Oxidation with Nickel Peroxide. I. Oxidation of Alcohols

KUNIO NAKAGAWA, RYUSEI KONAKA, AND TADASI NAKATA

Division of Engineering Chemistry, Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka, Japan

Received December 4, 1961

Nickel peroxide, readily obtainable by the treatment of nickel salts with sodium hypochlorite in alkaline solution, was shown to be a useful oxidizing agent for several types of organic compounds. Thus the oxidation of primary alcohols with nickel peroxide in an aqueous alkaline solution afforded the corresponding carboxylic acids, while carbonyl compounds were obtained on oxidation of primary or secondary alcohols by this reagent in organic solvents.

Although such metal oxides as manganese dioxide, selenium dioxide, lead dioxide, silver oxide, mercuric oxide, etc. have often been used as oxidizing agents in the field of organic chemistry, the action of nickel peroxide as an oxidizing agent on organic compounds has not yet been reported in the literature except for a German patent[1] in which only the oxidation of toluene to benzaldehyde or benzoic acid was described. We have studied the action of nickel peroxide[2] on a variety of alcohols in alkaline solution or in organic solvents and found that it is a convenient and useful oxidizing agent for obtaining carboxylic acids or carbonyl compounds from corresponding alcohols.

Nickel peroxide can readily be obtained by the treatment of an aqueous solution of nickel sulfate with sodium hypochlorite in an alkaline solution and the activity is about 0.35×10^{-2} g.-atom of available oxygen per gram.[3] Since it has remarkably broad surface compared with its weight, the available oxygen in nickel peroxide can be used effectively in the reactions. Owing to this character of the reagent, the oxidation of alcohols with nickel peroxide can advantageously be completed in a short time with 1.0 to 1.5 equivalent amounts of the oxidizing agent.

The oxidizing power of nickel peroxide for alcohols was affected by alkalinity of the solvent and temperature. While oxidation of alcohols by this reagent in organic solvents afforded the corresponding carbonyl compounds, primary alcohols in an aqueous alkaline solution were further oxidized to carboxylic acids. Therefore oxidation of alcohols with nickel peroxide may be divided into two procedures, determined by the presence or absence of alkali in the reaction mixture.

Oxidation in Alkaline Solution.—With nickel peroxide in an alkaline solution, saturated aliphatic primary alcohols were oxidized to the corresponding acid in good yields, while the oxidation of straight-chain alcohols proceeded more rapidly than that of the branched-chain isomers. In the case of the alcohols which are only slightly soluble in water, for instance, octyl alcohol, the reaction proceeded obviously at a slower rate. Reaction rates of oxidation of saturated aliphatic alcohols are listed in Table I.

TABLE I

REACTION RATES OF OXIDATION[a] FOR SATURATED ALIPHATIC ALCOHOLS

Alcohol	React. Temp.	Time, Hr. 0.5	1.0	3.0	5.0
EtOH	30°		96.6	97.3	99.4
n-PrOH	30°		74.9	93.0	96.6
n-BuOH	30°		81.6	94.1	96.9
i-BuOH	30°	47.8	59.1	72.7	84.9
i-BuOH	0°	19.6	20.1	29.0	40.3
n-AmOH	30°			83.2	96.8
i-AmOH	30°			69.7	77.5
n-OctOH	30°				58.5

[a] All oxidations were carried out using nickel peroxide at 1.5 times the theoretical amount, and the number in the columns indicates per cent yields of the carboxylic acids.

The oxidation of allyl alcohol proceeded very rapidly and resulted in partial cleavage of its double bond even at a low temperature giving formic acid and carbon dioxide along with acrylic acid. But the oxidation of propargyl alcohol gave propiolic acid in about 50% yield at a low temperature due to the stability of the triple bond, as compared with the double bond. However, cinnamyl alcohol, whose double bond is stabilized by conjugation with the benzene ring, underwent smooth oxidation to give cinnamic acid in an excellent yield, accompanying a small amount of benzoic acid.

