

An Efficient and Practical System for the Catalytic Oxidation of Alcohols, Aldehydes, and α,β -Unsaturated Carboxylic Acids

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Upon exposure to commercial bleach (~5% aqueous sodium hypochlorite), nickel(II) chloride or nickel(II) acetate is transformed quantitatively into an insoluble nickel species, nickel oxide hydroxide. This material consists of high surface area nanoparticles (ca. 4 nm) and is a useful heterogeneous catalyst for the oxidation of many organic compounds. The oxidation of primary alcohols to carboxylic acids, secondary alcohols to ketones, aldehydes to carboxylic acids, and α,β -unsaturated carboxylic acids to epoxy acids is demonstrated using 2.5 mol % of nickel catalyst and commercial bleach as the terminal oxidant. We demonstrate the controlled and selective oxidation of several organic substrates using this system affording 70–95% isolated yields and 90–100% purity. In most cases, the oxidations can be performed without an organic solvent, making this approach attractive as a “greener” alternative to conventional oxidations.

Introduction

Nickel oxide hydroxide has been known to oxidize a host of organic substrates. One of the first examples appeared in a patent from 1901.¹ Among the substrates that can be oxidized using nickel oxide hydroxide are alcohols, aldehydes, phenols, amines, and oximes. However, early reports demonstrated oxidations of organic compounds using 1–1.5 equiv of nickel. In 1975, George and Balachandran published an extensive review covering the major reactions that can be carried out using stoichiometric nickel oxide hydroxide.² Only two reports exist that demonstrate the *catalytic* application of nickel oxide hydroxide on organic substrates with excess bleach (~5% aqueous sodium hypochlorite) as the oxidant. Weijlard reported the first example in 1945; nicotine and vitamin C were oxidized using a catalytic amount of a nickel(II) salt (3–5 mol %) and excess sodium hypochlorite.³ In 1996, Bekkum et al. reported that larger amounts of nickel oxide hydroxide (15–120 mol %) and excess

bleach would cleave the diols in several sugars to give carboxylic acids.⁴

We reasoned that many of the reactions carried out using stoichiometric nickel oxide hydroxide² could be carried out instead with a catalytic amount of nickel in the presence of excess sodium hypochlorite. The known stoichiometric reactions offer considerable literature precedent, but their catalytic analogues^{3,4} are essentially unexplored. This reasoning led to our recent finding of the only other catalytic example with this oxidation system. We utilized nickel(II) salts (2.5 mol %) and excess bleach to oxidize several α,β -unsaturated carboxylic acids to epoxy acids (Scheme 1a).⁵ Methylene chloride was employed to dissolve the reactant.

Of particular interest to our group is the facile oxidation of alcohols using relatively benign and inexpensive catalysts. Typically, oxidations can be accomplished in the lab through

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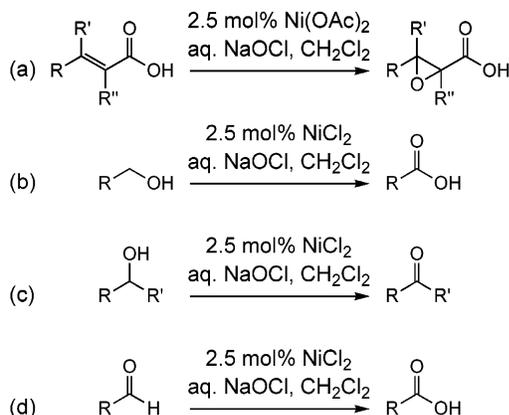
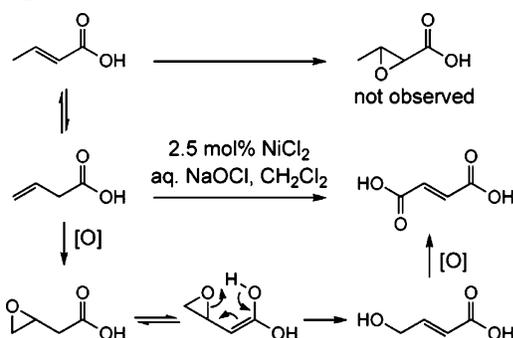
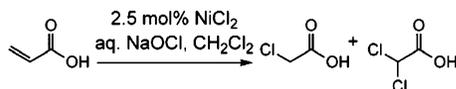
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SCHEME 1. Oxidation of Organic Substrates with Catalytic Nickel(II) Salts and Aqueous Bleach

