Nickel Peroxide Oxidation of Organic Compounds

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Contents

I. Introduction

Numerous examples of the oxidation of organic compounds using nickel peroxide are reported in the literature. One of the early reports appeared in a German patent,[1] in which the oxidation of toluene to benzaldehyde and benzoic acid was described. Weijlard[2] reported that diacetone-2-keto-L-gulonic acid, an intermediate in the synthesis of vitamin C, was obtained from diacetone-L-sorbose in good yields by the addition of nickel salts in a solution of sodium hypochlorite. Nakagawa[3] had suggested that the black oxide of nickel formed by the treatment of sodium hypochlorite with nickel sulfate was responsible for this type of oxidation. Since then, several workers have used this reagent for oxidizing different organic substrates.[4a]

The oxidation of organic compounds using nickel peroxide is assumed to proceed through a free-radical pathway.[4-10] Isotopic and esr studies using radical scavengers support this view.[5-10] Nickel peroxide has a large surface area as compared to its weight, and hence it serves as a better oxidizing agent when compared to other oxidizing agents such as manganese dioxide. In addition, only smaller quantities of the reagent (1.0–1.5 equiv) are needed for oxidation. The present review primarily deals with the oxidation of different organic substrates using nickel peroxide, and the literature coverage extends up to December 1973.

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II. Compounds

A. Alcohols

The oxidation of alcohols by nickel peroxide is affected by the alkalinity of the solvent medium and also the reaction temperature.[11] While the oxidation of alcohols in organic solvents like benzene and petroleum ether affords the corresponding carbonyl compounds, primary alcohols in aqueous alkaline solutions are further oxidized to the corresponding carboxylic acids.

1. Oxidation in Aqueous Alkaline Medium

Saturated aliphatic primary alcohols are readily converted to the corresponding carboxylic acids on treatment with nickel peroxide, in alkali medium.[11] Table I summarizes the results of oxidation of several primary alcohols in aqueous alkaline medium. In general, the oxidation of straight-chain alcohols proceeds more rapidly than that of the corresponding branched chain isomers. Unsaturated alcohols, on the other hand, undergo oxidative cleavage in some cases. Allyl alcohol, for example, gives a mixture of acrylic acid, formic acid, and carbon dioxide.[11] The oxidation of propargyl alcohol, however, gives mainly propiolic acid. Similarly, cinnamyl alcohol undergoes smooth conversion to cinnamic acid.

In the case of alcohols possessing an active methylene group, the methylene group is, in part, simultaneously oxidized at room temperature. However, at lower temperatures, the hydroxylic function alone is affected. Thus, the oxidation of 3-phenyl-1-propanol at 0° gives mainly 3-phenylpropionic acid along with traces of benzoic acid, whereas at 30° a much higher yield of benzoic acid is obtained.[11]

Nickel peroxide has been used for the synthesis of orotic acid and thioorotic acid derivatives.[12] Thus, the oxidation of 6-hydroxymethyl-1-methyluracil (**16**) with nickel peroxide is reported to give 1-methylorotic acid (**16a**). Similarly, 6-hydroxymethyl-1-methylthiouracil (**17**) gives 1-methyl-2-thioorotic acid (**17a**). With excess of nickel peroxide, however, 1-methylorotic acid (**16a**) is formed from **17** (Table I).

Benzylic alcohols are easily oxidized to the corresponding carboxylic acids on treatment with nickel peroxide. Thus, benzyl alcohol and *o*-methylbenzyl alcohol give benzoic acid and *o*-toluic acid, respectively.[11] Oxidation of *m*-methylbenzyl alcohol and *p*-methylbenzyl alcohol at low temperatures gives *m*-toluic and *p*-toluic acids, respectively. At higher temperatures, however, both metaphthalic acid and terephthalic acids, respectively, are formed, along with the corresponding monocarboxylic acids.[11]

The oxidation of α-furfuryl alcohol with acidic oxidizing agents results in ring-opening reactions, but with nickel peroxide pure α-furoic acid is readily obtained.[11]

2. Oxidation in Organic Solvents

Alcohols are readily converted to the corresponding car-

TABLE I. Oxidation of Alcohols in Alkaline Medium

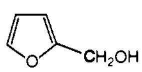
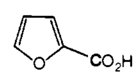
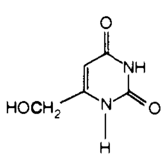
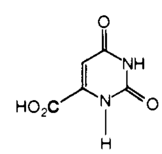
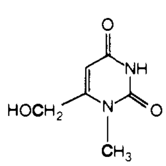
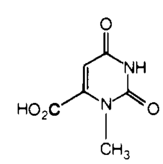
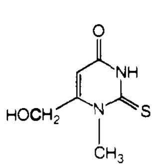
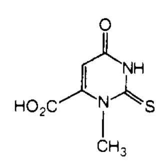
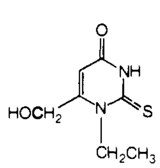
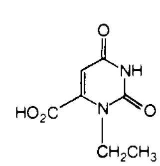
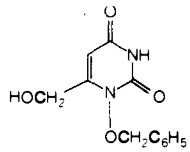
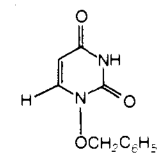
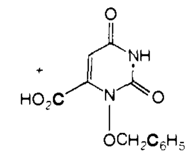
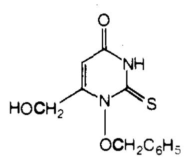
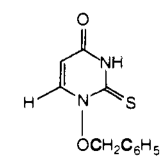
Starting material	Ratio of substrate: NiO_2[a]	Solvent	Temp, °C	Time, hr	Product	Yield, %	Ref
CH_3CH_2OH (**1**)	1.5	Water	30	3	CH_3CO_2H	97	11
	1.5	Water	30	5	CH_3CO_2H	99	
$CH_3CH_2CH_2OH$ (**2**)	1.5	Water	30	3	$CH_3CH_2CO_2H$	93	11
	1.5	Water	30	5	$CH_3CH_2CO_2H$	97	
$CH_3CH_2CH_2CH_2OH$ (**3**)	1.5	Water	30	3	$CH_3CH_2CH_2CO_2H$	94	11
	1.5	Water	30	5	$CH_3CH_2CH_2CO_2H$	97	
$CH_3CH(CH_3)CH_2OH$ (**4**)	1.5	Water	30	3	$CH_3CH(CH_3)CO_2H$ (**4a**)	73	11
	1.5	Water	30	5	**4a**	85	
	1.5	Water	0	3	**4a**	29	
	1.5	Water	0	5	**4a**	40	
$CH_3CH_2CH_2CH_2CH_2OH$ (**5**)	1.5	Water	30	3	$CH_3CH_2CH_2CH_2CO_2H$ (**5a**)	83	11
	1.5	Water	30	5	**5a**	97	
$CH_3(CH_2)_6CH_2OH$ (**6**)	1.5	Water	30	5	$CH_3(CH_2)_6CO_2H$	59	11
$CH{\equiv}CCH_2OH$ (**7**)	1.1	Water	5	0.5	$CH{\equiv}CCO_2H$	50	11
$C_6H_5CH{=}CHCH_2OH$ (**8**)	2.0	Water	50	6	$C_6H_5CH{=}CHCO_2H$	81	11
$C_6H_5CH_2CH_2CH_2OH$ (**9**)	1.5	Water	30	10	$C_6H_5CH_2CH_2CO_2H$ + $C_6H_5CO_2H$	57 18	11
	1.5	Water	0	30	Same as above	71 8	
$C_6H_5CH_2OH$ (**10**)	1.1	Water	30	3	$C_6H_5CO_2H$	93	11
	1.5	Water	30	3	$C_6H_5CO_2H$	97	
o-$CH_3C_6H_4CH_2OH$ (**11**)	1.1	Water	30	3	*o*-$CH_3C_6H_4CO_2H$	92	11
	1.5	Water	30	3	*o*-$CH_3C_6H_4CO_2H$	97	11
m-$CH_3C_6H_4CH_2OH$ (**12**)	1.5	Water	30	4	*m*-$CH_3C_6H_4CO_2H$ + *m*-$HO_2CC_6H_4CO_2H$	40	11
	1.0	Water	30	7	*m*-$CH_3C_6H_4CO_2H$	60	
p-$CH_3C_6H_4CH_2OH$ (**13**)	1.5	Water	30	3	*p*-$HO_2CC_6H_4CO_2H$ + *p*-$CH_3C_6H_4CO_2H$	12 63	11
	1.0	Water	30	7	*p*-$CH_3C_6H_4CO_2H$	81	11
 (14)	1.5	Water	30	3		90	11
 (15)	2.0	NaOH(aq)	Room temp	24		33	12
 (16)	2.0	NaOH(aq)	Room temp	24	 (16a)	73	12
 (17)	6.1	NaOH(aq)	Room temp	3.5	 (17a)	72	12
	Excess	NaOH(aq)	Room temp	24	**16a**	67	
 (18)	Excess	NaOH(aq)	Room temp	24	 (18a)	78	12

TABLE I (Continued)

Starting material	Ratio of substrate: NiO_2[a]	Solvent	Temp, °C	Time, hr	Product	Yield, %	Ref
 (19)		NaOH(aq)	Room temp	6	 (19a)	24	12
					+  (19b)	64	12
 (20)	Excess	NaOH(aq)	Room temp	18	**19b**	77	12
	2.0	NaOH(aq)	Room temp	1	 (20a)	76	12
	6.0	NaOH(aq)	Room temp	22	**19a**	74	12

[a] Based on available oxygen.

bonyl derivatives when treated with nickel peroxide in organic solvents such as benzene or petroleum ether (Table II).[11] The oxidation of saturated aliphatic alcohols, employing equivalent amounts of the oxide and alcohol, give poor yields of the carbonyl compounds, and most of the available oxygen in the oxidizing agent gets lost as oxygen.[11]

It is interesting to note that in the oxidation of alcohols with nickel peroxide using chloroform as solvent, no carbonyl compounds are formed, but hexachloroethane has been isolated in appreciable amounts.[11] It is apparent that chloroform is undergoing an oxidative dimerization in the presence of nickel peroxide.

Benzylic alcohols and their α-substituted analogs have been oxidized to give the corresponding carbonyl derivatives.[11] Thus, benzyl alcohol and benzhydrol are oxidized to benzaldehyde and benzophenone, respectively. Because of its mild and selective nature, nickel peroxide has been used in the oxidation of heterocyclic alcohols like furfuryl alcohol to give the corresponding aldehydes.[11,13]

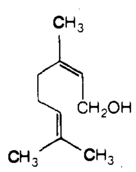
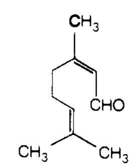
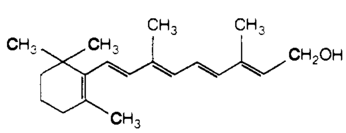
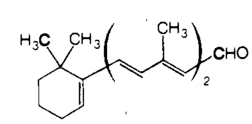
Nickel peroxide is an excellent reagent for the oxidation of allylic alcohols. The simplest α,β-unsaturated alcohol, allyl alcohol,[14,15] is oxidized to acrolein while cinnamyl alcohol[15] is oxidized to cinnamaldehyde. It has been reported that the oxidation of geraniol (**28**) with nickel peroxide gives a 81% yield of citral (**28**a) in 6 hr.[11] Similarly, the oxidation of vitamin A (**29**) with nickel peroxide[11] gives a 83% yield of retinene (**29a**) in 1 hr as compared with the manganese dioxide oxidation[18] which requires 18 hr (Table II).