In the cases of alcohols possessing an active methylene group in the molecule, the methylene group was in part simultaneously oxidized at room temperature to give compounds with less carbon atoms. When the reaction temperature was lowered in such cases, however, the oxidation of a carbinol group proceeded so predominantly that the corresponding acid was obtained in good yield. Thus the oxidation of γ-phenylpropyl alcohol at 0° afforded 70.5% yield of γ-phenylpropionic acid together with a small amount of benzoic acid,

---

[1] German Patent 127,388 (1900).

[2] Nickel peroxide is the name expediently applied to designate the black, hydrous, higher oxides of nickel which are formed by reaction between a strong oxidizing agent, such as one of the hypochlorites, and freshly precipitated nickelous hydroxide, and its structure can not be discussed in detail at present.

[3] A considerable portion of the available oxygen in nickel peroxide is lost gradually when it is heated, but if it is stored at room temperature under protection against atmospheric moisture, activity of the reagent remains unchanged for a long time.

TABLE II

OXIDATION OF SOME AROMATIC ALCOHOLS

Alcohol	Nickel Peroxide[a]	Temperature, °C.	Time, Hr.	Product	Yield, %
$CH{\equiv}CCH_2OH$	1.1	5	0.5	$CH{\equiv}CCOOH$	50.0
$C_6H_5CH{=}CHCH_2OH$	2.0	50	6.0	$C_6H_5CH{=}CHCOOH$	81.0
$C_6H_5CH_2CH_2CH_2OH$	1.5	30	10.0	$C_6H_5CH_2CH_2CO_2H$	56.7[b]
				$C_6H_5CO_2H$	17.6
$C_6H_5CH_2CH_2CH_2OH$	1.5	0	30.0	$C_6H_5CH_2CH_2CO_2H$	70.5
				$C_6H_5CO_2H$	7.5
$C_6H_5CH_2OH$	1.1	30	3.0	$C_6H_5CO_2H$	93.0
$C_6H_5CH_2OH$	1.5	30	3.0	$C_6H_5CO_2H$	96.7
o-$CH_3C_6H_4CH_2OH$	1.1	30	3.0	o-$CH_3C_6H_4CO_2H$	92.0
o-$CH_3C_6H_4CH_2OH$	1.5	30	3.0	o-$CH_3C_6H_4CO_2H$	97.0
m-$CH_3C_6H_4CH_2OH$	1.5	30	4.0	m-$CH_3C_6H_4CO_2H$	40.2
				m-$C_6H_4(CO_2H)_2$	5.9
m-$CH_3C_6H_4CH_2OH$	1.0	5	7.0	m-$CH_3C_6H_4CO_2H$	60.0
				m-$C_6H_4(CO_2H)_2$	0
p-$CH_3C_6H_4CH_2OH$	1.5	30	3.0	p-$CH_3C_6H_4CO_2H$	62.5
				p-$C_6H_4(CO_2H)_2$	12.0
p-$CH_3C_6H_4CH_2OH$	1.0	5	7.0	p-$CH_3C_6H_4CO_2H$	81.0
				p-$C_6H_4(CO_2H)_2$	0.
α-Furfuryl alcohol	1.5	30	3.0	α-Furoic acid	90.0

[a] Ratio of nickel peroxide to alcohol based on the available oxygen. [b] Yields were determined by quantitative gas chromatography.

whereas at 30° it gave 56.7% yield of γ-phenylpropionic acid and 17.6% yield of benzoic acid.

Benzylic alcohols were far more readily oxidized to carboxylic acids. Benzyl alcohol and *o*-methylbenzyl alcohol, even employing only a slight excess of the theoretical amount of nickel peroxide, gave an excellent yield of benzoic acid and *o*-methylbenzoic acid, respectively. Oxidation of *m*- and *p*-methylbenzyl alcohols was carried out with an equivalent amount of nickel peroxide at a low temperature and yielded the corresponding acids along with the unchanged alcohols, but when the reaction temperature was raised and more peroxide was employed, it resulted in formation of dicarboxylic acids as by-product. On the other hand, oxidation of *o*-methylbenzyl alcohol with an excess amount of nickel peroxide did not give any detectable amount of the dicarboxylic acid, but afforded monocarboxylic acid as the sole product.

The results of the oxidation of alcohols containing an aromatic nucleus in the molecule were summarized in Table II.