SCHEME 2. Oxidation of 3-Butenoic Acid to Fumaric Acid and Proposed Mechanism

SCHEME 3. Oxidation of Acrylic Acid


the stoichiometric use of Collins reagent,⁶ Jones' reagent,⁷ pyridinium chlorochromate (PCC),⁸ or potassium permanganate.⁹ These routes are generally undesirable due to the large amounts of toxic-metal-containing waste that they produce in addition to the fact that the reagents are always used in excess to ensure reaction completion. They do, however, tend to be selective and very reliable. Many industrial organic oxidations can be accomplished with oxygen or hydrogen peroxide using heterogeneous catalysts, but the reaction conditions can often lead to over-oxidation of the product to give carbon dioxide and water.¹⁰ Nevertheless, heterogeneous systems are industrially useful for synthesizing commodity chemicals from abundant feedstocks because modest selectivity is often compensated by the low cost of the oxidant, usually oxygen gas. However, with complex and expensive alcohols (fine chemical synthesis), a more selective route is desirable.

Herein we report the facile oxidation of primary alcohols, secondary alcohols, aldehydes, and α,β -unsaturated acids to give carboxylic acids, ketones, carboxylic acids, and epoxy acids, respectively, using rather inexpensive and commonly available reagents. The oxidation proceeds rapidly in the presence of

various nickel(II) salts and excess bleach under ambient conditions and appears to be quite general, giving predictable products with high yields (70–95%) and high purities (90–100%) in most cases (Scheme 1). With a few exceptions, these oxidations can be performed without the use of an organic solvent. For the oxidation of water-insoluble organics, a small amount of added dichloromethane (or diethyl ether in certain cases) greatly facilitates the reaction.

Results and Discussion

In order to obtain relevant data for activity and selectivity comparisons, we decided to perform each oxidation reaction under our standard conditions—which called for a small amount of dichloromethane to dissolve the organic—and then perform a separate set of experiments excluding all organic solvent from the reaction. The results could then be compared to determine the impact, if any, of the organic solvent. Since the active form of the nickel oxide hydroxide catalyst is insoluble under our reaction conditions,⁵ it is reasonable to assume that the oxidation is occurring on the catalyst surface. Thus, we surmised that liquid alcohols could be oxidized without the use of an organic solvent, whereas water-insoluble solid alcohols would require dissolution in an organic solvent. In most cases, this prediction holds true. An organic substrate that is either a liquid or water-soluble can be oxidized without the use of organic solvents. This is clearly advantageous because it reduces the amount of waste generated and it eliminates the need for a potentially toxic organic solvent. This reaction appears to be quite general, oxidizing both aliphatic and aromatic alcohols quite cleanly. Additionally, aldehydes are readily oxidized to carboxylic acids with this catalytic system.

Oxidation of Primary Alcohols. The oxidation of primary alcohols proceeds smoothly under the standard reaction conditions to give the corresponding carboxylic acids following acidic workup. Isolated yields for these reactions were generally good ranging from 68 to 89%, and initial purities were high (80–98% by gas chromatography, GC), indicating that the reaction generates few byproducts (Table 1). Since these alcohols are all liquids and/or water soluble, similar results were expected when the organic solvent was excluded from the reaction. Indeed, the different reaction conditions resulted in very similar isolated yields and GC purities. These five tested substrates are readily oxidized to the carboxylic acids without the need for organic solvent.

