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Mild and Efficient Oxidation of Aromatic Alcohols and Other Substrates Using NiO₂/CH₃COOH System

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Abstract: A variety of aromatic alcohols were efficiently oxidized to their corresponding aldehydes and ketones in good to excellent yields using nickel peroxide activated by acetic acid. Some thiols and amines were also readily oxidized by this oxidant under mild conditions.

Keywords: Oxidation, Nickel peroxide, Alcohols, Catalyst.

Introduction

The oxides and oxyanions of vanadium, chromium, manganese¹ and even iron² have proven to be useful oxidants. These oxides and some of the heavy metal oxides^{3,4} have been widely used in oxidation of organic substrates. However, there are a number of drawbacks against the classical oxidants (CrO₄²⁻, MnO₄⁻) and their use in organic synthesis. These include lack of selectivity, the requirement of a strong acid or base as catalyst and above all their high toxicity for man and environment⁵. Therefore, the development of efficient and less polluting oxidants is highly encouraged.

The powerful common oxidants are mostly derived from metals located around the middle of the first transition series. In contrast, the metals at the end of the first transition series are not capable of forming high-valent oxides and thus remain less studied. However, among these metals, nickel can readily form peroxide (NiO₂) which was used for oxidation of several substrates⁶. One of the first groups to study nickel peroxide pointed out that it is not a reliable oxidant for aliphatic alcohols in organic solvents⁶. This group has also reported that aromatic alcohols can be only converted to their carbonyl compounds by nickel peroxide with good yields under heating conditions in benzene. George *et al.*⁷ have also studied the oxidation of some organic compounds using nickel peroxide in benzene but the reported results were not satisfactory. In 1974, George and Balachandran published an excellent review covering most of the research which was carried out using nickel peroxide as oxidant⁸. Since then, only sporadic reports have appeared in the literature dealing with oxidation of various organic substrates by nickel peroxide⁹⁻¹².

We have, therefore, investigated the oxidation of various organic substrates by nickel peroxide in the presence of different materials as promoters to find out a suitable activator for this oxidant. We have observed that the oxidation of a series of alcohols to aldehydes and ketones, oxidative coupling of thiols to disulfides and oxidation of some amines proceed rapidly and efficiently by nickel peroxide in the presence of acetic acid.

Experimental

Preparation of nickel peroxide

A solution of KOH (22.4 g) in 100 mL of water was chilled and chlorine gas (generated from 20 g of KMnO_4 and 120 mL of concentrated HCl) was slowly bubbled over for one hour period with stirring. To the resulting yellow solution of KClO , was added 11.63 g (0.04 mol) of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ portion-wise in 20 min while stirred in an ice bath. A fine black precipitate formed which was filtered and washed with deionized water and dried at 110°C for 3 h to afford 3.42 g of NiO_2 (95% yield).

Oxidation of organic substrates

To a solution of 1.0 mmol of an organic substrate and 1.0 mmol of acetic acid in 15 mL of *n*-hexane, 4 mmol of nickel peroxide was added while stirred magnetically. The suspension was allowed to react and the reaction was monitored by TLC. After a desired time the reaction was stopped, the heterogeneous solution was filtered and the spent NiO_2 was washed with CH_2Cl_2 . After removing of the solvent the product was isolated and characterized by comparing its spectroscopic data with an authentic sample.

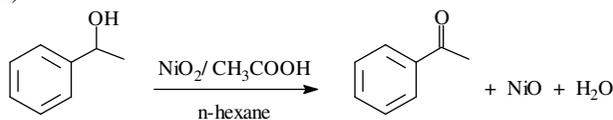
Recovery of nickel peroxide

The spent nickel peroxide was first washed with acetone and then with water to remove the adhered organic compounds and often impurities. The solid was then stirred with KClO solution (about ten times the quantity of NiO_2) for 30 min. The recovered NiO_2 was filtered, washed with water and kept dried for new oxidation process.

Results and Discussion

We have used the method introduced by Nakagawa *et al.*⁶ with some modification for the preparation of nickel peroxide. All the oxidation reactions, except some experiments, were carried out in *n*-hexane at room temperature.

To start our investigations on the oxidation of organic substrates with nickel peroxide, we have selected 1-phenyl ethanol as a probe substrate. Thus, 1-phenyl ethanol (1.0 mmol) and nickel peroxide (4.0 mmol) were suspended in *n*-hexane (15 mL) together with acetic acid (1.0 mmol) as catalyst. The suspension was stirred for a desired time and the reaction was monitored by TLC. The products were then isolated and characterized by comparison of their spectroscopic data with those reported in the literature. The results are gathered in Table 1, for various materials as catalyst. The stoichiometric oxidation is expressed as follows (Scheme 1).