It has been reported that the oxidation of α-furfuryl alcohol with acidic oxidants resulted in the opening of the ring, and in the case of oxidation with potassium permanganate[4] the resulting α-furoic acid was so contaminated that it was hardly purified successfully. However, in the oxidation with nickel peroxide at room temperature, α-furoic acid was readily obtained pure in a good yield. The oxidation of aldehydes with nickel peroxide afforded the carboxylic acids. But, owing to alkalinity in the reaction mixture, aldehydes bearing a hydrogen atom in its alpha-position resulted occasionally in the formation of by-products as a result of aldol condensation. On the other hand, benzaldehyde and furfural yielded the corresponding carboxylic acids in good yields.

Oxidation in Organic Solvents.—Manganese dioxide is an excellent reagent for the oxidation of allylic and benzylic alcohols and their congeners to unsaturated aldehydes and ketones,[5] and several different types of the dioxide have been employed for this purpose. However, relatively large amounts of manganese dioxide are necessary for completion of the oxidation due to the mildness of the oxidizing power of this reagent. On the other hand, the oxidation with nickel peroxide in organic solvents proceeded somewhat rapidly, even with a little excess of the theoretically required amounts.

In the present series of experiments, benzene, ether, and petroleum ether can be used as suitable solvents. However, in the case of chloroform, an exothermic reaction took place to give hexachloroethane. This fact means that the trichloromethyl radical can be formed by abstraction of a hydrogen atom from chloroform, and nickel peroxide may be used as an initiator in the field of radical telomerization. The oxidation of various types of alcohols with nickel peroxide was investigated as follows.

The oxidation of saturated aliphatic alcohols with nickel peroxide was carried out in ether or benzene, employing an equivalent amount of the oxidizing agent to the alcohol, and interrupted at the time when the color of nickel peroxide changed from black to grayish green.

The carbonyl compounds thus formed were identified and assayed as their 2,4-dinitrophenyl-

---

(4) J. Volhard, *Ann.*, **261**, 379 (1911).

(5) R. J. Gritter and T. J. Wallace, *J. Org. Chem.*, **24**, 1051 (1959); R. J. Highet and W. C. Wildman, *J. Am. Chem. Soc.*, **77**, 4399 (1955); M. Harfenist, A. Babley, and W. A. Lazier, *J. Org. Chem.*, **19**, 1608 (1954).

hydrazone, and the acidic by-products were titrated with 0.1 *N* sodium hydroxide solution. The reaction turned out to give a very poor yield of the carbonyl compounds and most of the available oxygen in the oxidizing agent was lost as oxygen gas. The results given in the Table III show clearly that nickel peroxide cannot be regarded as a reliable oxidizing agent for saturated aliphatic alcohols in organic solvents.

TABLE III

OXIDATION OF SATURATED ALIPHATIC ALCOHOLS[a] WITH NICKEL PEROXIDE[b]

Alcohol	Solvent	Temp., °C.	Time, Hr.	Yield of Carbonyl Compd.,[c] %	Yield of Acid, %
n-PrOH	Ether	25	12	3.2	0.18
	Benzene	20	10	0.6	0.23
i-PrOH	Ether	25	35	4.2	..
n-BuOH	Ether	36	15	5.8	0.23
i-BuOH	Ether	36	32	6.2	0.20

[a] All oxidations were done with 50 g. of a 10% by weight solution. [b] Nickel peroxide was used in an amount equivalent to that of the alcohol. [c] As 2,4-dinitrophenylhydrazone.

Benzyl alcohol in benzene solution was treated with an equivalent or a slight excess of nickel peroxide, and the filtrate was assayed by quantitative gas chromatography using β-phenylethyl alcohol as a marker. The results of this reaction are shown in Table IV.