B. Phenols

Numerous reports have appeared on the oxidation of both natural and synthetic phenolic antioxidants employing a variety of oxidizing agents.[17,18] The products formed in these oxidations depend considerably on the nature of the oxidizing agents and the reaction conditions. Phenol (**30**) is reported to undergo oxidation to give polymeric materials. However, a compound such as *p*-cresol (**31**), on treatment with nickel peroxide in benzene solution or in aqueous alkaline medium, gives rise to a mixture of compounds consisting of the ketone **31a**, the ortho isomer **31b**, and a trimer **31c**, in addition to polymeric materials (Table III).[19] The oxidation of 2,6-xylenol (**35**) in benzene gives rise to poly(2,6-dimethylphenylene ether) (**35b**) and a small amount of 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone (**35a**). However, only the polymeric material **35b** is isolated, if the oxidation is carried out in aqueous sodium hydroxide solution (Table III).[19] In contrast, the manganese dioxide oxidation of 2,6-xylenol gives a mixture of both monomeric and dimeric products.[20] A tail-to-tail dimer, 2,2′,6,6′-tetramethyl-4,4′-biphenol (**35c**), is reported to be formed when a molar excess of xylenol is treated with the oxide. Also, a head-to-tail dimer, 4-(2,6-xylenoxy)-2,6-xylenol (**35d**), is formed in the form of its oligomer which reacts further with the oxide to give a mixture of products consisting of a polymeric material, small amounts of 2,6-xylenol, and the diphenoquinone, **35a** (Scheme I). Similarly, 2,6-dimethylbenzoquinone (**38**a) and 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone (**35a**) are obtained on oxidation of the xylenol trimer (**38**) with nickel peroxide (Table III).[21] 3,5-Disubstituted fuchsones (**41**a) have been obtained on oxidation of the corresponding 3,5-disubstituted-4-hydroxytriphenylmethanes (**41**) (Table III).[22]

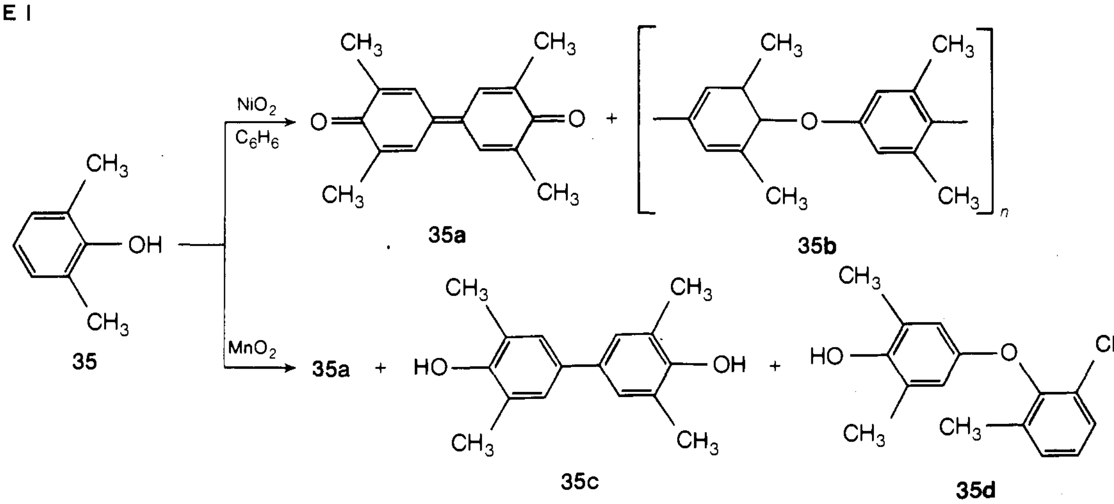
Treatment of *p*-chlorophenol (**32**) with nickel peroxide in benzene yields polymers and oligomers.[23] Similarly, 2,6-dichlorophenol (**37**) gives rise to poly(2,6-dichlorophenylene ether),[24] whereas 2,4,6-trichlorophenol (**39**) gives a mixture of 2,6-dichloro-1,4-benzoquinone (**39a**) and 2-chloro-6-(2,4,6-trichlorophenoxy)-1,4-benzoquinone (**39b**) and 2,6-bis(2,4,6-trichlorophenoxy)-1,4-benzoquinone (**39c**) (Table III).[17] The reactions of o- and *p-tert*-butylphenols (**33** and **34**) with nickel peroxide give polymeric products,[25] while 2,5-di-*tert*-butylphenol (**36**) gives a quantitative yield of 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (**36a**) (Table III).[18] An interesting reaction is observed in the case of the oxidation of catechol (**44**) which is converted by nickel peroxide in basic medium to *cis,cis*-muconic acid (**44a**), arising through a fission of the aromatic ring (Table III).[26]

TABLE II. Oxidation of Alcohols in Organic Solvents

Starting material	Ratio of substrate: NiO_2[a]	Solvent	Temp, °C	Time, hr	Product	Yield, %	Ref
$CH_3(CH_2)_2OH$ (**2**)	1.0	Ether	25	12	CH_3CH_2CHO + $CH_3CH_2CO_2H$	3.2 0.2	11
	1.0	C_6H_6	20	10	CH_3CH_2CHO + $CH_3CH_2CO_2H$	0.6 0.2	11
$(CH_3)_2CHOH$ (**21**)	1.0	Ether	25	35	CH_3COCH_3	4.2	11
$CH_3(CH_2)_3OH$ (**3**)	1.0	Ether	36	15	$CH_3(CH_2)_2CHO$ + $CH_3(CH_2)_2CO_2H$	5.8 0.2	11
$(CH_3)_2CHCH_2OH$ (**4**)	1.0	Ether	36	32	$(CH_3)_2CHCHO$ $(CH_3)_2CHCO_2H$	6.2 0.2	11
$C_6H_5CH_2OH$ (**10**)	1.2	C_6H_6	50	3	C_6H_5CHO	91[b]	11
$C_6H_5CHOHCH_3$ (**22**)	1.2	C_6H_6	50	3	$C_6H_5COCH_3$	51	11
$CH_2=CHCH_2OH$ (**23**)	1.2	C_6H_6	50	...	$CH_2=CHCHO$	79	11
$C_6H_5CH=CHCH_2OH$ (**24**)	1.2	C_6H_6	50	1	$C_6H_5CH=CHCHO$	86	11
$C_6H_5COCHOHC_6H_5$ (**25**)	1.2	C_6H_6	50	5	$C_6H_5COCOC_6H_5$	98	11
$C_6H_5CHOHC_6H_5$ (**26**)	1.2	C_6H_6	50	6	$C_6H_5COC_6H_5$ (**26a**)	98	11
o-$CH_3C_6H_4CH_2OH$ (**11**)	1.0	C_6H_6	50	3	o-$CH_3C_6H_4CHO$	76	11
m-$CH_3C_6H_4CH_2OH$ (**12**)	1.0	C_6H_6	50	3	m-$CH_3C_6H_4CHO$	58	11
p-$CH_3C_6H_4CH_2OH$ (**13**)	1.0	C_6H_6	50	3	p-$CH_3C_6H_4CHO$	65	11
	2.0	C_6H_6	50	3	p-$CH_3C_6H_4CHO$	81	
14	1.2	C_6H_6	30	10	2-Furaldehyde	78	11
$C_6H_5CH_2CH_2OH$ (**27**)	1.2	C_6H_6	80	1	$C_6H_5CH_2CHO$	13	11
$C_6H_5(CH_2)_3OH$ (**9**)	1.2	C_6H_6	50	4	$C_6H_5CH_2CH_2CHO$	12	11
 (28)	1.2	C_6H_6	50	6	 (28a)	81	11
 (29) Vitamin A_1	1.2	Pet. ether	30	1	 (29a) Retinene	83	11

[a] Based on available oxygen. [b] Yield corresponds to the optimum conditions of temperature, time, and ratio of nickel peroxide to the alcohol.

SCHEME I



An unusual oxidative dealkylation has been reported in the case of 2,6-di-*tert*-butyl-4-methylphenol.[25] Treatment of **40** in benzene at room temperature with nickel peroxide gives a mixture of products, consisting of **40a–f** (Scheme II). A similar oxidative dealkylation is reported in the manganese dioxide oxidation of mesitol.[27] The oxidation of 4-cyanocatechol (**45**) is reported to give rise to an *o*-quinone intermediate which has been trapped in presence of 2,3-dimethylbutadiene (**46**) to give the adduct **45a** (Scheme II).[28]

C. Polyhydroxy Compounds

Lead tetraacetate and periodic acid are commonly employed in the cleavage of 1,2-glycols. It has been shown that

TABLE III. Oxidation of Phenols

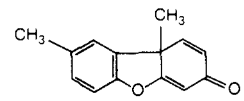
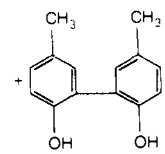
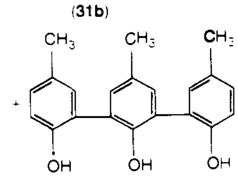
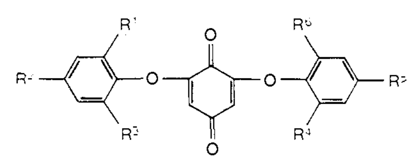
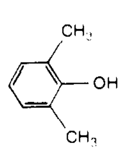
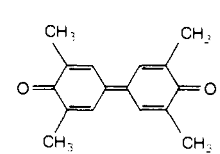
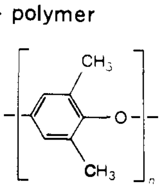
Substrate	NiO_2 used[a]	Solvent	Temp, °C	Time, hr	Product	Yield, %	Ref
C_6H_5OH (**30**)	0.0532	NaOH(aq)	<60	2	Polymer (soluble in C_2H_5OH) + polymer (insoluble in C_2H_5OH)	61 29	19
p-$CH_3C_6H_4OH$ (**31**)	0.0464	NaOH(aq)	<50	5	 (**31a**) (Pummerer's ketone) +  (**31b**) +  (**31c**) + polymer (soluble in CH_3OH) + polymer (insoluble in CH_3OH)	1 27 62	19
31	0.0464	C_6H_6	50	5	Pummerer's ketone + polymer (soluble in $CHCl_3$) + polymer (insoluble in $CHCl_3$)	2 17 48	
p-ClC_6H_4OH (**32**)	0.0464	NaOH(aq)	50	5	Polymer (mol wt 5000)	40	23
32	0.0464	C_6H_6	50	5	 (1) $R^1 = R^3 = R^4 = R^5 = R^6 =$ p-ClC_6H_4O–; $R^2 = Cl$ (2) $R^1 = R^5 = p$-ClC_6H_4O–; $R^2 = Cl$; $R^3 = R^4 = R^6 = H$ (3) $R^1 = R^3 = R^4 = R^6 = H$; $R^2 = R^5 = Cl$ + polymer (mol wt 2000)	38	23
o-$(CH_3)_3CC_6H_4OH$ (**33**)		C_6H_6 or NaOH(aq)	<40		Polymer (soluble in CH_3OH) + polymer (insoluble in CH_3OH) (one-third of oxygen in present as OH)	29 63	25
p-$(CH_3)_3CC_6H_4OH$		C_6H_6 or NaOH(aq)			Polymer		25
 (**35**)	0.0532	C_6H_6	45	3	 (**35a**) + polymer  (**35b**)	2.5	19

TABLE III (Continued)

