactant RNO_2 (R)	Product (RNH_2) Yield (%)
Cyclohexyl	68
Cyclohexenyl	66
C_8H_{17}	61
$CH_3CHOHCH_2CH_2C(CH_3)_2$	76
$HOCH_2CH_2C(CH_3)_2$	64
$CH_3OOCCH_2CH_2C(CH_3)_2$	50
$H_2NCH_2CH_2CH_2NHCH_2CH_2C(CH_3)_2$	69

a) Reductions were carried out with preformed Ni_2B in presence of excess $NaBH_4$.

5. Reduction of other Nitrogenous Functional Groups: Azoxy, Azo, Nitroso, Hydrazo and Hydroxylamines

The combination of $NiCl_2$ with $NaBH_4$ in CH_3OH was shown to reduce nitroso-, azoxy-, azo- and hydroxylaminobenzenes to hydrazobenzenes. Prolonged reduction of the hydrazobenzenes at room temperature led to the corresponding anilines.[24a] The reduction of the above functional groups with Ni_2B in acidic or basic media gives aniline as the main product (*Table* 13).[24c]

Table 13. Reduction of Nitroso, Azoxy, Azo and Hydrazobenzene with Equimolar Ni_2B

Compound	Medium	$C_6H_5NH_2$(Yield %)
$C_6H_5N=O$	3N HCl	71
$C_6H_5N=O$	15N NH_4OH	94
$C_6H_5N(O)=NC_6H_5$	3N HCl	58
$C_6H_5N(O)=NC_6H_5$	15N NH_4OH	94[a]
$C_6H_5N=NC_6H_5$	3N HCl	14[b]
$C_6H_5N=NC_6H_5$	15N NH_4OH	66
$C_6H_5NHNHC_6H_5$	3N HCl	14
$C_6H_5NHNHC_6H_5$	15N NH_4OH	83

a) Azobenzene (5 %) was also obtained. b) Hydrazobenzene (69 %) was the major product.
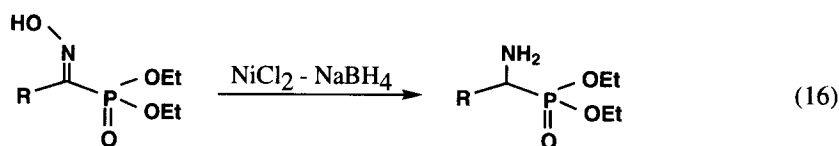
In 1984, Ipaktschi[29] observed that saturated and unsaturated oximes were exhaustively reduced to saturated amines at -30° using $NiCl_2$-$NaBH_4$/CH_3OH (*Table* 14). While the mechanism was not established, the $NiCl_2$ method was shown not to involve heterogeneous hydrogenation. α-Ketoxime of camphorquinone (**IV**) was reduced to the corresponding *exo*, *exo*-amino alcohol (**V**) in a two-step one-pot procedure using $NaBH_4$ and $NiCl_2\cdot6H_2O$ (*Eq.* 15).[30] Hydroxyiminophosphonates

$$\text{(15)}$$
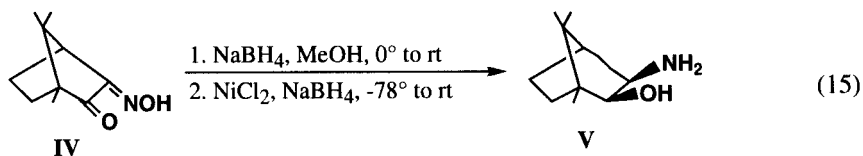
have been reduced with $NaBH_4$- $NiCl_2$ in methanol ($Eq.16$).[31] Reduction of aromatic oximes to amines with borohydride exchange resin (BER)-nickel acetate has also been reported.[32]

Table 14. Reduction of Oximes with $NiCl_2/NaBH_4$

Substrate	Product	Yield %
		94
		92
	(1:2)	92
	(62:38)	92
$C_3H_5-\overset{NOH}{\underset{\|}{C}}-C_3H_5$	$C_3H_5-\overset{NH_2}{\underset{\|}{CH}}-C_3H_5$	70
$PhCH_2CH_2C{=}NOH$ $\|$ CH_3	$PhCH_2CH_2\overset{}{\underset{\|}{CH}}NH_2$ CH_3	95
	(1 : 1)	90
		95

16

$$\underset{\substack{\text{R}}}{\overset{\substack{\text{HO}\\|\\\text{N}}}{\|}}\underset{\substack{\|\\\text{O}}}{\overset{\text{OEt}}{\underset{\text{OEt}}{\text{P}}}}\quad\xrightarrow{\text{NiCl}_2 - \text{NaBH}_4}\quad\underset{\substack{\text{R}}}{\overset{\substack{\text{NH}_2}}{}}\underset{\substack{\|\\\text{O}}}{\overset{\text{OEt}}{\underset{\text{OEt}}{\text{P}}}}\qquad(16)$$

6. Reduction of Azides and Acyl Azides

In 1987, Sharma and Sharma[33] reported the reduction of alkyl, cycloalkyl and steroidal azides to amines with nickel boride. Ketones, esters, epoxides and double bonds were not reduced under their reaction conditions (*Eq.* 17).

