poured into 40 mL of H_2O and basified with 20% NaOH (to pH 12). This solution was stirred 4 h and then extracted with ether to remove any epoxide and unreacted starting material. Acidification of the aqueous layer, followed by extraction with ether, drying and removal of solvent, and esterification with diazomethane provided a 79% yield (based on unreacted starting material) of keto ester **7**.

Alternatively, the basic aqueous layer was treated with 2 equiv of 30% H_2O_2, stirred for 4 h, and worked up to provide a near quantitative conversion to the dimethyl ester **8**.

The procedures described appear to represent a general route to keto acids (or esters) or to dicarboxylic acids (or esters) from α-alkylidenecyclanones, which are generally available. Optimization of reaction conditions to reduce competing epoxidation, and extension to three- and five-membered rings are projected.

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Supplementary Material Available: NMR, IR, and mass spectral and elemental analyses of compounds **5**, **7**, **8**, **10**, **11**, **12**, and **14** (4 pages). Ordering information is given on any current masthead page.

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Nickel(II) Bromide Catalyzed Oxidations of Primary and Secondary Alcohols to Carbonyl Compounds by Benzoyl Peroxide

Summary: Primary and secondary alcohols are oxidized to their respective carbonyl compounds in high yield by benzoyl peroxide through the action of nickel(II) bromide, which serves as an effective mediative catalyst and as an alcohol template in these transformations.

Sir: Numerous processes for the conversion of alcohols to carbonyl compounds through oxidation by active halogen[1-6] or peracid[7] reagents have been recently reported. Although each of these methods is generally suitable for the production of ketones from secondary alcohols, their application to primary alcohols usually results in overoxidation. Only the chlorine–dimethyl sulfoxide oxidative procedure[6] appears to offer the required selectivity and efficiency for this sensitive transformation. However, we have found that direct oxidation of alcohols by benzoyl peroxide in the presence of nickel(II) bromide (eq 1) is a conveniently

$$R_2CHOH + (C_6H_5COO)_2 \xrightarrow{NiBr_2} R_2C{=}O + 2C_6H_5COOH \tag{1}$$

employed alternative to this process. As we now report, the combination of inexpensive benzoyl peroxide with catalytic amounts of nickel(II) bromide serves not only as an effective reagent for the conversion of secondary alcohols to ketones but, through employment of nickel(II) as an alcohol template, also provides convenient access to aldehydes.

Table I. Isolated Yields of Ketones from Oxidations of Representative Secondary Alcohols by Benzoyl Peroxide in the Presence of Nickel(II) Bromide[a]

alcohol	ketone	yield, %[b]
2-adamantanol	2-adamantanone	85
benzhydrol	benzophenone	85
cyclobutanol	cyclobutanone	93[c]
cyclopropylphenylmethanol	cyclopropyl phenyl ketone	81
cyclooctanol	cyclooctanone	90
2-decalol	2-decalone	98
2,4-dimethyl-3-pentanol	2,4-dimethyl-3-pentanone	84
1,2-diphenylethanol	2-phenylacetophenone	94
1-phenylethanol	acetophenone	90

[a] Reactions usually performed with dibromo(1,2-dimethoxyethane)nickel(II). [b] Isolated weight yield of ketone; no other oxidized product could be detected by NMR or GLC analysis. [c] Isolated as the 2,4-dinitrophenylhydrazone derivative.[10]

In a typical oxidation procedure, a homogeneous solution of 1,2-diphenylethanol (1.98 g, 10.0 mmol), benzoyl peroxide (3.07 g, 12.7 mmol), and either anhydrous nickel(II) bromide or dibromo(1,2-dimethoxyethane)nickel(II)[8] (2.6 mmol) in 20 mL of anhydrous acetonitrile is heated at 60 °C for 24 h. The reaction solution is then cooled and aqueous potassium iodide is added to decompose excess peroxide. Following extraction with ether, subsequent acid and base washings of the ether solution, and solvent removal, 2-phenylacetophenone is obtained as the sole reaction product (1.84 g, 9.40 mmol, 94% yield). Isolated yields of carbonyl compounds formed in similar reactions with representative secondary alcohols are given in Table I. In all cases quantitative conversion of the secondary alcohol to the corresponding ketone is observed by analyses performed prior to product isolation. Benzoic acid is the sole product from peroxide reduction, and nickel(II) bromide may be quantitatively recovered from the reaction solutions.

Although acyl peroxides are potentially capable of serving as two-electron donors in alcohol oxidations, prior studies of thermal, electrophilic, and selected metal ion catalyzed decompositions of acyl peroxides have indicated that these reactions occur with the formation of acyloxy radicals as reaction intermediates.[11] Benzoyl peroxide[12] and related acyl peroxides[13] or peresters[14] undergo induced radical chain decomposition and, in the limited number of cases that have been examined, oxidize secondary alcohols to ketones in relatively high yield, but only when

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(8) Anhydrous nickel(II) bromide is effective as the oxidation catalyst even when used in amounts as low as 5 mol % relative to the reactant alcohol. However, because of the limited solubility of anhydrous $NiBr_2$ in acetonitrile, the soluble dimethoxyethane complex (available from Alfa or conveniently synthesized[9]) may be preferred.