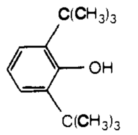
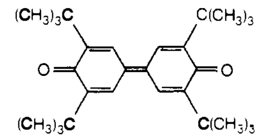
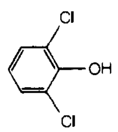
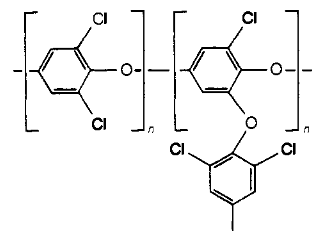
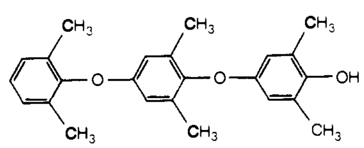
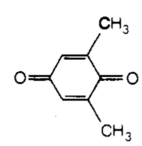
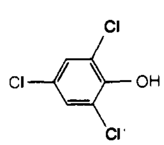
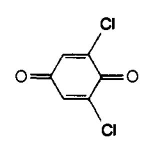
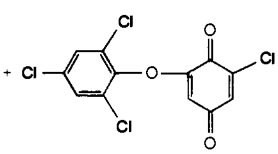
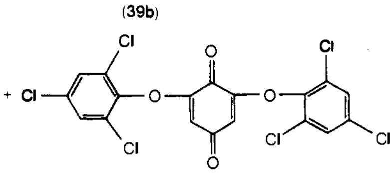
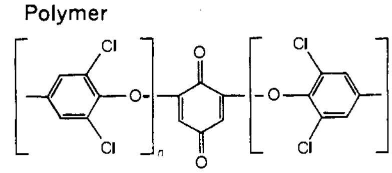
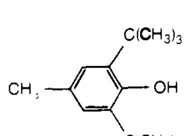
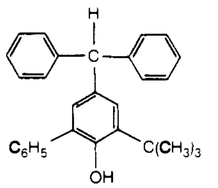
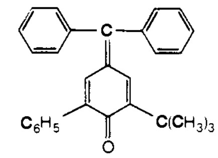
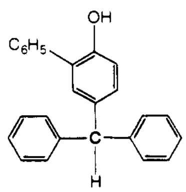
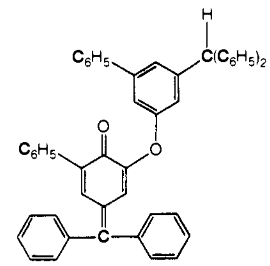
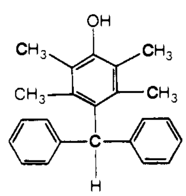
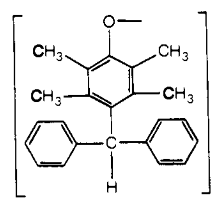
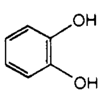
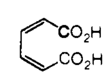
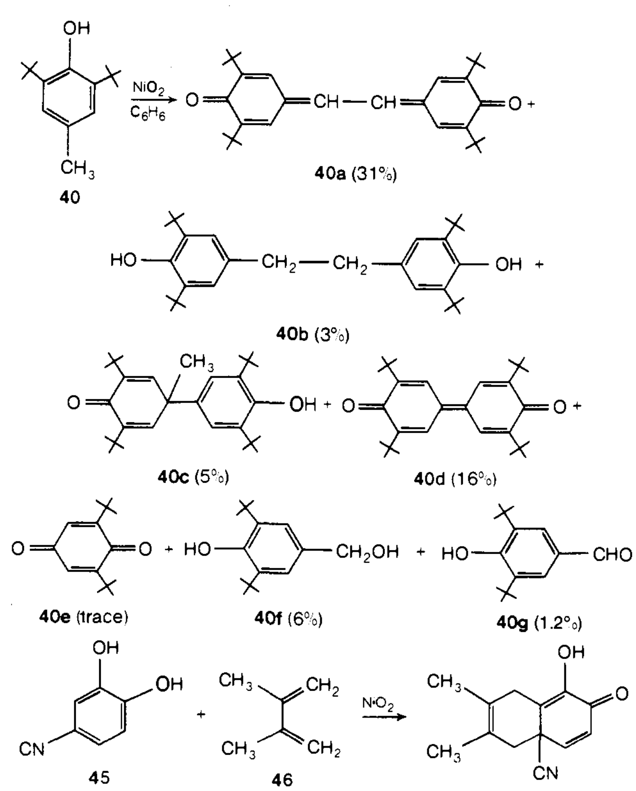
Substrate	NiO_2 used[a]	Solvent	Temp, °C	Time, hr	Product	Yield, %	Ref
35	0.0500	NaOH(aq)		5	Polymer	33	19
 (36)	0.0523	C_6H_6	50	5	 (36a)	99	24
 (37)	0.0523	C_6H_6	<50	10	Polymer (soluble in $CHCl_3$) + polymer (insoluble in $CHCl_3$)  (ratio of chain polymer to branched polymer is 2:1)	2 67	24
37	0.0523	NaOH(aq)	50	5	Polymer (soluble in $CHCl_3$) + polymer (insoluble in $CHCl_3$) (ratio of chain polymer to branched polymer is 2:3)	35 30	24
 (38)		CH_3CO_2H	Reflux	2	 (38a) + 35a	25	21
 (39)		C_6H_6		5	 (39a) +  (39b) +  (39c)	3 5 22	23
39		NaOH(aq)		5	Polymer 	94	23
 (40)	1.5	C_6H_6	40		Mixture of products consisting of **40a–g** (see Scheme II)		25

TABLE III (Continued)

Substrate	NiO$_2$ used[a]	Solvent	Temp, °C	Time, hr	Product	Yield, %	Ref
 (41)		C_6H_6	Room temp	3	 (41a)	94	22
 (42)		C_6H_6	Room temp	3.5	 (42a)	19	22
 (43)		C_6H_6	Room temp	0.5	 (43a)		22
 (44)					 (44a)		26

[a] f = effective oxygen/total NiO$_2$.

SCHEME II



nickel peroxide brings about the oxidation of a wide variety of polyhydroxy compounds such as α-glycols, α-hydroxy acids, α-oxo alcohols, and α-oxo acids (Table IV).[26] It is interesting to note that the oxidation in organic solvents gives oxidative fragmentation products. Thus, for example, phenylethylene glycol on oxidation with nickel peroxide in benzene solution gives benzaldehyde, whereas benzoic acid is formed as the only product when the oxidation is carried out in aqueous medium. Similarly, *cis*-cyclohexanediol gives adipaldehyde in benzene medium. α-Hydroxy acids are reported to undergo oxidative decarboxylation. Mandelic acid, for example, gives benzaldehyde on oxidation with nickel peroxide in benzene solution. In aqueous medium, however, the product formed is benzoic acid.[26]

D. Carbonyl Compounds

Oxidation of aldehydes with nickel peroxide in alkaline medium gives rise to carboxylic acids.[11] Thus, benzaldehyde (**61**) is converted smoothly to benzoic acid (**61a**). Similarly, furfural (**62**) is oxidized to furoic acid (**62**a) (Table V). Aldehydes containing α-hydrogen atoms, on the other hand, are reported to give aldol condensation products and this may be due to the alkalinity of the reaction mixture.

An interesting oxidative dimerization has been reported in the nickel peroxide oxidation of isobutyraldehyde (**74**) leading to the formation of a mixture of both C–C and C–O dimers **74a** and **74b**, respectively (Table V).[29] The same oxidative dimerization has been observed with manganese dioxide also.[29] Similar oxidative dimerizations have been observed in the case of 2-methylbutyraldehyde (**75**) and 2-ethylbutyraldehyde (**76**) (Table V).

TABLE IV. Oxidation of Polyhydroxy Compounds

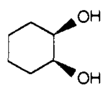
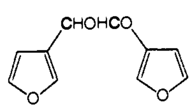
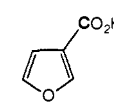
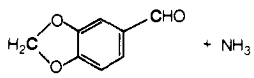
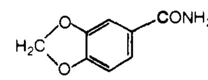
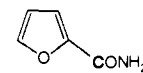
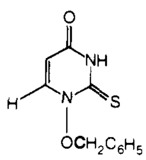
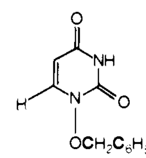
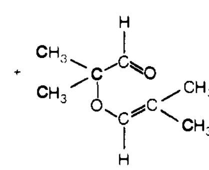
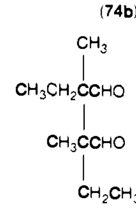
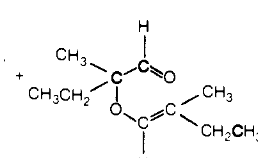
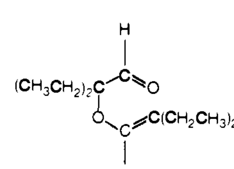
Substrate	Ratio of substrate: NiO_2	Solvent	Temp, °C	Time, hr	Product	Yield, %	Ref
$C_6H_5CHOHCHOHC_6H_5$ (**47**)	1.1	C_6H_6	50	1	C_6H_5CHO	85	26
	1.1	C_6H_6	50	5	C_6H_5CHO	81	26
	1.1	Ether	35	0.5	C_6H_5CHO	90	26
	1.1	NaOH(aq)	50	8	$C_6H_5CO_2H$	97	26
$C_6H_5CHOHCH_2OH$ (**48**)	1.1	C_6H_6	50	2	C_6H_5CHO	90	26
		NaOH(aq)	50	5	$C_6H_5CO_2H + CO_2$	92	26
$(CH_3)_2C(OH)—C(OH)(CH_3)_2$ (**49**)	1.1	C_6H_6	70	3	CH_3COCH_3	61	26
	1.1	C_6H_6	30	81	CH_3COCH_3	70	26
		NaOH(aq)	30	24	$CH_3COCH_3 + CO_2$	10	26
$CH_3CHOHCHOHCH_3$ (**50**)	1.1	C_6H_6	50	5	CH_3CHO	30	26
		NaOH(aq)	50	7	CH_3CO_2H	90	26
 (**51**)	1.1	C_6H_6	50	5	$OHC(CH_2)_4CHO$	17	26
$C_6H_5CHOHCO_2H$ (**52**)	1.1	C_6H_6	50	1.5	C_6H_5CHO	78	26
	1.1	H_2O	10	7	C_6H_5CHO	51	26
$C_6H_5CHOHCO_2CH_3$ (**53**)	1.1	C_6H_6	50	11	$C_6H_5COCO_2CH_3$	63	26
$CH_3CHOHCO_2H$ (**54**)	1.1	H_2O	50	7	CH_3CHO	13	26
$CH_3CHOHCO_2CH_2CH_3$ (**55**)	1.1	C_6H_6			No reaction		26
$C_6H_5CHOHCOC_6H_5$ (**56**)		NaOH(aq)	50	5	$C_6H_5CO_2H$	99	26
		NaOH(aq)	80	8	$C_6H_5CO_2H$	95	26
 (57)		NaOH(aq)	30	5		91	26
$CH_3CHOHCOCH_3$ (**58**)		NaOH(aq)	50	5	CH_3CO_2H	67	26
$CH_3(CH_2)_2CHOHCO(CH_2)_2CH_3$ (**59**)		NaOH(aq)	50	5	$CH_3(CH_2)_2CO_2H$	68	26
$C_6H_5CHOHCO_2H$ (**52**)		NaOH(aq)	50	5	$C_6H_5CO_2H$	90	26
$CH_3CHOHCO_2H$ (**48**)		NaOH(aq)	50	7	CH_3CO_2H	92	26
CH_3COCO_2H (**54**)		NaOH(aq)	50	10	CH_3CO_2H	75	26
$C_6H_5COCO_2H$ (**60**)		NaOH(aq)	50	3	$C_6H_5CO_2H$	98	26