$$\text{RN}_3 \quad \xrightarrow[\text{10-25 min}]{\text{NiCl}_2, \text{NaBH}_4, \text{MeOH}} \quad \text{RNH}_2 \qquad (17)$$

Recently borohydride exchange resin (BER)-nickel acetate has also been reported to reduce azides to amines.[34] Reduction of acyl azides to amides with nickel chloride-sodium borohydride in methanol has also been reported (*Eq.* 18).[35] When X was nitro group, only 20% of the amide was obtained du to competing reduction of the nitro group.

$$\underset{\text{X}}{\text{}}\overset{\text{CON}_3}{\text{}}\quad\xrightarrow{\text{NiCl}_2, \text{NaBH}_4, \text{MeOH}}\quad\underset{\text{X}}{\text{}}\overset{\text{CONH}_2}{\text{}}\qquad(18)$$
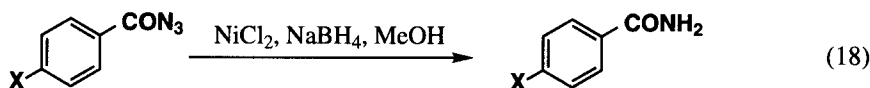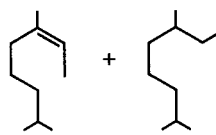
II. DEOXYGENATION REACTIONS
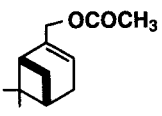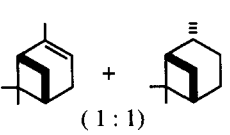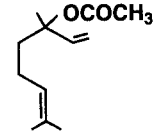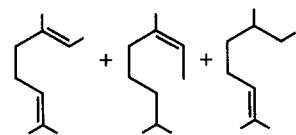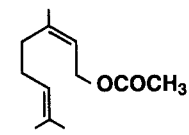
1. Ethers, Esters and Anhydrides

While P-2 Ni does not hydrogenolyze allylic, propargyllic and benzylic substituents, recent developments in boride chemistry have made this transformation possible. In 1984, Ipaktschi[36] found that $NiCl_2/NaBH_4/CH_3OH$ constituted an effective system for reductive removal of allylic, propargyllic and benzylic groups from acetate esters (*Table* 15).

Equimolar amounts of the unsaturated ester and $NiCl_2$, when treated with $NaBH_4$ (10 equiv.) for 30 min at 0°, afforded a mixture of alkenes and alkanes. Likewise, cinnamyl alcohol furnished 1: 1 mixture of 1-phenylpropane and 1-phenylpropene. Interestingly, *p*-methoxybenzyl acetate was reduced in CH_3OD to a 35:65 mixture of mono- and undeuterated 4-methylanisole. More highly deuterated species were not detected.

Using nickel boride prepared in anhydrous diglyme from $NiCl_2$ and $NaBH_4$, Sarma and Sharma[37] showed that the ease of reductive removal of allylic substituents followed the order: OC OH < $OSiMe_3$ < $OCOCH_3$ < $OCOCF_3$. In comparing nickel boride with Raney nickel, the former was judged superior for reductive removal of an allylic group from allylic acetates whereas the latter more efficiently deoxygenated allylic benzyl ethers. Reductions of 3β-acetoxycholest-4-ene, run in CH_3OD, resulted in only 20% deuterium incorporation. The same workers reported the reductive cleavage of allylic alcohols to alkenes in a one-pot process *via* the trimethylsilyl ethers (*Table* 16).[38]

Table 15. Reduction of Allylic and Propargyllic Acetates using $NiCl_2/NaBH_4$

Reactant	Product	Yield %
$PhCH=CHCH_2OCOCH_3$	$PhCH_2CH_2CH_3$	93
$PhCH=C(CH_3)CH_2OCOCH_3$	$PhCH_2CH(CH_3)_2$	>95
$PhCH=CHCH(CH_3)CH_2OCOCH_3$	$PhCH_2CH_2CH_2CH_3$	87

(1 : 1) >95

(38 : 19 : 43) 92

(60 : 40) 90

$Me_2C - C \equiv C - CMe_2$
  | |
$MeOCO$ $OCOMe$

$Me_2C = CH-CH_2-CMe_2$
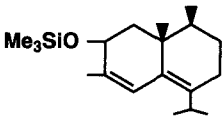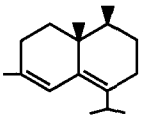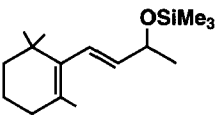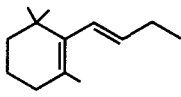 |
                    $OCOMe$ 85
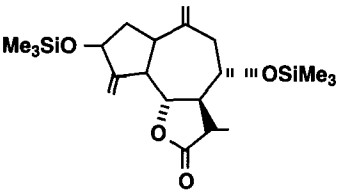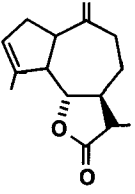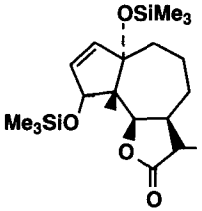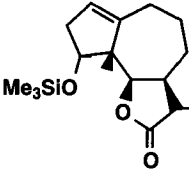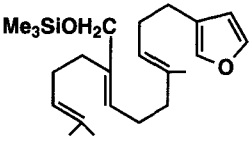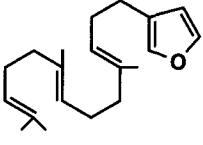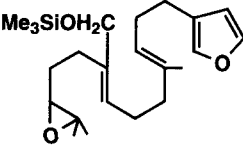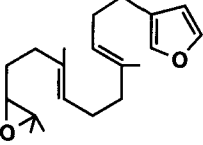
Toluene p-sulfonates of phenols, enolizable 1,3-diketones and 3-ketoesters have been reported to undergo facile deoxygenation with sodium borohydride-nickel chloride in methanol to give the aromatic compounds, mono alcohols and esters, respectively.[39] The reductions have been reported in methanol or methanol-chloroform (1: 1) using a molar ratio of 1:1: 20 or 1:1:5 under ice cooling (*Eq.* 19). p,p'-Dinitrobenzhydryl ether of cholestrol has been reported to undergo nickel boride catalyzed hydrogenation followed by mild acid hydrolysis to give cholestrol.[40]