TABLE IV

OXIDATION OF BENZYL ALCOHOL TO BENZALDEHYDE

Nickel Peroxide[d]	Temp., °C.	Time, Hr.	Recovery of Benzyl Alcohol, %	Yield of Benzaldehyde, % X^a	Y^b	Z^c	Yield of Benzoic Acid, %
1.0	70	3	12.1	74.4	76.0	86.4	1.4
1.1	50	3	5.7	84.2	85.4	90.5	1.3
1.2	30	6	2.7	88.4	90.4	92.9	1.6
1.2	50	3	0.9	88.3	90.8	91.6	1.8
1.2	80	1	0.7	90.2	92.0	92.6	2.2
1.5	50	3	0	73.1	75.8	75.8	2.9

[a] *X* shows the value calculated by the hydrazone method and based on the amount of starting alcohol. [b,c] *Y* and *Z* are both calculated by the gas chromatographic method, where the former is based on the amount of starting alcohol and the latter represents the yield corrected for recovered alcohol. [d] Ratio of nickel peroxide to alcohol based on the available oxygen.

This table shows that the best procedure is to treat a benzene solution of benzyl alcohol with nickel peroxide at the ratio of 1.1:1.2, which is calculated on the basis of the available oxygen in the oxidizing agent.

When more than this ratio of nickel peroxide was employed the unchanged alcohol could not be detected at all from the reaction mixture, but the yield of benzaldehyde was a little decreased owing to the adsorption on the surface of a large amount of nickel peroxide. When a smaller amount of nickel peroxide was used, unchanged benzyl alcohol was found in large amounts in the products. Comparison of the oxidizing power of nickel peroxide with that of manganese dioxide[6] for benzyl alcohol is shown in Table V.

TABLE V

COMPARISON WITH MnO_2 FOR OXIDATION OF BENZYL ALCOHOL

Oxydant[a]	Available Oxygen/ ROH[b]	Temp., °C.	Time, Hr.	Yield of Benzaldehyde, %	Recovery of ROH, %
MnO_2	1.0	70	3	26.7	72.3
Nickel peroxide	1.0	70	3	76.0	12.1
MnO_2	1.2	50	3	27.6	..
Nickel peroxide	1.2	50	3	90.8	0.9
MnO_2	2.0	50	3	33.5	..

[a] Available oxygen content in manganese dioxide was determined by the method indicated in the case of nickel peroxide. All oxidations were done in benzene solution. [b] Ratio of oxidizing agent to alcohol based on the available oxygen.

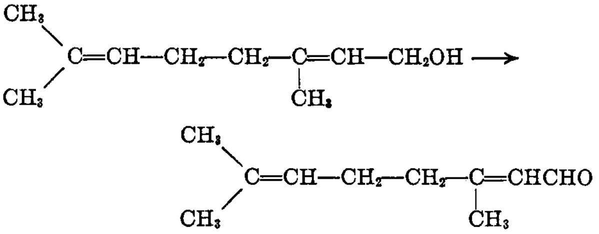
Judging from these results, it was concluded that the oxidizing power of nickel peroxide for benzyl alcohol was stronger than that of manganese dioxide, and only a slight excess of the oxidizing agent was enough to complete the oxidation.

Other aromatic alcohols were treated in similar manner. As summarized in Table VI, when the carbinol group is located at the α-position of the aromatic ring or the double bond, the alcohols are easily oxidized to the corresponding carbonyl compounds.

On the other hand, oxidation of β-phenylethyl and γ-phenylpropyl alcohol turned out to give as poor a yield as the saturated aliphatic alcohols and the reactions proceeded partly through oxidation of the methylene group adjacent to the aromatic ring, giving a small quantity of benzaldehyde.

The oxidation of allyl alcohol to acrolein was carried out in ether solution. The amount of the recovered alcohol and the yield of acrolein were determined respectively by gas chromatography or their 2,4-dinitrophenylhydrazone. In the series of experiments, the maximum yield of acrolein was 79%.

It has been reported that oxidation of geraniol with manganese dioxide[7] to citral resulted in a low yield even with a long reaction time of more than ninety hours. However, oxidation with nickel



$$(CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}\underset{CH_3}{\underset{|}{C}}{=}CH{-}CH_2OH \longrightarrow (CH_3)_2C{=}CH{-}CH_2{-}CH_2{-}\underset{CH_3}{\underset{|}{C}}{=}CHCHO$$

---

(6) The manganese dioxide was prepared according to a method of Attenburrow, *J. Chem. Soc.*, 1094 (1952).

(7) M. Harfenist, A. Bavley, and W. A. Lazier, *J. Org. Chem.*, **19**, 1608 (1954).