TABLE V. Oxidation of Carbonyl Compounds

Substrate	Ratio of substrate: NiO_2	Solvent	Temp, °C	Time, hr	Product	Yield, %	Ref
C_6H_5CHO (**61**)					$C_6H_5CO_2H$ (**61a**)		11
2-Furaldehyde (**62**)					2-Furoic acid (**62a**)		11
p-ClC_6H_4CHO (**63**) + NH_3	1.3	Ether	−25	4	p-$ClC_6H_4CONH_2$ +	92	31
					p-$ClC_6H_4CO_2H$	5	
	1.3	Ether	−20	4	p-$ClC_6H_4CONH_2$ +	89	31
					p-$ClC_6H_4CO_2H$	9	
	1.3	Ether	0	4	p-$ClC_6H_4CONH_2$ +	72	31
					p-$ClC_6H_4CO_2H$	17	
63 + NH_3	1.3	Ether	10	4	p-$ClC_6H_4CONH_2$ +	57	31
					p-$ClC_6H_4CO_2H$ +	29	
					p-ClC_6H_4CN	5	
63 + NH_3	1.3	Ether	20	4	p-$ClC_6H_4CONH_2$ +	37	31
					p-$ClC_6H_4CO_2H$ +	28	
					p-ClC_6H_4CN +	14	
					p-ClC_6H_4CHO	16	
63 + NH_3	1.3	Ether	35	4	p-$ClC_6H_4CONH_2$ +	5	31
					p-$ClC_6H_4CO_2H$ +	15	
					p-ClC_6H_4CN +	34	
					p-ClC_6H_4CHO	42	
63 + NH_3	1.3	C_6H_6	80	4	p-$ClC_6H_4CONH_2$ +	9	31
					p-$ClC_6H_4CO_2H$ +	26	
					p-ClC_6H_4CN +	51	
					p-ClC_6H_4CHO	10	
o-ClC_6H_4CHO (**64**) + NH_3	1.3	Ether	−20	4	o-$ClC_6H_4CONH_2$	77	31

TABLE V (Continued)

Substrate	Ratio of substrate: NiO_2	Solvent	Temp, °C	Time, hr	Product	Yield, %	Ref
61 + NH_3	1.3	Ether	−20	4	$C_6H_5CONH_2$	89	31
m-$NO_2C_6H_4CHO$ (**65**) + NH_3	1.3	Ether	−20	4	*m*-$NO_2C_6H_4CONH_2$	88	31
p-CNC_6H_4CHO (**66**) + NH_3	1.3	Ether	−20	4	*p*-$CNC_6H_4CONH_2$	77	31
p-$(CH_3)_2NC_6H_4CHO$ (**67**) + NH_3	1.3	Ether	−20	4	*p*-$(CH_3)_2NC_6H_4CONH_2$	58	31
p-$CH_3OC_6H_4CHO$ (**68**) + NH_3	1.3	Ether	−20	4	*p*-$CH_3OC_6H_4CONH_2$.	88	31
p-$CH_3C_6H_4CHO$ (**69**) + NH_3	1.3	Ether	−20	4	*p*-$CH_3C_6H_4CONH_2$	87	31
 + NH_3 (70)	1.3	Ether	−20	4		86	31
$C_6H_5CH{=}CHCHO$ (**71**) + NH_3	1.3	Ether	−20	4	$C_6H_5CH{=}CHCONH_2$	85	31
62 + NH_3	1.3	Ether	−20	4	 (72)	86	31
 (**20a**)		NaOH(aq)	Room temp	18	 (**19a**)	54	12
$(CH_3)_2CHCHO$ (**74**)		THF			$(CH_3)_2CCHO$ | $(CH_3)_2CCHO$ (**74a**)		29
					+  (**74b**)		
$CH_3(CH_3CH_2)CHCHO$ (**75**)		THF			 (**75a**)		29
					+  (**75b**)		
$(CH_3CH_2)_2CHCHO$ (**76**)		Dioxane–pyridine			$(CH_3CH_2)_2CCHO$ | $(CH_3CH_2)_2CCHO$ (**76a**)		29
					 (**76b**)		

It has been reported that the oxidation of aldehydes with lead tetraacetate, in presence of ammonia, gives rise to nitriles.[30] Nakagawa and coworkers have shown that alcohols and aldehydes can be directly converted to the corresponding amides, if the nickel peroxide oxidation is carried out in an ether solution containing ammonia at −20°. At higher temperatures, however, the yields of the amides are lower and the corresponding nitriles are formed as major products. Corey and coworkers[32] have recently reported that manganese dioxide in presence of sodium cyanide oxidizes aldehydes to the corresponding acids or esters, when the reaction is carried out in acetic acid or alcohol, respectively. Cyanohydrins which are supposed to be the intermediate in these reactions get oxidized to the corresponding acyl cyanides. These acyl cyanides are subsequently transformed to either acids or esters in presence of the appropriate solvents.

E. Amines

1. Primary Amines

Aliphatic and aromatic primary amines are oxidized by nickel peroxide,[33] and two modes of reactions have been observed in these cases (Table VI). Aromatic primary amines are readily converted to the corresponding symmetrical azo compounds. Aliphatic primary amines, on the other hand, give rise to the corresponding nitriles. Thus, benzylamine, furfurylamine, and *n*-heptylamine are oxidized to the corresponding nitriles by nickel peroxide.[33] Phenylethylamine (**105**), under similar conditions, is oxidized to *trans*-α,α'-stilbenedicarbonitrile (**105a**) (Table VI).[4]

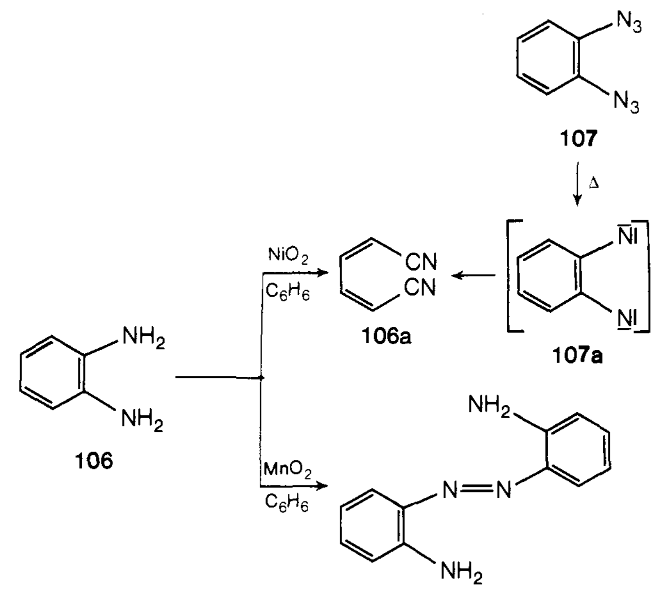
A detailed study of the oxidation of aromatic primary amines with manganese dioxide has been made by Barakat and coworkers[34] who have found that nitroanilines are not oxidized readily to the corresponding azo compounds unlike other aromatic amines. However, the oxidation with nickel peroxide leads to the formation of azo compounds, without the formation of resinous materials.[33] It has been observed that in the oxidation of chloroanilines, anisidines, and toluidines, only poor yields of the azo compounds are formed,[33] as compared with the manganese dioxide oxidation of these amines.

Nickel peroxide oxidation of o-phenylenediamine (**106**) results in the cleavage of the aromatic ring to give *cis,cis*-1,4-dicyano-1,3-butadiene (**106a**) which has been characterized through its Diels–Alder adduct.[35] In contrast, the oxidation of o-phenylenediamine (**106**) with manganese dioxide gives 2,2′-diaminoazobenzene.[36] Similarly, the oxidation of 1,2-diaminonaphthalene (**119**) gives the corresponding dinitrile (**119a**). However, the analogous dinitrile could not be isolated from the nickel peroxide oxidation of 2,3-diaminonaphthalene (**120**).[35] The formation of the dinitrile **106a** in the oxidation of o-phenylenediamine (**106**) may be proceeding through the dinitrene intermediate (**107a**), which is a reported intermediate in the thermal decomposition of 1,2-diazidobenzene (**107**) (Scheme III).[37]

2. Secondary Amines

A secondary amine like diphenylamine (**122**) on oxidation with nickel peroxide yields tetraphenylhydrazine (**122a**) and polydiphenylamines (**122b**) in which each nitrogen atom is bonded to the para position of another diphenylamine molecule.[38] 4-Methyldiphenylamine (**123**) under similar conditions gives the hydrazine derivative (**123a**) and *N*-(*p*-tolyl)-*p*-benzoquinone monoimine (**123b**) (Table VII). Similarly, the oxidation of carbazole (**124**) gives 9,9′-bicarbazole (**124a**), 9,3′,9′,9″-tercarbazole (**124b**) and some polymeric materials.[39] Secondary amines like *N*-methylbenzylamine and *N*-methylpiperonylamine are reported[40] to give rise to the corresponding imines when oxidized with manganese dioxide, whereas products like formaldehyde, acetaldehyde, and azobenzene are formed in the oxidation of *N*-ethylaniline.[41]

SCHEME III



Manganese dioxide oxidation of *N*-benzylanilines has been reported to give rise to the corresponding benzylideneanilines.[42] On the contrary, nickel peroxide oxidation gives two types of oxidative dimers, in addition to benzylideneanilines.[43] Thus, *N*-benzylaniline (**134**) gives benzylideneaniline (**134a**) and *N*-benzyl-*N*-phenyl-*N*′-benzylidene-*p*-phenylenediamine (**134b**) (Table VII).[43] Similarly, *N*-benzyl-o-toluidine (**135**) gives benzylidene-o-toluidine and *N*-benzyl-*N*-(o-tolyl)-*N*′-benzylidene-2-methyl-*p*-phenylenediamine (**135a**) and the corresponding Schiff's base (**135b**). On the other hand, the oxidation of *N*-benzyl-*p*-toluidine (**136**) gives *N,N*′-dibenzyl-*N,N*′-di(*p*-tolyl)hydrazine (**136a**) and benzylidine-*p*-toluidine (**136b**).[43] Likewise, other *N*-benzylanilines **137, 138,** and **139** give the corresponding hydrazine derivatives and Schiff's bases (Table VII). The oxidation of dibenzylamine (**140**) yields a mixture of *N*-benzylidenebenzylamine (**140a**), benzaldehyde (**140b**), and benzonitrile (**140c**).[43]

Tertiary amines have so far not been oxidized by nickel peroxide, whereas numerous reports have appeared in the literature which deal with the oxidation of these compounds using manganese dioxide.[44]

F. Compounds Containing Activated C–H Bonds

Nickel peroxide oxidation of hydrocarbons containing activated C–H bonds is extremely slow under mild conditions, while under drastic conditions these hydrocarbons are oxidized to the corresponding carboxylic acids.[4] In the oxidation of toluene, for example, further addition of nickel peroxide after 8 hr results in an increased yield of benzoic acid. Manganese dioxide, on the other hand, does not oxidize simple hydrocarbons like toluene, xylene, and ethylbenzene. In the cases of cumene and bibenzyl, the yield of benzoic acid is low when compared to the nickel peroxide case. Thus, it appears that the oxidizing power of nickel peroxide is greater than that of manganese dioxide.