$\qquad$ (19)
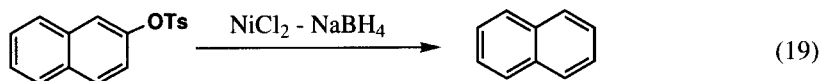
2. Aldehydes

Russell *et al.* have shown that borohydride reduced nickel does effect hydrogenation of both carbon-oxygen and carbon-carbon bonds in unsaturated aldehydes. However, the carbonyl group is hydrogenated more slowly than the olefinic group over the nickel boride catalyst (*Table* 17).[41]

**Table 16.** Nickel Boride reducation of Trimethylsilyl Ethers of Allyl Alcohols

Substrate	Product	Time (hrs	Yield (%)
		3	60
		3	60
		1	80
		1.5	80
		2	75
		6	30

Recently, it has been shown that aldehydes can be reduced in the presence of ketonic moieties using Ni_2B-CTMS (chlorotrimethylsilane). It was proposed that trimethylsilane can be generated *in situ* from reaction of CTMS with Ni_2B, which in turn accomplishes the reaction.[42] A demonstrative example is shown below (*Eq.* 20). Borohydride exchange resin (BER)-nickel acetate, on the other hand, has been reported to reduce aromatic aldehydes to hydrocarbons in methanol.[43]
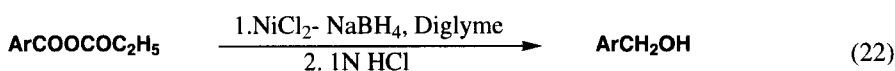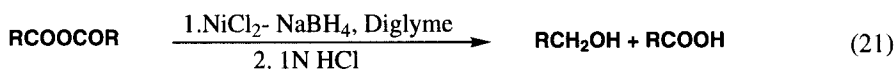
Table 17. Reduction of α,β-Unsaturated Aldehydes with Hydrogen over Nickel Boride[a]

Reactant	P-2 Ni(mmol)	Time (hrs)[b]	Product
Acrolein	5	0.5	Propionaldehyde
Crotonaldehyde	5	8	Butyraldehyde
Crotonaldehyde	20	0.75	Butyraldehyde
Cinnamaldehyde	20	1	Hydrocinnamaldehyde
Tiglaldehyde	20	1	2-Methylbutyraldehyde
Propionaldehyde	50	15	Propyl alcohol
Butyraldehyde	50	21	Butyl alcohol
Hydrocinnamaldehyde	20	4	3-Phenylpropanol
2-Methylbutyraldehyde	20	7.5	2-Methylbutanol
Benzaldehyde	10	48	Benzyl alcohol
Furfural	5	12	Furfuryl alcohol

a) 100 mmol of reactant, 30 psi initial H_2 pressure, ambient temperature, in 50 mL of 95% ethanol; b) Time for uptake of 100 mmol of H_2 in hrs.
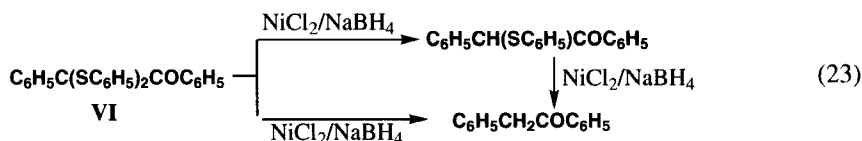

$$(20)$$
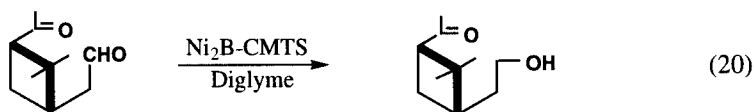
Symmetric and mixed anhydrides of carboxylic acids have also been reduced with nickel boride.[44] Symmetric anhydrides gave the corresponding alcohols and acids (*Eq.* 21) unlike mixed anhydrides of aromatic acids and carbonic acids which gave benzylic alcohols (*Eq.* 22).