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Table II. Isolated Product Yields from Oxidations of Representative Primary Alcohols by Benzoyl Peroxide in the Presence of Nickel(II) Bromide[a]

alcohol	$[NiBr_2]/[alcohol]$	time, h	RCHO, %[b]	$RCOOCH_2R$, %[b]
benzyl alcohol	0.50	24	96	0
cyclopropylmethanol	0.50	48	76[c]	0
1-heptanol	0.25	24	0	81
	2.5	48	92	8
3-phenyl-1-propanol	1.0	24	34	14
	2.5	48	58	0
1-phenylcyclobutylmethanol	1.0	72	59	18
	2.5	72	64	<1

[a] Reactions performed in anhydrous acetonitrile at 60 °C. [b] Isolated product yield. [c] Isolated as the 2,4-dinitrophenylhydrazone derivative.

the alcohol is employed as the reaction solvent. Peroxide decomposition in primary alcohols produces aldehydes in low yield, and dilution of the alcohol leads to a decrease in the yield of carbonyl compounds formed in these oxidations.[14a] In contrast, nickel(II) bromide catalyzes and effectively mediates the oxidation of alcohols by benzoyl peroxide when these reactants are employed in stoichiometric amounts. Formation of the corresponding carbonyl compounds (Table I) occurs without interference from oxidative cleavage, β-scission, or other processes normally associated with one-electron oxidations or with homolytic decomposition of benzoyl peroxide. By analogy with prior studies of peroxide decompositions catalyzed by metal halide salts[15] and our observation that the nickel(II) bromide–benzoyl peroxide combination reacts rapidly with cyclohexene to form the corresponding *trans*-1,2-dibromocyclohexane and nickel(II) benzoate,[16] alcohol oxidation by the combination of benzoyl peroxide with nickel(II) bromide may be represented as involving the intermediacy of benzoyl hypobromite, whose concentration is effectively mediated by nickel(II) bromide (eq 2–4).

$$NiBr_2 + (C_6H_5COO)_2 \rightarrow C_6H_5COOBr + (C_6H_5COO)NiBr \quad (2)$$

$$R_2CHOH + C_6H_5COOBr \rightarrow R_2C{=}O + C_6H_5COOH + HBr \quad (3)$$

$$HBr + (C_6H_5COO)NiBr \rightarrow NiBr_2 + C_6H_5COOH \quad (4)$$

Significantly, although alternatively employed metal salts such as lithium bromide do cause oxidation of secondary alcohols to ketones, complex product mixtures are obtained and the oxidation process is not catalytic in the metal salt. Investigations are underway to thoroughly define the mechanism of the nickel(II) bromide catalyzed oxidation process.

If the rapid oxidation of aldehydes that has been observed in previously reported processes that utilize active halogen[1–5] or peracid[7] reagents is recognized as resulting from alcohol, modified alcohol,[1] or water addition to the carbonyl group with subsequent oxidation of the aldehyde derivative, then selective oxidation of primary alcohols to aldehydes should be feasible when reaction conditions are chosen that inhibit carbonyl addition. Successful processes for the oxidation of primary alcohols to aldehydes, such as the chlorine–dimethyl sulfoxide procedure[6] and the trityl cation catalyzed oxidation of trityl alkyl ethers,[17] have relied on suitable modifications of the alcohol functionality that promote subsequent oxidation while also inhibiting carbonyl addition from the reactant alcohol derivative. Alcohol association with nickel(II) bromide[9b,18] should similarly inhibit carbonyl addition and thus serve to protect the aldehyde from further oxidation.

Although benzyl alcohol is converted to benzaldehyde in 76% yield under reaction conditions identical with those employed for oxidations of secondary alcohols (Table I, $[NiBr_2]/[ROH] \leq 0.25$), aliphatic alcohols such as 1-heptanol are oxidized to esters under these same reaction conditions. 1-Heptanol, for example, is converted to 1-heptyl heptanoate in 81% isolated yield. However, by increasing the proportion of nickel(II) bromide relative to the alcohol, the yield of aldehyde product is dramatically increased. Product yields from oxidations of representative primary alcohols (Table II) demonstrate the effectiveness of nickel(II) bromide as a mediative template for oxidations of primary alcohols. Except for oxidations of activated alcohols such as benzoyl alcohol, optimum oxidative conversion of primary alcohols to aldehydes occurs when between 1.5 and 2.5 mol equiv of nickel(II) bromide (based on alcohol) is employed.

Investigations are underway to determine the scope and selectivity of this oxidative transformation.

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Registry No. 2-Adamantanol, 700-57-2; benzhydrol, 91-01-0; cyclobutanol, 2919-23-5; cyclopropylphenylmethanol, 1007-03-0; cyclooctanol, 696-71-9; 2-decalol, 825-51-4; 2,4-dimethyl-3-pentanol, 600-36-2; 1,2-diphenylethanol, 614-29-9; 1-phenylethanol, 98-85-1; 2-adamantanone, 700-58-3; benzophenone, 119-61-9; cyclobutanone 2,4-dinitrophenylhydrazone, 3349-70-0; cyclopropyl phenyl ketone, 3481-02-5; cyclooctanone, 502-49-8; 2-decalone, 4832-17-1; 2,4-dimethyl-3-pentanone, 565-80-0; 2-phenylacetophenone, 451-40-1; acetophenone, 98-86-2; benzyl alcohol, 100-51-6; cyclopropylmethanol, 2516-33-8; 1-heptanol, 111-70-6; 3-phenyl-1-propanol, 122-97-4; 1-phenylcyclobutylmethanol, 70775-57-4; benzaldehyde, 100-52-7; benzaldehyde 2,4-dinitrophenylhydrazone, 1157-84-2; heptanal, 111-71-7; benzenepropanal, 104-53-0; 1-phenylcyclobutanecarboxaldehyde, 1469-83-6; heptyl heptanoate, 624-09-9; 3-phenylpropyl benzenepropanoate, 60045-27-4; (1-phenylcyclobutyl)methyl 1-phenylcyclobutanecarboxylate, 70775-58-5; nickel(II) bromide, 13462-88-9; dibromo(1,2-dimethoxyethane)nickel(II), 28923-39-9.

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