Diphenylmethane (**141**), on oxidation with nickel peroxide in refluxing benzene,[4] gives a 56% yield of benzophenone (**141a**), whereas in the absence of any solvent and around 110°, a 79% yield of benzophenone is obtained.[43] Similarly, fluorene (**142**) gives fluorenone (**142a**) on treatment with nickel peroxide (Table VIII). Pratt and Suskind[45] have studied

TABLE VI. Oxidation of Primary Amines

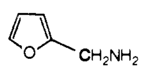
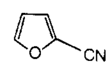
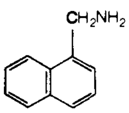
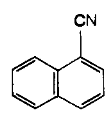
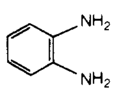
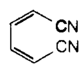
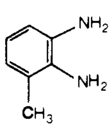
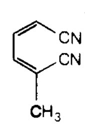
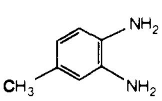
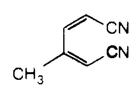
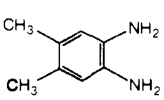
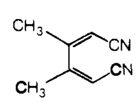
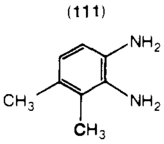
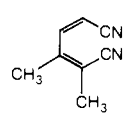
Substrate	Ratio of substrate: NiO_2	Solvent	Temp, °C	Time, hr	Product	Yield, %	Ref
$C_6H_5NH_2$ (**77**)	1.5	C_6H_6	80	6	$C_6H_5N{=}NC_6H_5$	44	33
o-$NO_2C_6H_4NH_2$ (**78**)	1.5	C_6H_6	80	6	RN=NR	20	33
m-$NO_2C_6H_4NH_2$ (**79**)	1.5	C_6H_6	80	6	RN=NR	41	33
p-$NO_2C_6H_4NH_2$ (**80**)	1.5	C_6H_6	80	6	RN=NR	64	33
o-$ClC_6H_4NH_2$ (**81**)	1.5	C_6H_6	80	6	RN=NR	20	33
m-$ClC_6H_4NH_2$ (**82**)	1.5	C_6H_6	21	7	RN=NR	21	33
p-$ClC_6H_4NH_2$ (**83**)	1.5	C_6H_6	80	6	RN=NR	28	33
o-$CH_3OC_6H_4NH_2$ (**84**)	1.5	C_6H_6	80	6	RN=NR	12	33
m-$CH_3OC_6H_4NH_2$ (**85**)	1.5	C_6H_6	80	6	RN=NR	14	33
p-$CH_3OC_6H_4NH_2$ (**86**)	1.5	C_6H_6	80	6	RN=NR	25	33
o-$CH_3C_6H_4NH_2$ (**87**)	1.5	C_6H_6	80	6	RN=NR	Trace	33
m-$CH_3C_6H_4NH_2$ (**88**)	1.5	C_6H_6	22	7	RN=NR	18	33
p-$CH_3C_6H_4NH_2$ (**89**)	1.5	C_6H_6	22	7	RN=NR	25	33
m-$CH_3COC_6H_4NH_2$ (**90**)	1.5	C_6H_6	22	7	RN=NR	33	33
$C_6H_5CH_2NH_2$ (**91**)	1.5	C_6H_6	60	1.5	C_6H_5CN	79	33
p-$CH_3OC_6H_4CH_2NH_2$ (**91a**)	1.5	C_6H_6	60	1.5	*p*-$CH_3OC_6H_4CN$	88	33
p-$CH_3C_6H_4CH_2NH_2$ (**92**)	1.5	C_6H_6	60	1.5	*p*-$CH_3C_6H_4CN$	75	33
m-$CH_3C_6H_4CH_2NH_2$ (**93**)	1.5	C_6H_6	60	1.5	*m*-$CH_3C_6H_4CN$	79	33
o-$CH_3C_6H_4CH_2NH_2$ (**94**)	1.5	C_6H_6	60	1.5	*o*-$CH_3C_6H_4CN$	77	33
p-$NO_2C_6H_4CH_2NH_2$ (**95**)	1.5	C_6H_6	60	1.5	*p*-$NO_2C_6H_4CN$	56	33
o-$NO_2C_6H_4CH_2NH_2$ (**96**)	1.5	C_6H_6	60	1.5	*o*-$NO_2C_6H_4CN$	87	33
p-$ClC_6H_4CH_2NH_2$ (**97**)	1.5	C_6H_6	60	1.5	*p*-ClC_6H_4CN	73	33
m-$ClC_6H_4CH_2NH_2$ (**98**)	1.5	C_6H_6	60	1.5	*m*-ClC_6H_4CN	70	
o-$ClC_6H_4CH_2NH_2$ (**99**)	1.5	C_6H_6	60	1.5	*o*-ClC_6H_4CN	87	
 (**100**)	1.5	C_6H_6	5	0.5		63	
 (**101**)	1.5	C_6H_6	60	1.5		91	
$CH_3(CH_2)_4CH_2NH_2$ (**102**)	1.5	C_6H_6	80	1.5	$CH_3(CH_2)_4CN$	73	
$CH_3(CH_2)_{10}CH_2NH_2$ (**103**)	1.5	C_6H_6	80	1.5	$CH_3(CH_2)_{10}CN$	81	
$CH_3(CH_2)_6CH_2NH_2$ (**104**)	1.5	C_6H_6	80	1.5	$CH_3(CH_2)_6CN$	96	
$C_6H_5CH_2CH_2NH_2$ (**105**)					$C_6H_5(NC)C{=}C(CN)C_6H_5$ (**105a**)		4
 (**106**)	2.0	C_6H_6	Room temp		 (**106a**)	14	35
 (**109**)	2.0	Ether	Room temp			8	35
 (110)	2.0	Ether	Room temp			9	35
 (111)	2.0	Ether	Room temp			13	35
 (112)	2.0	Ether	Room temp			6	35

TABLE VI (Continued)

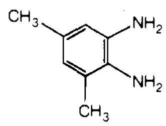
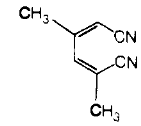
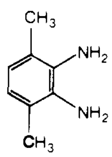
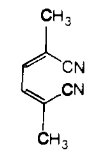
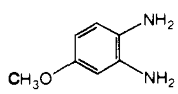
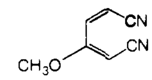
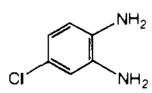
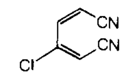
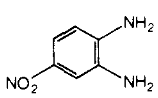
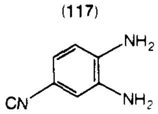
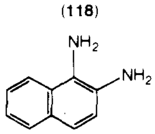
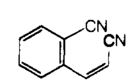
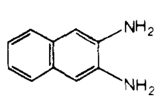
Substrate	Ratio of substrate: NiO_2	Solvent	Temp, °C	Time, hr	Product	Yield, %	Ref
 (113)	2.0	Ether	Room temp			7	35
 (114)	2.0	Ether	Room temp			7	35
 (115)	2.0	Ether	Room temp			12	35
 (116)	2.0	Ether	Room temp			6	35
 (117)	2.0	Ether	Room temp		No reaction		35
 (118)	2.0	Ether	Room temp		No reaction		35
 (119)	2.0	C_6H_6	Room temp		 (119a)	26	35
 (120)	2.0	Ether	Room temp		No reaction		35
$H_2N(CH_2)_6NH_2$ **(121)**	1.5	C_6H_6	80	1.5	$NC(CH_2)_4CN$	23	

TABLE VII. Oxidation of Secondary Amines

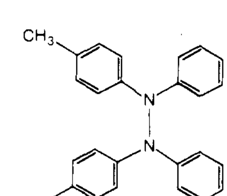
Substrate	Ratio of substrate: NiO_2	Sol-vent	Temp, °C	Time, hr	Product	Yield, %	Ref
$(C_6H_5)_2NH$ **(122)**	1.3	C_6H_6		4	$N(C_6H_5)_2$ | **(122a)** $N(C_6H_5)_2$	52	38
					+ $[(C_6H_5)_2N-]_n$ **(122b)**	12	
p-$CH_3C_6H_4NHC_6H_5$ **(123)**	1.3	C_6H_6		4	 (123a)	46	38

TABLE VII (Continued)

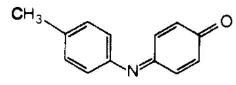
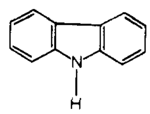
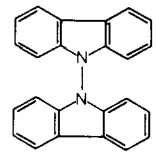
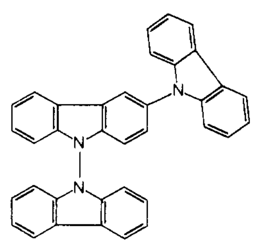
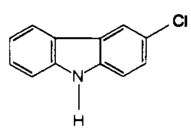
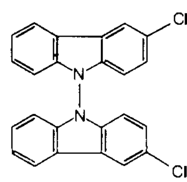
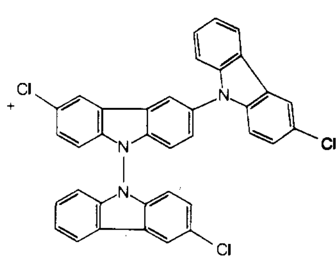
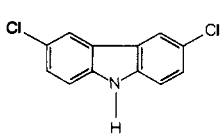
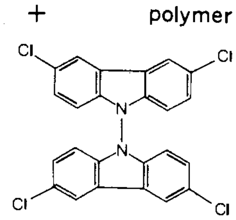
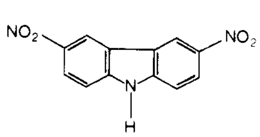
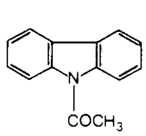
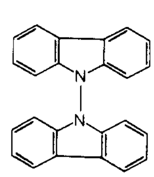
Substrate	Ratio of substrate: NiO_2	Sol- vent	Temp, °C	Time, hr	Product	Yield, %	Ref
					+  (123b)	23	
 (124)	1.5	Ether			 (124a)		39
					+ polymer		
					 (124b)		
 (125)	1.5	Ether			 (125a)	43	39
					+  (125b)	14	39
					+ polymer	27	
 (126)	1.5	Ether			 (126a)	96	39
 (127)	1.5	Ether			Starting material	97	39
 (128)	1.5	Ether			 (128a)	0.8	39

TABLE VII (Continued)

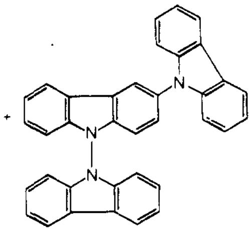
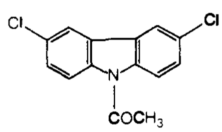
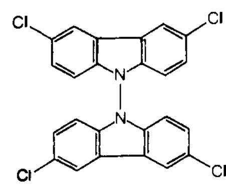
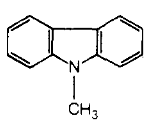
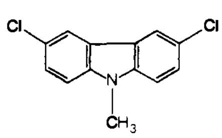
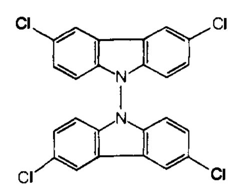
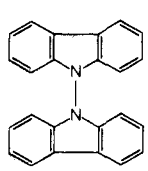
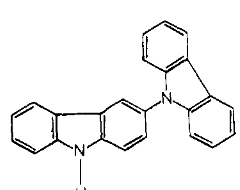
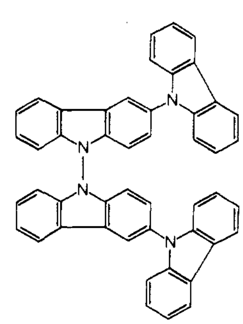
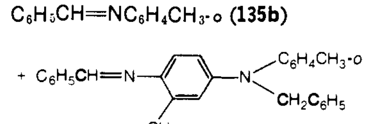
Substrate	Ratio of substrate: NiO_2	Sol-vent	Temp, °C	Time, hr	Product	Yield, %	Ref
					+  (128b)	0.8	
					+ starting material	75	
 (129)	1.5	Ether			 (129a)	57	39
					+ starting material	29	
 (130)	1.5	Ether			Starting material	94	39
 (131)	1.5	Ether			 (131a)	1	39
					+ starting material	65	
 (132)	1.5	Ether			Starting material	96	39
 (133)	1.5	Ether			 (133a)		39
$C_6H_5CH_2NHC_6H_5$ (134)		C_6H_6	22	4	p-$(C_6H_5CH{=}N)C_6H_4N(C_6H_5)CH_2C_6H_5$ (134b)	45	43
					+ $C_6H_5CH{=}NC_6H_5$	5	
					$C_6H_5CH{=}NC_6H_4CH_3$-o (135b)	3	
$C_6H_5CH_2NHC_6H_4CH_3$-o (135)		C_6H_6	Room temp	5	 (135a)	45	43

TABLE VII (Continued)