$$RCOOCOR \xrightarrow[\text{2. 1N HCl}]{\text{1.NiCl}_2\text{- NaBH}_4,\text{ Diglyme}} RCH_2OH + RCOOH \qquad (21)$$

$$ArCOOCOC_2H_5 \xrightarrow[\text{2. 1N HCl}]{\text{1.NiCl}_2\text{- NaBH}_4,\text{ Diglyme}} ArCH_2OH \qquad (22)$$
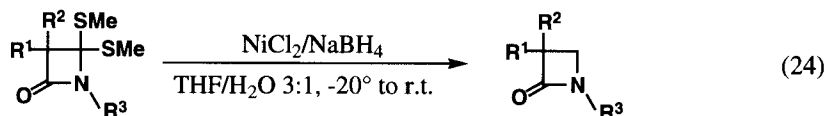
III. DESULFURIZATION REACTIONS

The first use of Ni_2B to desulfurize organic structures was reported in 1963 when Truce and Perry reduced thioketals and thioacetals with an excess of $NiCl_2$-$NaBH_4$ in EtOH under N_2 at reflux.[45] For example, diphenylmercaptol (**VI**) was reduced with this reagent to give phenyl benzyl ketone. It was found possible to replace one or both sulfur atoms of the mercaptol by H_2 simply by varying the amount of nickel boride (*Eq.* 23).

$$C_6H_5C(SC_6H_5)_2COC_6H_5 \begin{array}{c} \xrightarrow{NiCl_2/NaBH_4} C_6H_5CH(SC_6H_5)COC_6H_5 \\ \downarrow NiCl_2/NaBH_4 \\ \xrightarrow{NiCl_2/NaBH_4} C_6H_5CH_2COC_6H_5 \end{array} \qquad (23)$$

VI

Reduction of α,β-unsaturated ethylene dithioketals to the corresponding olefins[46] and 4,4-bis(methylthio)-β-lactams to 4-unsubstituted-2-azetidinones (Eq. 24) have also been reported.[47]

$$R^1 \underset{O}{\overset{R^2 \quad SMe}{\vert\vert}} \underset{N}{\vert} SMe \quad \xrightarrow[\text{THF/H}_2\text{O 3:1, -20° to r.t.}]{\text{NiCl}_2/\text{NaBH}_4} \quad R^1 \underset{O}{\overset{R^2}{\square}} \underset{R^3}{N} \qquad (24)$$

This method was later extended to the desulfurization of mercaptans, sulfides and sulfoxides in good yield (Table 18).[48] Though the yields of desulfurization are somewhat inferior, it offers several advantages over Raney Ni, e.g., (i) the ease of preparation of Ni_2B, (ii) the boride could selectively remove a single sulfur atom from a thioketal, (iii) desulfurization could be accomplished in the presence of sulfones and (iv) the non-pyrophoric nature of nickel boride which is less hazardous.

Table 18. Desulfurization with Raney Nickel and Nickel Boride[a]

Compound	% Yield of toluene	
	Nickel boride	Raney nickel
p-Toluenethiol	60	91
p-Tolyldisulfide	37	85
p-Tolylsulfide	72	86
p-Tolylsulfoxide	80	>99
p-Tolylsulfone	0	88
p-Phenylsulfonylphenyl p-tolylsulfide	84	91

a) Substrate: $NiCl_2:NaBH_4$ = 1: 10:30 in aqueous ethanol under reflux for 7 hrs.

A later study described the desulfurization of heterocyclic materials with Ni_2B at reflux in ethylene glycol or in aqueous solution at 200° (autoclave). However, the yields were not as high as those obtained using Raney Ni.[49] Paz et al. have also used $NiCl_2/NaBH_4$ to desulfurize sulfur-containing amino acids of peptides for mass spectrometric sequencing of peptides which otherwise creates difficulties.[50a] Synthesis of desoxopeptides from endothiopeptides by nickel boride has been recently reported.[50b] Some representative examples are given in Table 19. However in most cases the yields are comparable to those obtained using Raney Ni as catalyst.
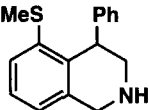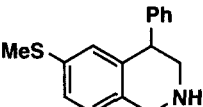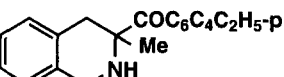
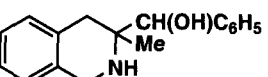**Table 19.** Desulfurization of Endothiopeptides[a]

Substrate	Product	% Yield
Boc-GlyC(=S)NHGly-OMe	Boc-Gly(CH$_2$NH)Gly-OMe	41
Boc-PheC(=S)NHGly-OMe	Boc-Phe(CH$_2$NH)Gly-OMe	41
Boc-AlaC(=S)NHPhe-OMe	Boc-Ala(CH$_2$NH)Phe-OMe	66
Z -LeuC(=S)NHLeu-OMe	Z -Leu(CH$_2$NH)Leu-OMe	56

a) Solvent:THF/MeOH (1: 1); Substrate:$NiCl_2:NaBH_4$ = 1: 8:24

In 1973, Boar et al.[51] reported desulfurization of ethylenedithioacetals and hemithioacetals with Ni_2B and observed that the rate of reduction decreased as borohydride decomposition raised the pH of the medium. Optimum reaction conditions were developed consisting of ethylene glycol or ethanol-boric acid as the solvent. They found that nickel boride is a better desulfurizing agent than Raney nickel in the synthesis of triterpen-2-enes.