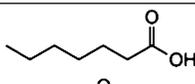
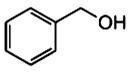
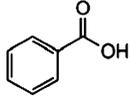
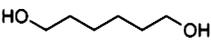
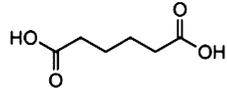
Oxidation of Secondary Alcohols. Secondary alcohols are oxidized to ketones in high yields and purities in most cases (Table 2). Again, in the case of liquid alcohols or water-soluble alcohols, no organic solvent is required, with one exception. The oxidation of racemic *sec*-phenethyl alcohol reached only 33% conversion after the 4 h reaction time in the absence of organic solvent (Table 2, entry 4). The balance of the material was determined to be starting material by GC. Curiously, running this reaction for longer periods of time did not improve the yield or the conversion. With organic solvent, the GC purity is high, but a low isolated yield of the corresponding ketone is obtained. Also, the substrate in Table 2 entry 8 (a mixture of diastereomers) did not react under either of the reaction conditions, suggesting that excessive steric bulk severely impedes oxidation. Finally, the cyclic vicinal diol 1,2-dihydroxycyclohexane (Table 2, entry 9, a mixture of diastereomers) undergoes carbon–carbon bond cleavage to afford the α,ω -dicarboxylic acid in high yield (90% isolated).

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TABLE 1. Oxidation of Primary Alcohols under Standard Reaction Conditions and without Organic Solvent

entry	substrate	product	standard conditions ^a			no organic solvent ^b		
			% crude yield	% GC purity	% isolated yield ^c	% crude yield	% GC purity	% isolated yield ^c
1			89	80	68	91	92	86
2			95	95	89	96	95	89
3			89	95	78	87	95	75
4			68	<i>n.d.</i>	68	72	<i>n.d.</i>	72
5			88	98	88	81	97	81

^a Standard reaction conditions: 2.5 mol % of NiCl₂, 45 mmol alcohol, 15 mL of CH₂Cl₂, 300 mL of ~5% aq. NaOCl, 2 h at 0 °C, then 2 h at 20 °C. ^b Organic solvent-free conditions: same, except no CH₂Cl₂. ^c The isolated products were at least 97% pure. GC = gas chromatography; *n.d.* = not determined.

Oxidation of Aldehydes. As expected, aldehydes are readily oxidized to the corresponding carboxylic acids under the standard reaction conditions. The four entries in Table 3 aptly demonstrate this conversion, which affords the carboxylic acids in high yield and high purity. The oxidation also proceeds rather well without the use of organic solvent. Notably, even very bulky aldehydes (Table 3, entry 4) are oxidized with facility. The same oxidation of pivaldehyde with traditional oxidants oxone¹¹ or H₂O₂¹² occurs with lower yields: 45 or 40%, respectively.

Epoxidation of α,β -Unsaturated Carboxylic Acids. We recently observed several examples of the epoxidation of α,β -unsaturated carboxylic acids using our standard reaction conditions.⁵ Thereafter, we decided to explore the possibility of epoxidizing these olefins without the use of organic solvent. All of our substrates dissolved readily in our aqueous reaction medium, and as targeted, the α,β -unsaturated carboxylic acids were readily epoxidized in yields and purities comparable to those synthesized in the presence of dichloromethane (Table 4). Note that the methallyl alcohol in entry 5 is most likely first oxidized to the α,β -unsaturated acid (methacrylic acid), which is subsequently epoxidized.

Other Oxidations Using Nickel Oxide Hydroxide/NaOCl: 3-Butenoic acid. While exploring the scope of this reaction, we observed several unusual reactions. Initially, our principal research interests were in applying nickel oxide hydroxide/NaOCl toward epoxidation catalysis. This catalyst system does not react with most standard olefins such as styrene and 1-hexene. However, as previously discussed, α,β -unsaturated carboxylic acids are readily epoxidized. We reasoned that the acid functional group was binding to the surface of the heterogeneous catalyst and thus positioning the olefin to accept an oxygen atom. The requirement of a directing group would explain the inertness of standard olefins. During the exploration of this hypothesis, we attempted to epoxidize 3-butenic acid