Scheme 1

Table 1. Oxidation of 1-phenyl ethanol to acetophenone by NiO₂ in the presence of different catalysts.

Entry	Catalyst	Time, h	Yield, %
1	Non	5	50
2	Al ₂ O ₃	6	45
3	CuSO ₄ .5H ₂ O	3	37
4	Silica gel	2.5	55
5	CH ₃ COOH	1.5	88
6	CF ₃ COOH	3.5	36
7	Al ₂ O ₃ , CH ₃ COOH	3	34
8	Al ₂ O ₃ , CF ₃ COOH	4	25
9	H ₂ O	3	43
10	Al ₂ O ₃ , H ₂ O	4	40
11	AlCl ₃	2.5	59
12	CH ₃ COOH	3 ^a	65
13	CH ₃ COOH, heat 60 °C	1.5	30

^aThe reaction was carried out with molar ratio 1:3 of alcohol : oxidant respectively

As it is seen, the best result is obtained by nickel peroxide/acetic acid combination (entry 5). It is interesting to note that some of the tested materials, such as alumina, CuSO₄.5H₂O and silica gel (entries 2-4) which showed activating effect on the oxidation of alcohols by other oxidants^{13,14}, did not affect nickel peroxide oxidizing power in our study. Nickel peroxide in the absence of any catalyst gives only 50% yield of acetophenone even after 5 h of reaction time (entry 1). This sluggish reaction might be due to high insolubility of NiO₂ in *n*-hexane. The obtained yields of acetophenone using other substances as catalyst such as stronger acid (CF₃COOH), combination of acids with alumina, trace of moisture, wet alumina or AlCl₃ (entries 6-11) were all rather poor. Moreover, performing the oxidation of 1-phenyl ethanol with NiO₂ in the presence of CH₃COOH at 60 °C did not bring about any improvement in the yield (entry 13). A control experiment using less amount of oxidant, 1:3 alcohol:oxidant instead of 1:4 molar ratio was also carried out. The result however was not satisfactory and only 65% yield of acetophenone was obtained (entry 12) compared with 88% yield of 1:4 molar ratio.

As acetic acid seemed to be the best catalyst among the tested materials in activating nickel peroxide, we have studied the oxidation of various alcohols, two amines and two thiols by our oxidation system. In all experiments, we have used a molar ratio of 1:4:1 of substrate, nickel peroxide and acetic acid respectively. Benzylic, substituted benzylic and allylic alcohols are readily converted to their corresponding carbonyl derivatives when treated with NiO₂ in the presence of acetic acid in *n*-hexane. As shown in Table 2, except a few cases, all of the examined aromatic alcohols give excellent yields of aldehydes or ketones in less than 3h reaction time. Moreover, the primary alcohols were not further oxidized to carboxylic acids which reveal the relative mildness of our oxidation system.

In addition to alcohols, we have also examined the oxidation of two amines and two thiols to check the efficiency of our oxidant. Thus, treating of *n*-hexane solution of aniline or benzyl amine with nickel peroxide in the presence of acetic acid afforded the corresponding diazo and nitrile compound respectively in good yields (entries 13,14), (Table 2). Similarly, reacting of thiophenol and *p*-methyl thiophenol with nickel peroxide/acetic acid in *n*-hexane gives rise to the production of the corresponding symmetrical disulfide products, resulting from oxidative coupling, with excellent yields (Table 2).

Table 2. Oxidation of some organic compounds with NiO₂ in *n*-hexane (unless otherwise mentioned)

Entry	Substrate	Product	Time, h	Yield ^a , %
1			1.5	98
2			1.5	82
3			3	70
4			1.5	88
5			1	79
6			2.5	72
7			4	53
8			1.5	93
9			2 ^b	75
10			3	55
11			2 ^c	84
12			2.5 ^b	80
13			3	58
14			1	85
15			1	94
16			3	76

^aIsolated yields. Spectroscopic analysis of the isolated compounds (IR, ¹H and ¹³CNMR) was in concordance with those reported in the literature. ^bThe reaction was carried out in ether.

^cThe reaction was carried out in CH₂Cl₂

In view of the obtained results, our oxidation system seemed to be a facile and efficient means for oxidation of various organic substrates. The yields and the reaction conditions are much superior to those previously reported^{7,11}. We have replaced the less polluting n-hexane solvent with the highly polluting benzene used by previous researchers⁶⁻⁸. There was no sign of over-oxidation of the alcohol in our system as it usually occurred with other oxidants¹⁵. Other advantages of worthwhile mentioning about our oxidation system are that both nickel peroxide and acetic acid are inexpensive and relatively environmentally benign materials. In addition, the spent nickel peroxide can be easily recovered and reused in oxidation of organic substrates, which is of particular interest to chemists.

Acknowledgements

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