Recently, nickel boride has been reported as a convenient and effective reagent for the reductive desulfurization of thioethers. Nickel boride selectively reduces alkylthio derivatives of benzaldehyde and benzyl alcohol to give good yields of benzyl alcohol as compared to Raney nickel which yields toluene (Table 20).[52a]

Table 20. Desulfurization of Thioethers with Nickel Boride

Substrate	Molar ratio (Substrate:$NiCl_2$:$NaBH_4$)	Product	% Yield
p-$MeSC_6H_4CHO$	1:10:30	$C_6H_5CH_2OH$	94
p-$EtSC_6H_4CHO$	1:6:60	$C_6H_5CH_2OH$	70
p-$MeSC_6H_4CH_2OH$	1:6:60	$C_6H_5CH_2OH$	77
p-$PhSC_6H_4CH_2OH$	1:6:60	$C_6H_5CH_2OH$	65
m-$MeSC_6H_4NHCH_2Ph$	1:6:60	$C_6H_5CH_2NHCH_2Ph$	70
p-$MeSC_6H_4NHMe$	1:6:30	$C_6H_5CH_2NHMe$	91
	1:10:30	4-Phenyl-1,2,3,4-tetrahydroquinoline	89
	1:6:30	4-Phenyl-1,2,3,4-tetrahydroquinoline	79
	1:6:30		91

Barton et al. [52b] carried out reductive removal of S-pyridyl group using nickel boride in presence of boric acid (Eq. 25).
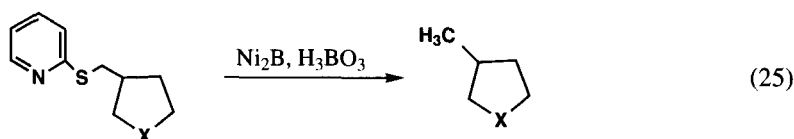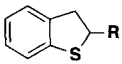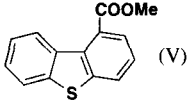

$$\text{(25)}$$
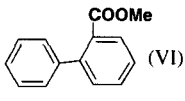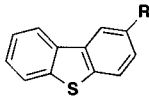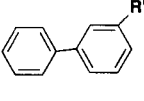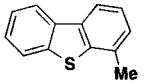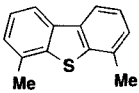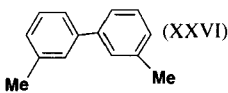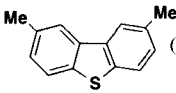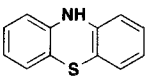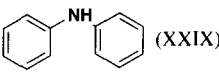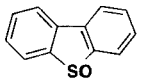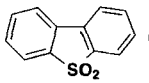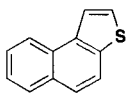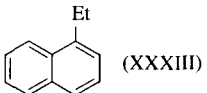
Table 21. Desulfurization of Benzo- and Dibenzothiophenes with Nickel boride

Substrate	Moles Ni(II)[a] per mole of substrate	Time (min)[b]	Product	Yield (%)
R = H (I)	14	15	R' = Et (II)	82
R = Me (III)	14	15	R' = n-Pr (IV)	62
(V) [COOMe]	14	60	(VI) [COOMe]	78
R = H (VII)	14	60	R' = H (VIII)	83
R = Me (IX)	14	60	R' = Me (X)	75
R = Cl (X)	14	60	R' = Cl (XII)	30
			+(VIII)	55
R = Br (XII)	14	60	VIII + VII	77+11
R = OH (XIV)	14	60	R' = OH (XV)	70
R = COOH (XVI)	14	60	R' = COOH (XVII)	74
R = NH₂ (XX)	14	60	R' = NH₂ (XXI)	81
R = NO₂ (XXII)	14	60	R' = NH₂ (XXII)	82
(XXIV) [Me]	21	60	(X)	63
(XXV) [Me, Me]	14	60	(XXVI) [Me, Me]	78
(XXVII) [Me, Me]	14	60	(XVI)	69
(XXVIII) [NH]	14	60	(XXIX) [NH]	68
(XXIV) [SO]	21	60	(VIII) + (VII)	75 + 6
(XXXI) [SO₂]	21	60	(VIII)	22
(XXXII)	21	60	(XXXIII) [Et]	75

a) Molar ratio of NiCl₂ 6H₂O to NaBH₄ was 1: 3. b) The solvent was 3:1 MeOH-THF. c) Reactions performed at 0° were for 15 min. and those performed at room temperature were for 60 min.

Finet *et al.* [52c] had successfully achieved the desulfurization of sterically hindered 3-*p*-methoxyphenyl- 3-phenylthiochroman-4-ones using an excess of nickel boride (*Eq.* 26). Desulfurization of thioethers with concomitant migration of double bonds in 1,5-dihydro-2H-imidazoles to give 4,5-dihydro-1H-imidazoles in high yields has been recently reported (*Eq.* 7).[18]