(Scheme 2). To our surprise, we obtained fumaric acid in high yield (75%, >99% *trans* isomer by ¹H NMR) rather than the expected epoxide. The fumaric acid was not further oxidized to the epoxide. This unusual transformation formally involves isomerization of the double bond and an oxidation of carbon 4. In independent experiments, we attempted to epoxidize fumaric acid and maleic acid. Consistent with the results obtained from the oxidation of 3-butenic acid, these attempts failed to yield epoxide and gave only starting material. If 3-butenic acid were first isomerized to 2-butenic acid (*cis* or *trans*), then it should simply be epoxidized as in Table 4, entry 2; this is not observed. An alternative mechanism calls for direct epoxidation and subsequent tautomerization. Ring opening of the epoxide/enediol tautomer generates an allylic alcohol, which under the reaction conditions should be oxidized to yield fumaric acid (Scheme 2). Support for this mechanism is found in our observation that 3-butenic acid epoxide, prepared independently with *m*-chloroperbenzoic acid, is converted with 69% yield to fumaric acid under our standard conditions. Additionally, since the oxidation of crotonic acid yields no fumaric acid, we must reason that 3-butenic acid is not isomerized to crotonic acid prior to being oxidized.

Other Oxidations Using Nickel Oxide Hydroxide/NaOCl: Acrylic Acid. Payne reported the sodium tungstate catalyzed epoxidation of α,β -unsaturated carboxylic acids with hydrogen peroxide in 1959,¹³ and Sharpless later optimized this reaction.¹⁴ However, it is curious that neither Payne nor Sharpless reported the epoxidation of acrylic acid with the tungsten-based system. The omission of this simple substrate led us to believe that its reaction with the tungsten system is poorly selective or altogether unfruitful. Our nickel system also

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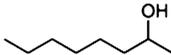
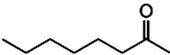
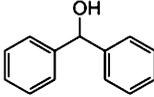
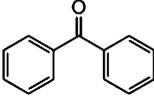
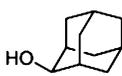
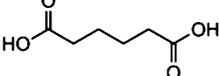
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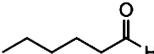
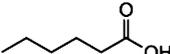
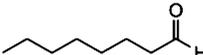
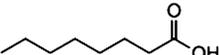
TABLE 2. Oxidation of Secondary Alcohols under Standard Reaction Conditions^a

entry	substrate	product	standard conditions ^a			no organic solvent ^b		
			% crude yield	% GC purity	% isolated yield ^c	% crude yield	% GC purity	% isolated yield ^c
1			71	>99	71	70	>99	70
2			65	94	59	66	97	66
3			72	82	52	89	92	75
4			33	90	29	55	33	<i>n.d.</i>
5			90	>99	90	<i>n.r.</i>	<i>n.r.</i>	<i>n.r.</i>
6			78	>99	78	<i>n.r.</i>	<i>n.r.</i>	<i>n.r.</i>
7 ^d			98	>99	98	<i>n.r.</i>	<i>n.r.</i>	<i>n.r.</i>
8			<i>n.r.</i>	<i>n.r.</i>	<i>n.r.</i>	<i>n.r.</i>	<i>n.r.</i>	<i>n.r.</i>
9			90	<i>n.d.</i>	90	88	<i>n.d.</i>	88

^a Standard reaction conditions: 2.5 mol % of NiCl₂, 45 mmol alcohol, 15 mL of CH₂Cl₂, 300 mL of ~5% aq. NaOCl, 2 h at 0 °C, then 2 h at 20 °C.

^b Organic solvent-free conditions: same, except no CH₂Cl₂. ^c The isolated products were at least 97% pure. GC = gas chromatography; *n.d.* = not determined; *n.r.* = no reaction, starting material recovered. ^d The organic solvent employed for 2-adamantanol was diethyl ether.