Substrate	Ratio of substrate: NiO_2	Sol-vent	Temp, °C	Time, hr	Product	Yield, %	Ref
$C_6H_5CH_2NHC_6H_4CH_3$-*p* (**136**)		C_6H_6	Room temp	2	*p*-$CH_3C_6H_4$ $CH_2C_6H_5$ N—N (**136a**) $C_6H_5CH_2$ $C_6H_4CH_3$-*p*	64	43
					+ $C_6H_5CH{=}NC_6H_4CH_3$ (**136b**)	24	
$C_6H_5CH_2NHC_6H_4OCH_3$-*p* (**137**)		C_6H_6	Room temp	2	*p*-$CH_3OC_6H_4$ $CH_2C_6H_5$ N—N (**137a**) $C_6H_5CH_2$ $C_6H_4OCH_3$-*p*		43
					+ $C_6H_5CH{=}NC_6H_4OCH_3$-*p* (**137b**)	37	
$C_6H_5CH_2NHC_6H_4Cl$-*p* (**138**)		C_6H_6	Room temp	4	*p*-ClC_6H_4 $CH_2C_6H_5$ N—N (**138a**) $C_6H_5CH_2$ C_6H_4Cl-*p*	20	43
					+ $C_6H_5CH{=}NC_6H_4Cl$-*p* (**138b**)	17	
$C_6H_5CH_2NHC_6H_4CH_3$-*m* (**139**)		C_6H_6	Room temp	4	*m*-$CH_3C_6H_4$ $CH_2C_6H_5$ N—N (**139a**) $C_6H_5CH_2$ $C_6H_4CH_3$-*m*	39	43
					+ $C_6H_5CH{=}NC_6H_4CH_3$-*m* (**139b**)	28	
		C_6H_6	Room temp	6	**139a**	48	43
					+ **139b**	36	
$C_6H_5CH_2NHCH_2C_6H_5$ (**140**)		C_6H_6	80	6	$C_6H_5CH_2N{=}CHC_6H_5$ (**140a**)	43	43
					+ C_6H_5CHO (**140b**)	48	
					+ C_6H_5CN (**140c**)	40	

TABLE VIII. Oxidation of Compounds Containing Activated C-H Bonds

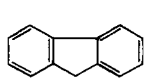
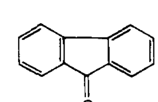
Substrate	Ratio of substrate: NiO_2	Solvent	Temp, °C	Time, hr	Product	Yield, %	Ref
$C_6H_5CH_2C_6H_5$ (**141**)		C_6H_6	80		$C_6H_5COC_6H_5$ (**141a**)	56	4
		No solv	110	5	$C_6H_5COC_6H_5$	79	43
 (**142**)		No solv	110	5	 (**142a**)	66	43
$(C_6H_5)_3CH$ (**143**)		C_6H_6	55	10	$(C_6H_5)_3COH$ (**143a**)	2	5
$(C_6H_5)_3CC(C_6H_5)_3$ (**144**)	0.6	C_6H_6	Room temp	2	$(C_6H_5)_3COH$	90	5
$C_6H_5N{=}NC(C_6H_5)_3$ (**145**)	1.1	C_6H_6	65		$(C_6H_5)_3COH$	56	5
					+ $HC(C_6H_5)_3$	48	
					+ $C_6H_5C_6H_5$	79	
$C_6H_5CH_2CN$ (**146**)		C_6H_6	27	4	C_6H_5 C_6H_5 CHCH (*meso*) (**147**) NC CN	9	46
					+ $C_6H_5CO_2H$	28	
					+ polymer (soluble in ether) Containing only N	11	
					+ polymer (insoluble in ether) Containing N and O	5	
					+ starting material	57	
146		C_6H_6	40	4	$C_6H_5CO_2H$	6	46

TABLE VIII (Continued)

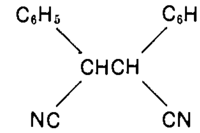
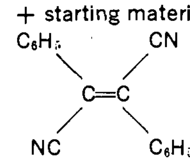
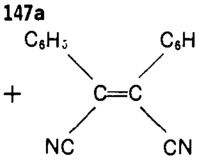
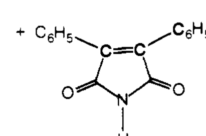
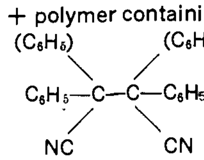
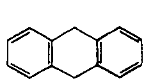
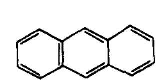
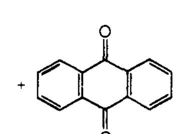
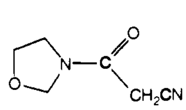
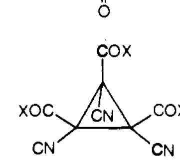
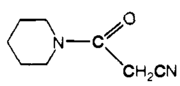
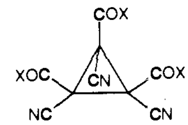
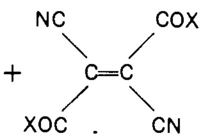
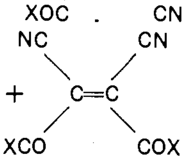
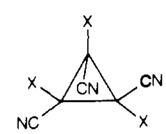
Substrate	Ratio of substrate: NiO_2	Solvent	Temp, °C	Time, hr	Product	Yield, %	Ref
					 (*meso*) **(147)**	7	
					+ polymer (soluble in ether)	24	
					+ polymer (insoluble in ether)	39	
					+ starting material	11	
146		C_6H_6	60	4	 **(147a)**	6	46
					+ $C_6H_5CO_2H$	1.4	
					+ polymer (soluble in ether)	39	
					+ polymer (insoluble in ether)	51	
146		C_6H_6	80	4	$C_6H_5CO_2H$	0.6	46
					+ **147a**		
					+ polymer (soluble in ether)	19	
					+ polymer (insoluble in ether)	52	
					+ starting material	4	
147		C_6H_6	40	4	**147a**	5	46
					+  **(147b)**	3	
					+ $C_6H_5CO_2H$	1.4	
					+ polymer	21	
					+ starting material		
147		C_6H_6	60	4	$C_6H_5CO_2H$	0.3	46
					+ **147a**	36	
					+ **147b**	8	
					+ polymer	4	
					+ starting material	1	
147		C_6H_6	80	4	$C_6H_5CO_2H$	1	46
					+ **147a**	27	
					+ **147b**	26	
					+ 	9	
					+ polymer containing N and O	9	
$(C_6H_5)_2CHCN$ **(148)**		C_6H_6	25	1	 **(148a)**	99	4, 5
 (149)		C_6H_6	Room temp	3		Major	5
					+ 	Minor	
 (150)	2.0	C_6H_6	Room temp	5 min	 (150a) (X = oxazolidinyl)	43	44

TABLE VIII (Continued)

Substrate	Ratio of substrate: NiO_2	Solvent	Temp, °C	Time, hr	Product	Yield, %	Ref
 (151)	3.0	C_6H_6	Room temp	30 min	 (151a) (X = piperidino) +  (151b) +  (151c)		44
151	...[a]	C_6H_6	Room temp	30 min	151a + 151b	10 10	44
151	...[b]	C_6H_6	Room temp	30 min	151b + 151c	8 4	44
$NCCH_2CO_2CH_2CH_3$ (152)	3.0	C_6H_6	Room temp	2	 X = $CO_2CH_2CH_3$	6	44

[a] Available oxygen, 2.7 mg-atoms/g of NiO_2. [b] Available oxygen, 2.3 mg-atoms/g of NiO_2.

the oxidation of several diarylmethanes with manganese dioxide, and they have shown that different products are formed in these reactions, depending on the reaction conditions. Thus, diphenylmethane on oxidation in a mixture of refluxing benzene and biphenyl gives tetraphenylethane as the only product, whereas, in the absence of any solvent around 120°, benzophenone is formed in appreciable amounts.[45] Similarly, fluorene gives 9,9′-bifluorenylidene on treatment with manganese dioxide.[45]

Tetraphenylsuccinonitrile is formed in quantitative amounts on treatment of diphenylacetonitrile with nickel peroxide for 1 hr.[4] The oxidation of phenylacetonitrile (**146**) gives a mixture of products consisting of *meso*-2,3-diphenylsuccinonitrile (**147**), *trans*-dicyanostilbene (**147a**), and benzoic acid along with polymeric materials.[48] The oxidation of *meso*-2,3-diphenylsuccinonitrile (**147**) itself leads to the same mixture of cyanostilbenes (**147a** and **147b**) (Table VIII) together with polymeric materials.[48] On the other hand, active manganese dioxide does not oxidize phenylacetonitrile.[48] Oxidation of triphenylmethane (**143**) with nickel peroxide results in the formation of triphenylcarbinol (**143a**) in poor yields.[5] In contrast, 9,10-dihydroanthracene (**149**) is readily oxidized to anthracene on treatment with nickel peroxide. In addition, a small amount of anthraquinone is also formed in the reaction. Tetraphenylsuccinonitrile (**148a**) is formed in quantitative amounts on treatment of diphenylacetonitrile (**148**) with nickel peroxide for 1 hr.[4] An interesting oxidative coupling reaction has been observed on treatment of *N*-(cyanoacetyl)-4,4-dimethyloxazolidine (**150**) with nickel peroxide, resulting in the formation of the cyclopropane derivative (**150a**) (Table VIII).[44] In contrast, *N*-(cyanoacetyl)piperidine (**151**) gives the cyclopropane derivative (**151a**) and two isomeric dimers (**151b** and **151c**), respectively (Table VIII).[44]

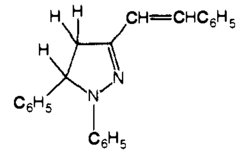
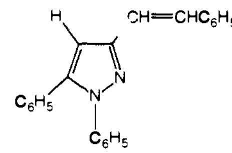
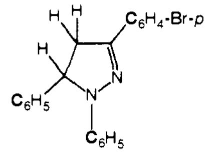
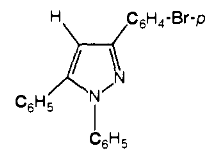
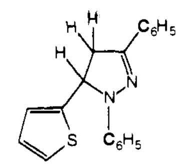
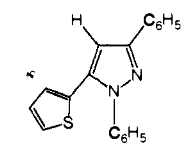
G. Heterocycles

Nickel peroxide has been used in the dehydrogenation of few heterocycles.[43] Thus, it has been shown that pyrazolines are converted to pyrazoles in excellent yields on treatment with nickel peroxide. Table IX summarizes the results of some of these studies. Similarly, the dehydrogenation of a cyclic hydrazide to give the corresponding cyclic azo compound has been recently observed.[89]

H. Telomerization and Polymerization Reactions

It has been observed that chloroform is converted to hexachloroethane in presence of nickel peroxide, and the reaction is assumed to proceed through trichloromethyl radicals.[11] Such halogenated alkyl radicals formed in similar oxidation reactions have been used in different telomerization and polymerization reactions.[47,48] Thus, it has been observed that in the reaction of 1-octene with bromoform in presence of nickel peroxide, a 1:1 addition product is formed. However, styrene in the presence of chloroform yields products with a higher degree of polymerization. Under analogous conditions, tetrabromomethane gives a 1:1 addition product in nearly quantitative yields. Tanaka and coworkers[49] have applied this type of telomerization reaction to the synthesis of terpenes, α-terpineol, linalool, myrcene, and dipentene by treating isoprene and prenyl chloride with nickel peroxide as initiator. In a reaction similar to the telomerization reaction, a mixture of 2,2,2-trichloro-1,1,1-tribromoethane, hexachloroethane, hex-

TABLE IX. Oxidation of Heterocycles

Substrate	Ratio of substrate: NiO_2	Solvent	Temp, °C	Time, hr	Product	Yield, %	Ref
 (153)		C_6H_6	80	3		76	43
 (154)		C_6H_6	80	3		95	43
 (155)		C_6H_6	80	3		93	43