$$\text{NiCl}_2.6\text{H}_2\text{O, NaBH}_4 \quad \text{EtOH-H}_2\text{O, Reflux 6 hrs} \tag{26}$$
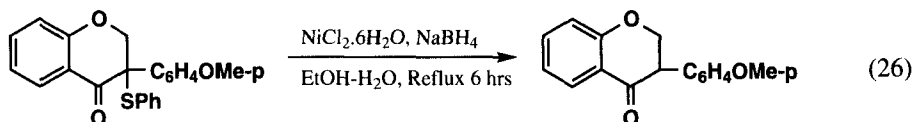
Nickel boride, prepared from the reduction of nickel chloride hexahydrate with sodium borohydride in methanol-tetrahydrofuran, reduces dibenzothiophenes to biphenyls and benzothiophenes to substituted benzenes. The reaction is rapid at or below room temperature and does not require protection from the atmosphere. Best results are obtained when the nickel boride is generated *in situ* in the presence of the sulfur compound. Hydroxyl, carboxyl, ester and amino groups are unaffected while chloro, bromo and nitro substituents are also reduced under these conditions (*Table* 21).[53]
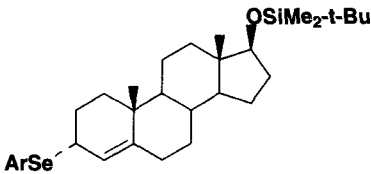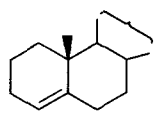
Back *et al.* [54] have reported desulfurization of a variety of alkylthio and arylthio groups under mild conditions using nickel boride generated *in situ* in methanol-THF (3:1). Phenyl, chloro and ester groups are not reduced under these conditions while iodo, bromo, nitrile, aldehyde, ketone, cyclopropane and olefinic functions are reduced either completely or partially (*Table* 22).

Table 22. Desulfurization of Organosulfur Compounds

Substrate	Molar ratio Substrate:Nickel boride	Product	% Yield
n-$C_{11}H_{23}SPh$	1:5	n-$C_{11}H_{24}$	90
n-$C_{12}H_{25}SH$	1:3.5	n-$C_{12}H_{26}$	86
$(n$-$C_{12}H_{25}S)_2$	1:3.5	n-$C_{12}H_{26}$	48
$(n$-$C_{12}H_{25})_2SO$	1:7	n-$C_{12}H_{26}$ & $(n$-$C_{12}H_{25})_2S$	67 23
$(n$-$C_{12}H_{25})_2SO_2$	1:7	n-$C_{12}H_{26}$	14
$PhS(CH_2)_{11}X$			
X = CN	1:3.5	n-$C_{12}H_{25}NH_2$	86
X = Cl	1:3.5	n-$C_{11}H_{23}Cl$	82
X = Br	1:7	n-$C_{12}H_{24}$	81
X = I	1:3.5	n-$C_{12}H_{24}$	85
$PhCH(SPh)CH_2CHO$	1:3.5	$PhCH_2CH_2CHO$ & $PhCH_2CH_2CH_2OH$	14 75
PhCOSPh	1:3.5	$PhCH_2OH$	91

In contrast to the common desulfurization reactions with nickel boride, borohydride exchange resin (BER)-Ni(OAc)$_2$ has been reported to bring about methanolysis and disproportionation of thioacetates to give the corresponding disulfides (*Eq.* 27).[55]

24

$$RSAc \xrightarrow[\text{MeOH, reflux, 1 hr}]{\text{BER -Ni(OAc)}_2} \xrightarrow{\text{rt, 3-9 hrs}} RSSR \qquad (27)$$
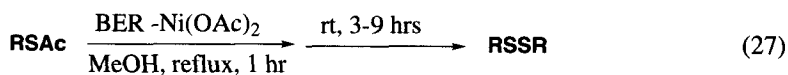
Table 23. Deselenization with Nickel Boride

Substrate	Molar ratio Substrate:NiCl$_2$:NaBH$_4$	THF: MeOH	Product	Yield (%)
n-C$_{12}$H$_{25}$SePh	1: 3: 9.3	1: 3	n-C$_{12}$H$_{26}$	98
X(CH$_2$)$_{11}$SePh				
X = Cl	1: 2:6.2	1: 3	n-C$_{11}$H$_{23}$Cl	82
X = I	1: 2:6.2	1: 3	n-C$_{11}$H$_{24}$	76
X = CN	1: 2.2:6.8	1: 3	n-C$_{11}$H$_{23}$CN	88
X = COOMe	1: 2.3:6.9	1: 1	n-C$_{11}$H$_{23}$COOMe	90
X = SPh	1: 2.2:6.8	1: 3	n-C$_{11}$H$_{23}$SPh	76
X = p-MeC$_6$H$_4$SOO$^-$	1: 1: 3.1	1: 3	HO(CH$_2$)$_{11}$SePh	32
X = Ts	1: 2:6.2	1: 3	n-C$_{11}$H$_{23}$Ts	92
PhSe(CH$_2$)$_9$CH = CH$_2$	1: 2:6.2	1: 3	n-C$_{11}$H$_{24}$	78
n-BuCH=C(SePh)-n-Bu	1: 3:9.3	1: 3	n-BuCH=CH-n-Bu	17
			+ n-C$_{10}$H$_{22}$	76
n-BuC(SePh)=C(Ts)-n-Bu	1: 4:12	1: 1	n-BuCH=C(Ts)-n-Bu	95
n-C$_8$H$_{17}$C(SePh)=CHTs	1: 2:6	1: 1	n-C$_{10}$H$_{21}$Ts	80
Cyclododecyl phenylselenide	1: 2.5:7.8	1: 6	Cyclododecane	94
Cyclododecyl p-nitro-phenylselenide	1: 6: 18	1: 1	Cyclododecane	71
α-(Phenylseleno)-cyclododecanone	1: 1.6:4.8	1:1	Cyclododecanone	93
β-(Phenylseleno)-cyclododecanone	1: 2.6:2	1: 2.4	Cyclododecanone & 2-Cyclododecenone	85 7
α-(Phenylseleno)-cyclododecyl chloride	1: 2:6	1: 1	Cyclododecane	100
α-(Phenylseleno)-cyclododecyl acetate	1: 2:6	1: 1	Cyclododecane & Cyclododecyl acetate	29
(PhSe)$_2$CH(CH$_2$)$_{10}$CH$_3$	1: 8:25	1: 1	n-C$_{12}$H$_{26}$	62