TABLE VI

OXIDATION[a] OF SOME AROMATIC ALCOHOLS

Alcohol	Nickel Peroxide[d]	Temp., °C.	Time, Hr.	Product Carbonyl Compd.	Yield,[b] %	M.P., °C.[e]
α-Phenylethyl alcohol	1.2	50	3	Acetophenone	50.7	250
Cinnamyl alcohol	1.2	50	1	Cinnamaldehyde	85.9	254
Benzoin	1.2	50	5	Benzil	98.3[c]	94[f]
Benzhydrol	1.2	50	6	Benzophenone	98.1[c]	48[f]
o-Methylbenzyl alcohol	1.0	50	3	*o*-Methylbenzaldehyde	75.8	193
m-Methylbenzyl alcohol	1.0	50	3	*m*-Methylbenzaldehyde	57.7	211
p-Methylbenzyl alcohol	1.0	50	3	*p*-Methylbenzaldehyde	64.5	241
p-Methylbenzyl alcohol	2.0	50	3	*p*-Methylbenzaldehyde	81.0	241
α-Furfuryl alcohol	1.2	30	10	Furfural	77.8	216
β-Phenylethyl alcohol	1.2	80	1	Phenylacetaldehyde	12.9	236
γ-Phenylpropyl alcohol	1.2	50	4	β-Phenylpropionaldehyde	11.6	259

[a] All oxidations were done in benzene solution. [b] Yields were calculated from weight of 2,4-dinitrophenylhydrazone. [c] Calculated from carbonyl compound itself. [d] Ratio of nickel peroxide to alcohol based on the available oxygen. [e] M.p. of 2,4-dinitrophenylhydrazone. [f] M.p. of carbonyl compound.

TABLE VII

YIELDS IN PER CENT, FROM THE OXIDATION OF VITAMIN A_1[a]

V.A. Mg./15 Ml.	150	100	50	30	25	25	10	100	67	33
Nickel Peroxide Mg.	50	50	50	50	100	20	50	250	167	84
Reaction Time, Min.										
10					69.7	11.7				
20					72.8	14.8				
60	20.4	30.7	50.6	65.0	82.7	25.5	66.3	81.5	77.4	72.5
120	24.2	34.2	56.6	74.6			65.0	80.1	78.1	72.5
180	26.1	38.4	66.2	76.5			67.9			

[a] All oxidations were done in petroleum ether at room temperature. The number in the columns indicates the per cent yield. Method of assay: ultraviolet absorption.

peroxide gave citral in a yield of 80.5% in only six hours. Similarly, oxidation of Vitamin A_1 with nickel peroxide, gave retinene in a good yield in a short reaction time.

All the oxidations of Vitamin A_1 were followed by ultraviolet analysis according to the usual manner. Table VII gives the results of these experiments. Thus although nickel peroxide and manganese dioxide are both considered to be oxidants of the same type, the oxidizing power of the former is somewhat stronger than that of the latter. Accordingly, a smaller amount of nickel peroxide, as compared with manganese dioxide, may be used for the same purpose. Moreover, nickel peroxide recovered after the oxidation reaction can be renewed with alkaline hypochlorite solution and repeatedly employed economically.

Experimental

Preparation of Nickel Peroxide.—A mixture of 300 ml. of 6% sodium hypochlorite solution and 42 g. of sodium hydroxide was added dropwise to 130 g. of nickel sulfate hydrate in 300 ml. of water, and stirred for 0.5 hr. at 20°. The resulting black nickel peroxide was collected by filtration, washed with enough water to remove active chlorine, and, after crushing the cake to powder, dried over anhydrous calcium chloride under reduced pressure.

Determination of Available Oxygen.—About 0.2 g. of nickel peroxide weighed accurately was added to 20 ml. of 36% acetic acid containing 2–3 g. of potassium iodide, entirely dissolved, and allowed to stand for 10 min. under closed protection against air. The liberated iodine was titrated by 0.1 *N* sodium thiosulfate solution. Available oxygen content is calculated as follows:

$$\frac{\mathrm{Na_2S_2O_3\ (ml.)}}{1000 \times \mathrm{peroxide\ (g.)} \times 10 \times 2} = \text{g.-atom oxygen/g. nickel peroxide}$$

Renewal of Nickel Peroxide.—After the oxidation reaction, nickel peroxide was collected by filtration, washed with water, stirred with 6% sodium hypochlorite solution (about ten times the quantity of nickel peroxide) for 20 min., filtered, washed with water, and dried.