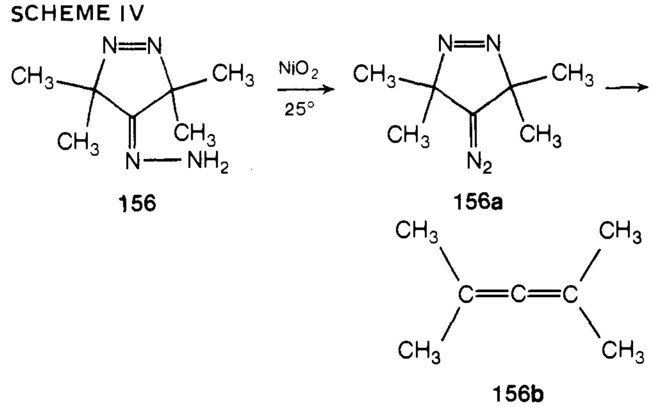
abromoethane, and tetrabromoethylene is formed on treatment of a mixture of chloroform, bromoform, and carbon tetrachloride with nickel peroxide.[50] Nickel peroxide has also been employed in the synthesis of stereospecific polymers.[51–60]

I. Hydrazones and Phenylhydrazones

Several hydrazones of aldehydes and ketones have been oxidized using nickel peroxide. Nickel peroxide oxidation[81] of benzophenone hydrazone, for example, yields diphenyldiazomethane in nearly quantitative amounts, whereas the same reaction with manganese dioxide[62] gives diphenyldiazomethane contaminated with small amounts of diphenylketazine. Similarly, other aldehyde and ketone hydrazones such as benzaldehyde hydrazone, fluorenone hydrazone, diethyl mesoxalate hydrazone, and acetone hydrazone are readily oxidized to the corresponding diazo compounds on treatment with nickel peroxide.[61] It might be mentioned in this connection that Barakat and coworkers[34] have observed that fluorenone hydrazone on treatment with manganese dioxide is converted to the corresponding azine. Aldehyde and ketone hydrazones, on the other hand, are oxidatively hydrolyzed to the corresponding carbonyl compounds.[83] It has been assumed that diazo compounds are involved as intermediates in these reactions.

Oxidation of benzil monohydrazone with nickel peroxide[4] around 0° is reported to give a nearly quantitative yield of the α-diazo ketone, whereas the room-temperature oxidation leads to a mixture of benzophenone and diphenylketene. Manganese dioxide oxidation of 1,2-diketone monohydrazones, similarly, have been reported to give rise to the corresponding α-diazo ketones.[84,85] The oxidation of a pyrazoline hydrazone such as 3,3,5,5-tetramethyl-1-pyrazolin-4-one hydrazone (**156**) with nickel peroxide has been shown to give tetramethylallene (**156c**).[68] It has been suggested that the diazoalkane intermediate (**156b**) is involved as an intermediate in this reaction (Scheme IV). 1,2-Diketone bishydrazones have been reported to give rise to the corresponding alkynes on treatment with nickel peroxide. Thus, the oxidation of benzil bishydrazone leads to the formation of tolan.[4] A similar oxidation of cyclohexane-1,2-dione bishydazone with manganese dioxide has been reported to give cyclohexyne.[87–89]

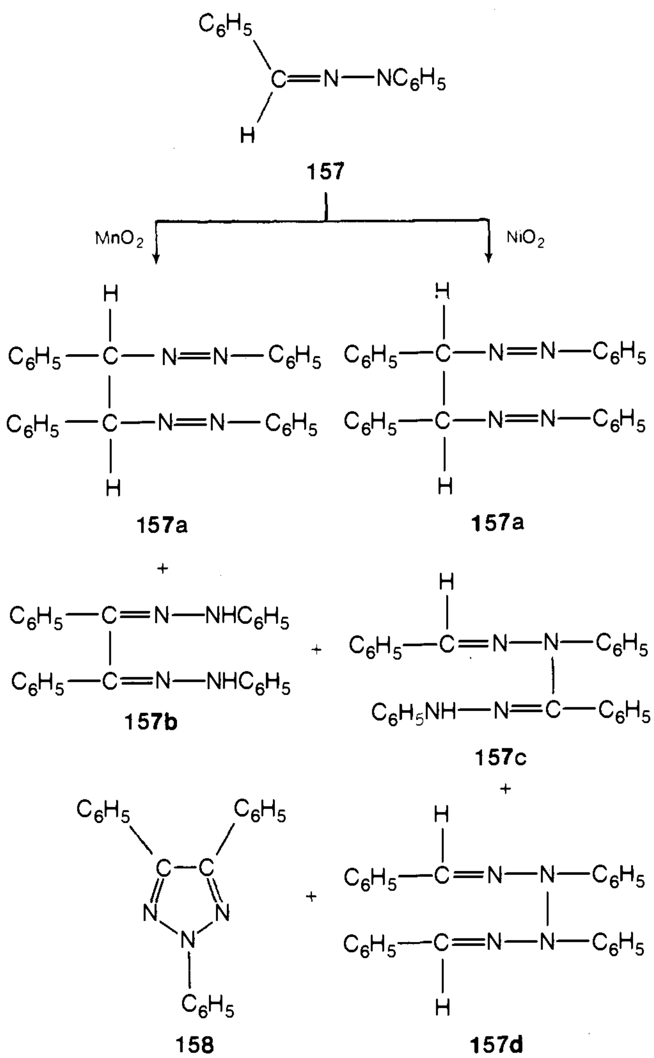
SCHEME IV



The oxidation of few aldehyde and ketone phenylhydrazones has been studied using nickel peroxide. Thus, benzophenone phenylhydrazone on oxidation in benzene medium is converted to a mixture of benzophenone and biphenyl.[43] The oxidation of aldehyde phenylhydrazones with manganese dioxide has been reported to give a mixture of several products. Thus, benzaldehyde phenylhydrazone (**157**) is converted to a mixture of 2,4,5-triphenyl-1,2,3-triazole (**158**) and several oxidative dimers consisting of 1,2-(bisphenylazo)-1,2-diphenylethane (**157a**), benzil osazone (**157b**), $N_\alpha,N_{\alpha'}$-diphenyl-N_β-benzalbenzhydrazine (**157c**), and 2,3-diphenyl-1,4-dibenzyltrazene (**157d**) (Scheme V).[70] Nickel peroxide oxidation of benzaldehyde phenylhydrazone (**157**), on the contrary, leads to the formation of only the C–C coupling product, **157a**.[43]

Chalcone phenylhydrazones give pyrazoles on oxidation with manganese dioxide in benzene solution.[71] Nickel peroxide oxidation of benzylideneacetone phenylhydrazones, on the other hand, gives rise to a mixture of *meso* and *dl* forms of 4,4′-bipyrazolines. The parent benzylideneacetone phenylhydrazone (**159a**), for example, gives a *dl* mixture of 1,1′,5,5′-tetraphenyl-3,3′-dimethyl-4,4′-bipyrazoline (**160a**), whereas 2-methylbenzylideneacetone phenylhydrazone (**159b**) under similar conditions gives *meso*-1,1′-diphenyl-3,3′-dimethyl-5,5′-di(o-tolyl)-4,4′-bipyrazoline (**161b**). Similarly, *meso*-4,4′-bipyrazolines are formed in the oxidation of 4-methyl- and 2-chlorobenzylideneacetone phenylhydrazones (**159d,e**) and furfurylideneacetone phenylhydrazone (**159h**). A

SCHEME V

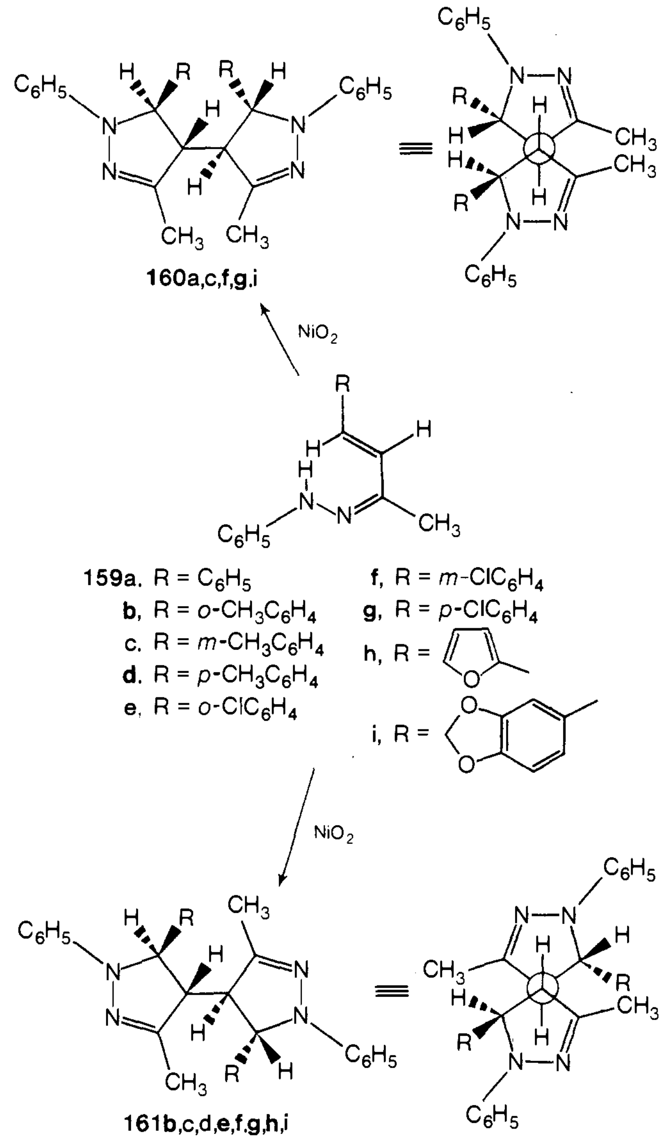


mixture of both *dl* and *meso* forms of 4,4′-bipyrazolines, however, is obtained in the oxidation of 3-methyl-, 3-chloro-, and 4-chlorobenzylideneacetone phenylhydrazones (**159c,f,g**) and piperonylideneacetone phenylhydrazone (**159l**) (Scheme VI).[72]

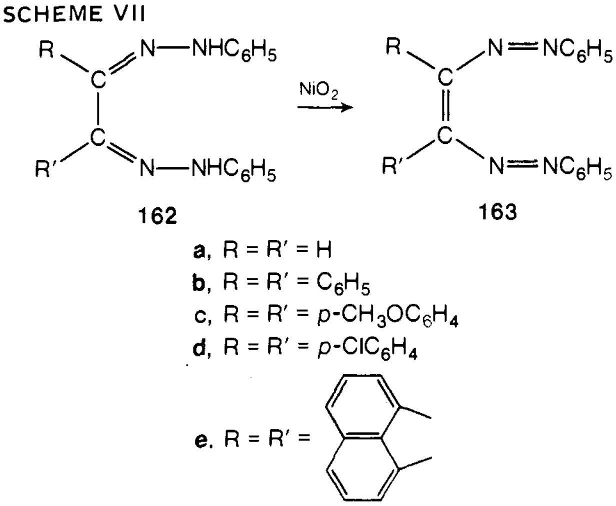
Several bisphenylhydrazones of 1,2-diketones have been oxidized by nickel peroxide. Thus, the oxidation of glyoxal bisphenylhydrazone (**162**a) in benzene at room temperature gives bisphenylazoethylene (**163a**). Similarly, the oxidation of benzil bisphenylhydrazone (**162b**), anisyl bisphenylhydrazone (**162c**), 4,4′-dichlorobenzil bisphenylhydrazone (**162d**), and acenaphthenequinone bisphenylhydrazone (**162e**) gives the corresponding bisazoolefins **163b–e** (Scheme VII).[73] In addition to the bisazoolefins, triazoles (**165b–d**) are also formed in the oxidation of the 1,2-diketone bisphenylhydrazones **163b–d**.[73-75] The formation of the triazoles **165b–d** has been shown to proceed through the zwitterionic intermediates **164b–d** derived from the corresponding bisazoolefins (**163b–d**) (Scheme VIII).[74,75]