TABLE 3. Oxidation of Aldehydes under Standard Reaction Conditions and without Organic Solvent

entry	substrate	product	standard conditions ^a			no organic solvent ^b		
			% crude yield	% GC purity	% isolated yield ^c	% crude yield	% GC purity	% isolated yield ^c
1			92	64	48	77	97	77
2			80	94	80	79	98	79
3			96	>99	96	98	>99	98
4			85	97	85	91	98	91

^a Standard reaction conditions: 2.5 mol % of NiCl₂, 45 mmol aldehyde, 15 mL of CH₂Cl₂, 300 mL of ~5% aq. NaOCl, 2 h at 0 °C, then 2 h at 20 °C.

^b Organic solvent-free conditions: same, except no CH₂Cl₂. ^c The isolated products were at least 94% pure. GC = gas chromatography.

fails to epoxidize this α,β -unsaturated carboxylic acid. Instead, it is fragmented and chlorinated, quite possibly via radical pathways known to operate with nickel oxide hydroxide.^{15–18} A 1:1 mixture of chloroacetic acid and dichloroacetic acid was

obtained from this reaction (overall yield is 78%), demonstrating the cleavage of carbon–carbon bonds along with chlorination (Scheme 3). In some cases—under seemingly identical reaction conditions—the chloroacetic acid/dichloroacetic acid ratio is as

TABLE 4. Epoxidation of α,β -Unsaturated Carboxylic Acids under Standard Reaction Conditions^a and without Organic Solvent^b

entry	substrate	product	% GC conversion	
			standard conditions ^a	no organic solvent ^b
1			97	95
2			45	42
3			71	71
4			75	85
5			81	89

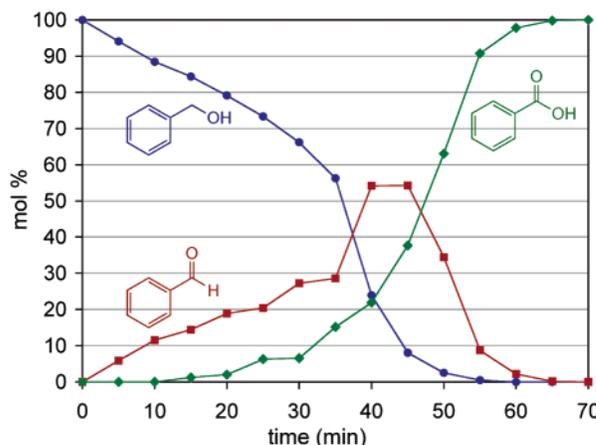
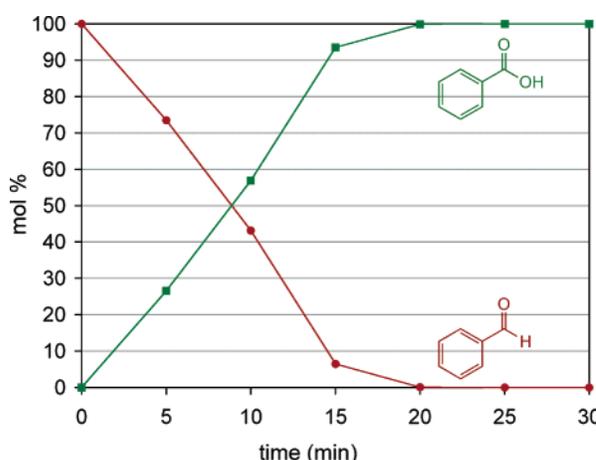
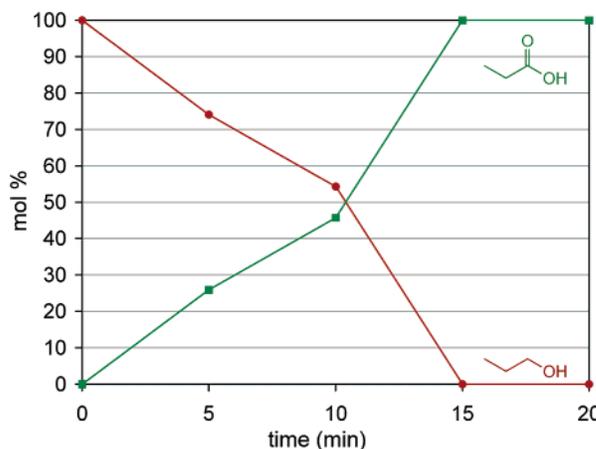
^a Standard reaction conditions: 2.5 mol % of NiOAc₂, 45 mmol olefin, 15 mL of CH₂Cl₂, 300 mL of ~5% aq. NaOCl, 2 h at 0 °C, then 2 h at 20 °C. See ref 5. ^b Organic solvent-free conditions: same, except no CH₂Cl₂. GC = gas chromatography.