Ar = o-NO$_2$C$_6$H$_4$	1: 3.6:10.8	3:1		82
Ar = p-NO$_2$C$_6$H$_4$	1: 3.6:10.8	3:1		91

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IV. DESELENIZATIONS

In 1984, Back published a convenient method for the reductive deselenization of alkyl, allyl, and alkenyl selenides with $NiCl_2$/NaBH$_4$ in THF-CH$_3$OH at 0°. Little or no alkene reduction was observed under these conditions and selenides could be cleaved in the presence of analogous sulfides, presumably because of the greater C-S bond strength.[56] Sulfones, ketones and acetates also resisted reduction (*Table* 23). The use of sodium borodeuteride in methanol-d afforded l-deutereododecane of high isotopic purity, indicating that the procedure, comprises a convenient method for the preparation of deuterated products.[56a]

V. MECHANISM

On the basis of deuterium labeling studies, Abe *et al.* [57] suggested that different mechanisms operate during the reduction reactions involving preformed nickel boride or nickel boride formed *in situ*. During the catalytic hydrogenation of methyl cinnamate, undeuterated product was obtained when preformed Ni$_2$B was used in MeOD, while no specificity of deuterium label was observed in case when Ni$_2$B was formed *in situ* using NiCl$_2$ and NaBH$_4$ in MeOD. The authors concluded that in the former case, Ni$_2$B just contributes to an initial activation of α,β-unsaturated carbonyl group in the substrate and the hydride transfer takes place from uncoordinated BH$_4^-$ (*Scheme* 1).
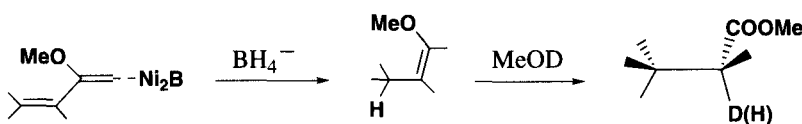
Scheme 1

In a parallel reaction using NiCl$_2$ and NaBD$_4$ in MeOH, 84-90% deuterium label was found at β-position even when Ni$_2$B was prepared *in situ*, indicating that the hydrogen added to β-position arises directly from starting NaBD$_4$. On the basis of the above results, they proposed a stepwise mechanism involving a homogeneous pentacoordinated Ni-complex containing borohydride (*Scheme* 2). Note that both mechanisms result in the *cis*-hydrogenation products as observed by the authors.

In a separate study, Back and coworkers[54-56] proposed a mechanism of deselenization and desulfurization reactions by nickel boride. They demonstrated *via* deuterium labeling that the hydrogen atom incorporated into the product during C-S or C-Se bond cleavage can originate from either the NaBH$_4$ or the protic solvent. The possibility of prior complexation of the substrate to nickel chloride followed by reduction by sodium borohydride was ruled out since this would require sodium borohydride as the sole source of label. It was further proved by the fact that the UV-VIS spectra of an equimolar mixture of NiCl$_2$.6H$_2$0 and dibenzothiophene was identical to the superimposed spectra of individual compounds. Since nickel boride catalyzes the formation of hydrogen gas from NaBH$_4$ and the protic solvent, under reaction conditions, it appears likely that dihydrogen is first produced (*Eq.* 1 and 2) and then adsorbed and activated on the nickel boride surface. This is consistent with the report

by Hawthorne and coworkers that fresh nickel boride has the composition $(Ni_2B)_2H_3$ and that hydrogen is gradually lost when it is heated.