Determination of Oxidation Rates for Saturated Aliphatic Alcohols.—To a solution of 0.04 mole of each alcohol and 2 g. of sodium hydroxide in 100 ml. of water, nickel peroxide (1.5 times the theoretical amount) was added under stirring on a magnetic stirrer, and the heterogeneous mixture was allowed to react for the given times at various temperatures. The solid was then separated from the reaction solution by suction filtration and washed with water. The combined filtrate was acidified with dilute sulfuric acid and a portion accurately weighed out from the solution was steam distilled. The volatile carboxylic acid in the distillate was titrated with 0.1 *N* sodium hydroxide solution.

Oxidation of Benzyl Alcohol in Alkaline Solution.—To a solution of 2.16 g. of benzyl alcohol and 1.0 g. of sodium hydroxide in 50 ml. of water, 16.0 g. of nickel peroxide (1.5 times the theoretical amount) was added while stirring on a magnetic stirrer, and the heterogeneous solution was allowed to react at 30° for 3 hr. The reaction mixture was filtered through a glass filter, nickel peroxide was washed with water, and, on acidifying, the filtrate deposited white needles which were collected and dried to give 2.1 g. of benzoic acid, m.p. 122.5° (reported 122.4°), undepressed on admixture with an authentic sample. In addition, by extracting the filtrate with ether, 0.26 g. of the crude acid was obtained, m.p. 122.0°.

Oxidation of Cinnamyl Alcohol in Alkaline Solution.—A mixture of 2.68 g. of cinnamyl alcohol, 1.0 g. of sodium hydroxide, and 23.5 g. of nickel peroxide (twice the theoretical amount) in 50 ml. of water was heated at 50° for 6 hr. as in the preceding method. The reaction solution was filtered, acidified, extracted with ether, and the crude product obtained (2.67 g., 90% purity) was recrystallized from a mixture of ether and petroleum ether to give 2.37 g. of cinnamic acid, m.p. 133° (reported 133°).

Anal. Calcd. for $C_9H_8O_2$: C, 72.95; H, 5.44. Found: C, 72.59; H, 5.50.

Oxidation of *o*-Methylbenzyl Alcohol in Alkaline Solution.—By the same procedure as for benzyl alcohol, a mixture of 1.22 g. of *o*-methylbenzyl alcohol, 0.5 g. of sodium hydroxide, and 8.6 g. of nickel peroxide (1.5 times the theoretical amount) gave 1.32 g. of *o*-methylbenzoic acid, m.p. 104° (reported 104–105°).

Oxidation of Furfuryl Alcohol in Alkaline Solution.—A mixture of 1.96 g. of furfuryl alcohol, 1.0 g. of sodium hydroxide, and 16 g. of nickel peroxide (1.5 times the theoretical amount) in 50 ml. of water was subjected to the oxidation followed as usual, which gave 2.02 g. of furoic acid as white crystals, m.p. 132–133° (reported 133–134°).

Oxidation of Furfural in Alkaline Solution.—To a solution of 1.92 g. of furfural and 1.0 g. of sodium hydroxide in 50 ml. of water was added 8.2 g. of nickel peroxide (1.5 times the theoretical amount) and stirred for 3 hr. at 30°. After removal of nickel peroxide, the filtrate was acidified and the acid which formed was recrystallized from water to give 1.9 g. of furoic acid, m.p. 132–133°.

The Oxidation of Benzyl Alcohol in Benzene.—A mixture of 5 g. of benzyl alcohol and the amount of nickel peroxide given in Table IV in 45 g. of benzene was stirred in a flask equipped with a condenser on a heating plate, and the reaction temperature was adjusted to ±1° of the temperature given in Table IV. After the desired time, stirring was stopped, and the reaction mixture was filtered to remove the solid, which was washed with benzene. An aliquot sample was taken from the combined filtrate, and identified and assayed by the 2,4-dinitrophenylhydrazone and gas chromatographic analysis.