high as 5:1. We were unable to determine the fate of the C₁ fragment that was apparently generated and lost during workup. On the basis of the behavior of acrylic acid, it seems that a vinylic methyl substituent is required for selective epoxidation of α,β -unsaturated carboxylic acids. Moreover, greater selectivity is effected when this methyl group is in the α position, as evidenced by the modest conversion (42% by GC) observed in the epoxidation of β -methyl acrylic acid (crotonic acid) versus that of α -methyl acrylic acids (85–95% by GC). For crotonic acid epoxidation, the radical fragmentation/chlorination pathway is partially operative, and the balance of the substrate is largely converted to chloroacetic acid and dichloroacetic acid.

Preliminary Kinetic Studies. In an effort to gain a better understanding of this catalyst system, the oxidation of benzyl alcohol was explored in greater detail. Gas chromatography (GC) was employed to determine the distribution of organic components present as a function of time at 5 min intervals for a reaction at a temperature of 20 ± 1 °C. In the case of benzyl alcohol, the reaction proceeds cleanly through a benzaldehyde intermediate, which is subsequently oxidized to benzoic acid. The concentration of benzoic acid is initially very low, while the concentration of benzaldehyde steadily increases, reaching its peak abundance around 40–45 min (Figure 1). The benzyl alcohol is completely oxidized to benzoic acid in about 70 min at room temperature.

Separately, the oxidation of benzaldehyde was also explored under these same reaction conditions. Benzaldehyde is oxidized rapidly by the catalyst, achieving complete conversion to benzoic acid in about 20 min (Figure 2). This time frame is consistent with data from the oxidation of benzyl alcohol (Figure 1), wherein the reaction is complete about 25 min following the peak concentration of benzaldehyde.

Analysis of Figures 1 and 2 should reveal the relative reactivity of benzyl alcohol versus that of benzaldehyde. The first 30 min of Figure 1 shows [benzyl alcohol] versus time to be linear. Since 45 mmol of substrate was employed and 33.8% was consumed during this time period, the initial rate can be calculated as $k_{\text{alcohol}} = (0.045 \text{ mol})(33.8\% \text{ conversion})/(30 \text{ min}) = 5.1 \times 10^{-4} \text{ mol/min}$. Similarly, the first 15 min of Figure 2 shows [benzaldehyde] versus time to be linear, and the initial rate can be calculated as $k_{\text{aldehyde}} = (0.045 \text{ mol})(93.6\% \text{ conver-$

**FIGURE 1.** Distribution versus time in the oxidation of benzyl alcohol with 2.5 mol % of NiCl₂/aqueous NaOCl at 20 ± 1 °C.**FIGURE 2.** Distribution versus time in the oxidation of benzaldehyde with 2.5 mol % of NiCl₂/aqueous NaOCl at 20 ± 1 °C.**FIGURE 3.** Distribution versus time in the oxidation of 1-propanol with 2.5 mol % of NiCl₂/aqueous NaOCl at 20 ± 1 °C. Propionaldehyde concentration was not determined.

sion)/(15 min) = $2.8 \times 10^{-3} \text{ mol/min}$. Thus, the oxidation of benzaldehyde is somewhat faster than the oxidation of benzyl alcohol under these conditions and $k_{\text{aldehyde}}/k_{\text{alcohol}} = 5.5$.