Scheme 2
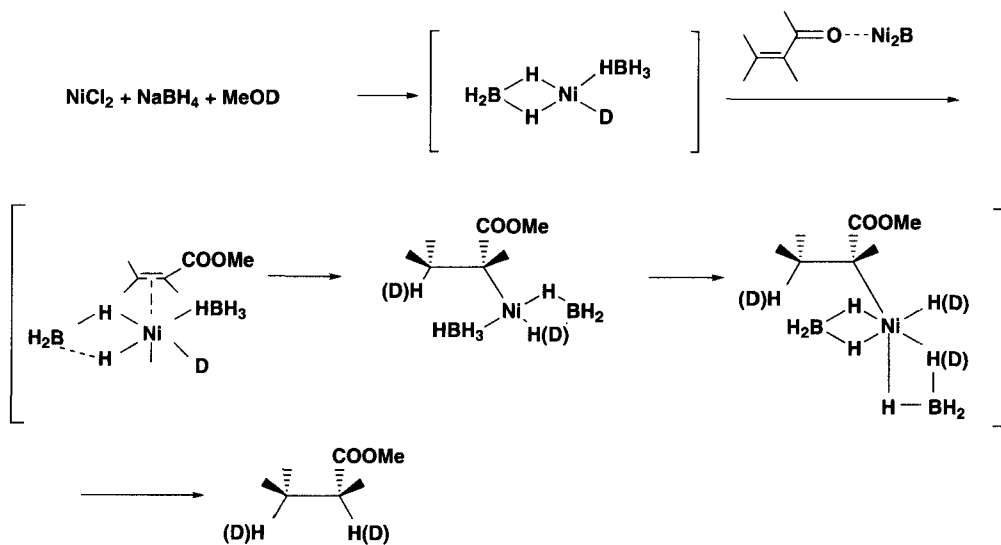
The rapid loss of reactivity of nickel boride upon aging in both deselenization and desulfurization experiments suggests that an essential transient intermediate-nickel hydride and not merely adsorbed hydrogen is formed on its surface. It was shown that the aging was neither due to the oxidative degradation of nickel boride by atmospheric oxygen nor was it due to the contamination of boride surface by spectator ions. The regeneration of the reactive species by treating preformed nickel boride with fresh $NaBH_4$ or with hydrogen gas supports this hypothesis. It is interesting to note, however, that aged nickel boride is still capable of catalyzing the decomposition of $NaBH_4$ and the hydrogenation of olefins suggesting that these processes do not require the same transient intermediate postulated in desulfurization and deselenization processes.

The possibility of free radical intermediates, produced by homolysis of C-S and C-Se bonds has been ruled out by the absence of deuterated products in the presence of deuterated methanol (d_1) and THF (d_8) as well as the absence of destabilizing effect of methyl substituents at the radical center. Stereochemical studies indicate that desulfurization with nickel boride occurs in a highly stereospecific fashion with retention of configuration. The epimers 3α- and 3β-(phenylthio)cholestane afforded 3α- and 3β-deuteriocholestane, respectively, demonstrating that the reaction proceeds with retention of configuration.

In the light of the above evidence Back et al. [53] have proposed an oxidative addition-reductive elimination process which involves a stereospecific oxidative addition of the C-S bond of the substrate to the nickel atom followed by a stereospecific reductive elimination of the C-H as shown in Scheme 3.
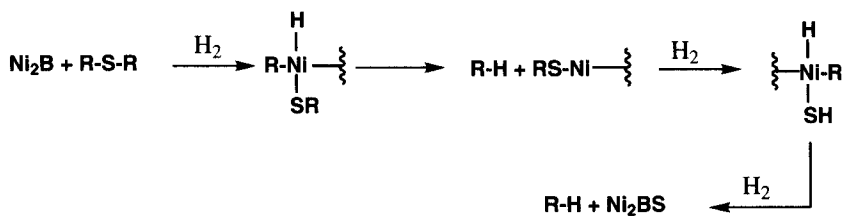
Scheme 3

It is believed that both the steps occur with retention of configuration. Since the reaction mixtures from dibenzothiophenes contain only the corresponding biphenyls along with unreacted starting materials and no significant amounts of thiol product, it is likely that the latter species undergo desulfurization more easily than the original dibenzothiophenes (*Eq.* 28). In an attempt to

$$(26)$$
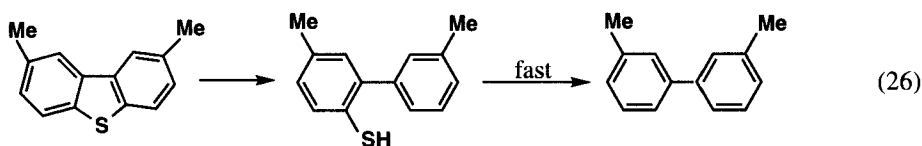
determine whether the complexation of the dibenzothiophene with the nickel boride or the C-S bond cleavage step was rate determining, it was found that dibenzothiophene containing the lighter ^{32}S isotope as compared to that with ^{34}S disappears faster, $K(^{32}S)/K(^{34}S) = 1.005$ to 1.006. This in turn is consistent with C-S bond cleavage as the rate determining step.

The role played by boron in nickel boride remains unclear although a previous study has indicated that it can reside in several different environments that affect the reactivity of the reagent and that it increases the electron density on the nickel. This would be expected to facilitate the oxidative addition step by stabilizing the increasing positive character of the nickel.

VI. CONCLUSION

It is apparent from the literature reviewed that nickel boride can reduce a variety of functional groups and is, in many cases, superior to other metal catalysts. Its advantages include its low cost, ease of preparation and handling, nonpyrophoric nature and simple removal from a reaction mixture by filtration.

We have also observed from this detailed survey of the reactions of nickel boride that it behaves differently under different reaction conditions. The product(s) depend greatly on (i) the molar ratio of the substrate to nickel boride or substrate to $NiCl_2$ to $NaBH_4$, (ii) whether the catalyst is preformed or formed *in situ*, (iii) the nickel salt used, (iv) the solvent/solvent mixture and (v) the temperature of the reactions. However, with the above factors in mind, nickel boride can be used as a key catalyst for new synthetic methods.

Nickel boride has shown tremendous potential for industrial applications. But the lack of mechanistic understanding in a variety of above reactions is a major obstacle as a result of which it

cannot be recycled. Informed use of the catalyst requires a thorough understanding of its surface properties under different solvent systems. We hope that this open area will be further investigated.

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