Gas Chromatographic Quantitative Analysis.—β-Phenylethylalcohol was chosen as a marker.

Apparatus: Shimadzu GC-1A equipped with a thermal conductivity cell. Column: U-shaped stainless steel column of 3 m. length and 6 mm. diameter, and packed with Silicone 550 packing. (30 weight % on 30–60 mesh Chromosorb P). Temperature: 140°. Carrier gas: hydrogen. Flow rate: 100 ml./min. The quantities of benzyl alcohol and benzaldehyde were calculated by the following equation

$$\frac{A}{B} \times 0.927 \times \text{weight of } \beta\text{-phenylethyl alcohol}$$

where A = area of peak for benzyl alcohol or benzaldehyde and B = area of peak for β-phenylethyl alcohol.

Oxidation of Cinnamyl Alcohol in Benzene.—Nickel peroxide (1.2 times the theoretical amount) was added to a solution of 3.028 g. of cinnamyl alcohol in 30 ml. of benzene, and heated at 50° for 1 hr. under stirring. The reaction solution was filtered to remove nickel peroxide and washed with 100 ml. of benzene. Then a one-tenth aliquot amount of the filtrate was weighed out and treated with 2,4-dinitrophenylhydrazine hydrochloride to give 0.4034 g. of cinnamaldehyde hydrazone, m.p. 254° (reported 255°).

Oxidation of Benzoin in Benzene.—A mixture of 5 g. of benzoin and nickel peroxide (1.2 times the theoretical amount) in 200 ml. of benzene was heated at 50° for 5 hr. The reaction mixture was filtered, washed with benzene, and the crude product obtained by removal of the solvent was recrystallized from dilute alcohol to give 4.87 g. of benzil, m.p. 94°.

Oxidation of Allyl Alcohol in Ether.—Nickel peroxide (1.5 times the theoretical amount) was added to a solution of 3.0 g. of allyl alcohol in 100 ml. of ether and stirred on a magnetic stirrer for 6 hr. at 20°. The reaction mixture was filtered, washed with ether, and a portion accurately weighed out from the combined filtrate was precipitated as acrolein 2,4-dinitrophenylhydrozone, m.p. 161° (reported 162°).

Oxidation of Geraniol.—A mixture of 5 g. of geraniol (purified *via* the calcium chloride adduct) and nickel peroxide (twice the theoretical amount) in 90 ml. of benzene was heated at 50° for 6 hr. The reaction mixture was filtered and washed with 100 ml. of benzene. Then a one-tenth aliquot amount of the filtrate was accurately weighed out and treated with 2,4-dinitrophenylhydrazine hydrochloride to give 0.866 g. of hydrazone, m.p. 108° (from ethanol) (reported 110°).

Oxidation of Vitamin A_1.—A petroleum ether solution of Vitamin A_1 (prepared from its palmitate) and the amount of nickel peroxide given in Table VII was stirred in a flask at room temperature. After the desired time, the reaction mixture was filtered, washed with the solvent, and the filtrate was concentrated to remove the solvent. The oily retinene obtained was dissolved in isopropyl alcohol and was assayed by its ultraviolet analysis according to the usual method; ultraviolet: $\lambda_{\max}^{i\text{-PrOH}}$ *i*-PrOH/max mμ ($E_{1\text{cm.}}^{1\%}$) 380 (1.400).

The product was further identified as its 2,4-dinitrophenylhydrazone, m.p. 208–209°.

Anal. Calcd. for $C_{26}H_{32}O_4N_4$: C, 67.21; H, 6.94; N, 12.06. Found: C, 66.25; H, 6.87; N, 12.04.

Oxidation of Chloroform.—To a stirred solution of 100 g. of chloroform was added 13.3 g. of nickel peroxide (0.316×10^{-2} g-atom oxygen/g.) and refluxed for 15 hr. After removal of nickel peroxide, the reaction solution was evaporated and the resulting residue was purified by sublimation to give 7.2 g. of hexachloroethane, m.p. 184–186° (in sealed tube). The yield based on the available oxygen content in nickel peroxide was 72.0%.

Acknowledgment.—The authors express their thanks to Prof. S. Ueo and Dr. K. Takeda for encouragement and helpful discussion.