Our initial kinetic studies indicate that aliphatic alcohols are oxidized more rapidly than benzylic alcohols. 1-Propanol is

quantitatively converted to propionic acid in just 15 min (Figure 3), compared to 70 min for benzyl alcohol. Unfortunately, we were unable to monitor the formation of the presumed propionaldehyde intermediate, as it is coincident with the solvent peak in the gas chromatogram. An initial rate analysis of Figure 3 suggests that $k_{\text{propanol}} = (0.045 \text{ mol})(100\% \text{ conversion})/(15 \text{ min}) = 3.0 \times 10^{-3} \text{ mol/min}$, which is similar to that of benzaldehyde and faster than that of benzyl alcohol by a factor of 5.9.

Conclusions

We have demonstrated a very effective, practical, and inexpensive method for oxidizing alcohols, aldehydes, and α,β -unsaturated carboxylic acids with readily available nickel(II) salts and commercial bleach. The nickel oxide hydroxide formed serves as a selective and high-yielding heterogeneous catalyst, converting both aliphatic and aromatic substrates to the expected product in most cases. These reactions can often be performed without organic solvents, thus improving the environmental impact of these oxidative transformations, which traditionally generate much organic and toxic metal waste. Future research will target the catalytic oxidation of other functional groups.

Experimental Section

Standard Procedure for the Oxidation of Primary Alcohols and Aldehydes. A 500 mL flask was charged with NiCl_2 hexahydrate (0.27 g, 1.14 mmol) and water (5 mL). A primary alcohol or an aldehyde (45 mmol) was added followed by (optional) dichloromethane (15 mL). The reaction was cooled in an ice bath, and cold bleach (300 mL) was added in a steady stream over 5 min. A fine black precipitate formed immediately. The resulting slurry was stirred for 2 h at 0 °C and 2 h at room temperature. The slurry was then acidified with 2 M hydrochloric acid until the aqueous layer was strongly acidic by pH paper. The aqueous layer was extracted with diethyl ether (3 × 100 mL). The combined organic extracts were dried over anhydrous MgSO_4 and filtered. Removal of the solvent by rotary evaporation and brief high vacuum gave the crude

product. The purities could generally be improved to >98% by distillation of the crude product or by recrystallization in the case of solids.

Standard Procedure for the Oxidation of Secondary Alcohols. A 500 mL flask was charged with NiCl_2 hexahydrate (0.27 g, 1.14 mmol) and water (5 mL). A secondary alcohol (45 mmol) was added followed by (optional) dichloromethane (15 mL). The reaction was cooled in an ice bath, and cold bleach (300 mL) was added in a steady stream over 5 min. A fine black precipitate formed immediately. The resulting slurry was stirred for 2 h at 0 °C and 2 h at room temperature. The aqueous layer was extracted with diethyl ether (3 × 100 mL). The combined organic extracts were dried over anhydrous MgSO_4 and filtered. Removal of the solvent by rotary evaporation and brief high vacuum gave the crude product. The purities could generally be improved to >98% by distillation of the crude product or by crystallization in the case of solids.

Standard Procedure for the Epoxidation of α,β -Unsaturated Carboxylic Acids. In a 500 mL round-bottom flask, sodium hydroxide (1.8 g, 45 mmol) was dissolved in water (10 mL), and an α,β -unsaturated carboxylic acid (45 mmol) was added followed by (optional) dichloromethane (15 mL). The flask was cooled in an ice bath, and a solution of nickel(acetate)₂ tetrahydrate (0.28 g, 1.14 mmol) in water (5 mL) was added. Cold bleach (300 mL) was added in a steady stream over 5 min. A fine black precipitate formed immediately. The resulting slurry was stirred for 2 h at 0 °C and 2 h at room temperature. The slurry was then acidified with 2 M hydrochloric acid until the aqueous layer was strongly acidic by pH paper. The aqueous layer was extracted with diethyl ether (3 × 100 mL). The combined organic extracts were dried over anhydrous MgSO_4 and filtered. Each product was then analyzed by GC.

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Supporting Information Available: Detailed experimental procedures and characterization data, along with details of the kinetic studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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