The oxidation of methylglyoxal bisphenylhydrazone (**166a**) at room temperature gives exclusively 1,2-bisphenylazopropylene (**167**a), whereas in refluxing benzene a mixture of **167a** and 1-phenyl-4-phenylazopyrazole (**168a**) is formed (Scheme IX). Similarly, the room-temperature oxidation of biacetyl bisphenylhydrazone (**166b**) gives 2,3-bisphenylazobut-2-ene (**167b**), whereas under refluxing conditions the pyrazole **168b** is formed. The oxidation of phenylmethylglyoxal bisphenylhydrazone (**166c**), on the other hand, gives the corresponding phenylazopyrazole **168c,** both at room temperature and under refluxing conditions (Scheme IX).[73] The room-temperature oxidation of benzylmethylglyoxal bisphenylhydrazone (**169**) gives a mixture of 3-phenylazo-3-buten-2-one phenylhydrazone (**170**) and 1,5-diphenyl-3-methyl-4-phenylazopyrazole (**171**). Under refluxing conditions in benzene, the oxidation of **169** gives a mixture of the phenylazopyrazole **171** and 1-phenyl-3-benzoyl-4-phenylazopyrazole (**172**) (Scheme X).[73] The oxidation of phenylglyoxal bisphenylhydrazone (**173**) is

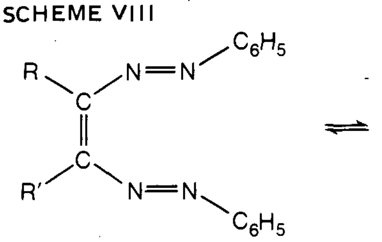
SCHEME VI



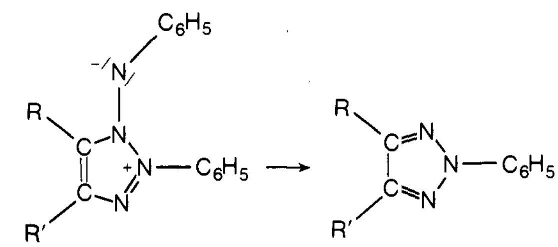
SCHEME VII



SCHEME VIII

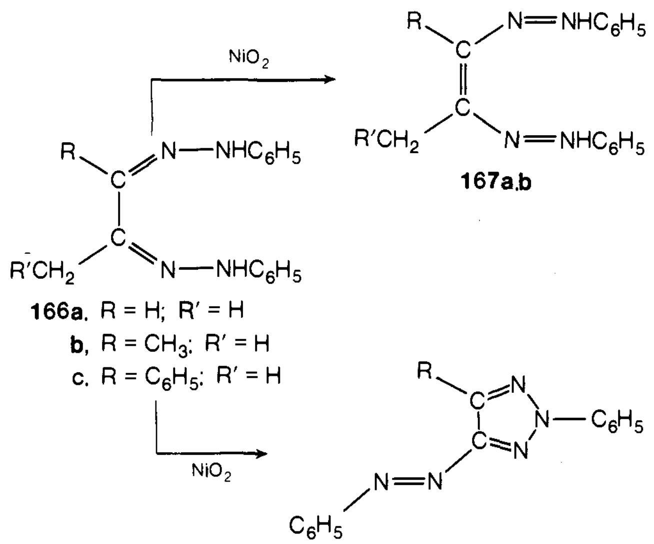


163b, R = R′ = C_6H_5
c, R = R′ = p-$CH_3OC_6H_4$
d, R = R′ = p-ClC_6H_4



164b,c,d **165b,c,d**

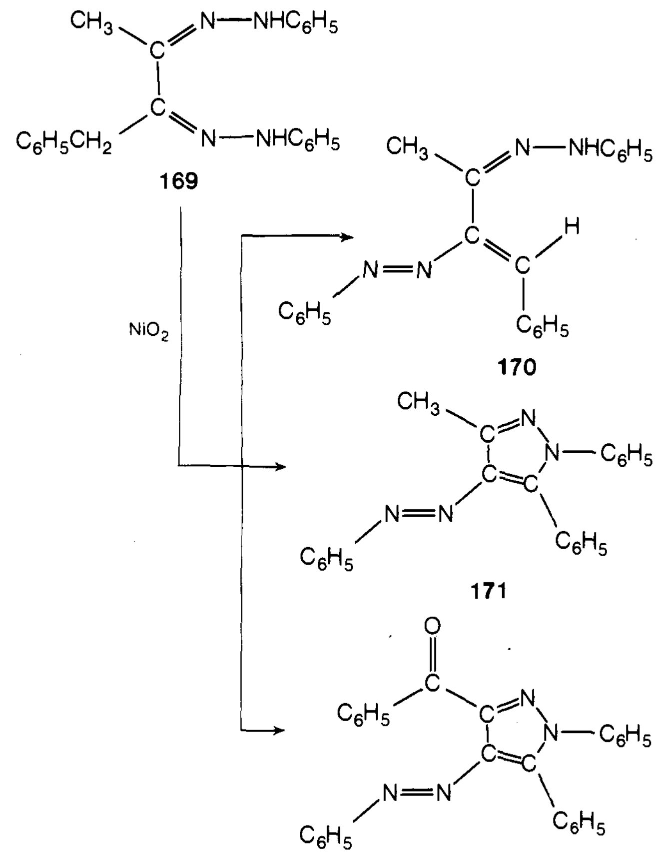
SCHEME IX



166a, R = H; R′ = H
b, R = CH_3; R′ = H
c, R = C_6H_5; R′ = H

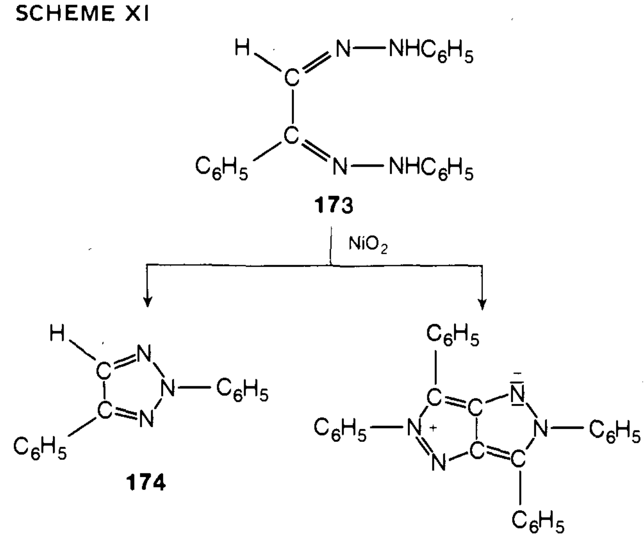
167a,b **168a,b,c**

SCHEME X



169 **170** **171** **172**

SCHEME XI



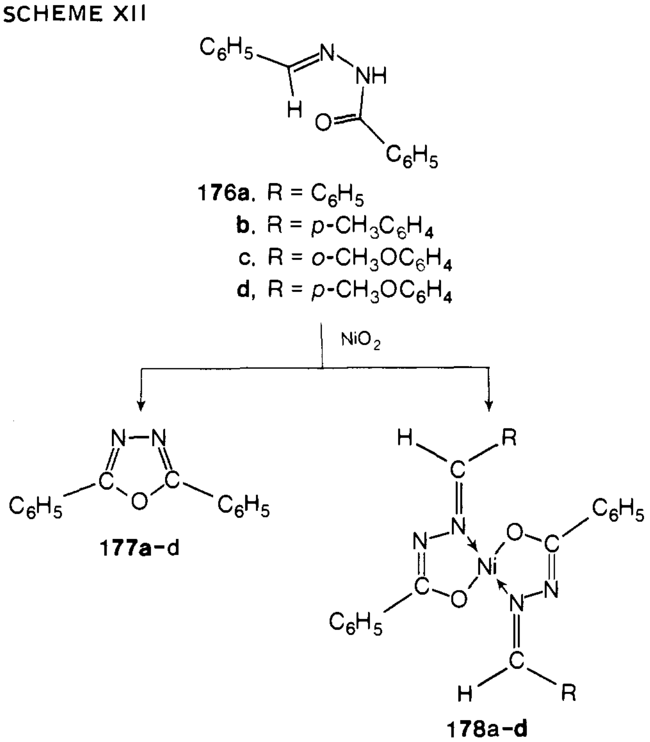
173 **174** **175**

shown to give a mixture of 2,5-diphenyl-1,2,3-triazole (**174**) and 2,3,5,6-tetraphenyl-1,2,4,5-tetraazapentalene (**175**) (Scheme XI).[73]

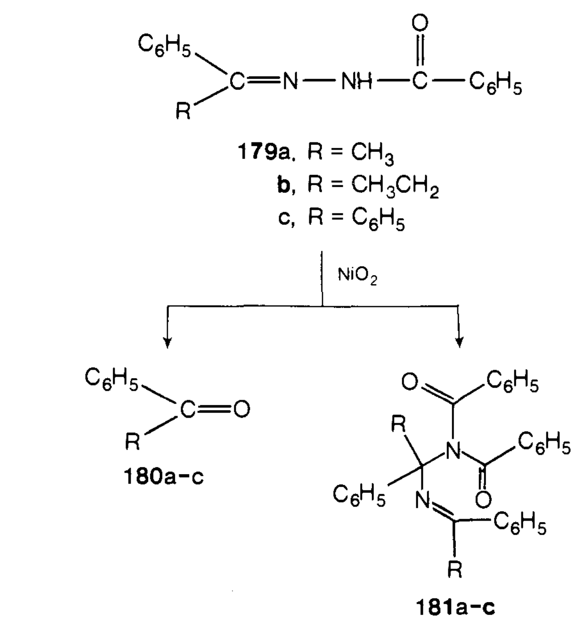
Nickel peroxide has also been used in the oxidation of several benzoylhydrazones of aldehydes, ketones, and 1,2-diketones.[78] The oxidation of benzaldehyde benzoylhydrazone (**176a**), for example, gives a mixture of 2,5-diphenyl-1,3,4-oxadiazole (**177a**) and a nickel complex, identified as the trans nickel bisbenzaldehyde benzoylhydrazone (**178a**). Similarly, *p*-tolualdehyde benzoylhydrazone (**176b**), o-methoxybenzaldehyde benzoylhydrazone (**176c**), and anisaldehyde benzoylhydrazone (**176d**) give the corresponding 1,3,4-oxadiazole derivatives (**177b–d**) and nickel complexes (**178b–d**) (Scheme XII).[78]

Acetophenone benzoylhydrazone (**179a**), on nickel peroxide oxidation, gives a mixture of acetophenone (**180a**) and methylbenzylidene-α-dibenzoylamino-α-methylbenzylamine (**181a**). Similarly, propiophenone benzoylhydrazone (**179b**) and benzophenone benzoylhydrazone (**179c**) give the corresponding ketones (**180b,c**) and Schiff's bases (**181b,c**) (Scheme XIII).[78] Biacetyl bisbenzoylhydrazone (**182a**) on oxidation in chloroform solution gives a mixture of 1-α-benzoyloxybenzylideneamino-4,5-dimethyl-1,2,3-triazole (**185a**) and a nickel complex **186a**. Similarly, benzil bisbenzoylhydrazone (**182b**) gives a mixture of the triazole **185b** and the nickel complex **186b**. In contrast, phenylmethylglyoxal bisbenzoylhydrazone (**182c**) gives only the triazole **185c** (Scheme XIV).[76] The formation of the triazoles **185a–c** in these reactions has been explained in terms of the intermediates **183a–c** and **184a–c** (Scheme XIV).[76] Phenylglyoxal bisbenzoylhydrazone (**187a**) gives a mixture of products consisting of 1-dibenzoylamino-4-phenyl-1,2,3-triazole (**188a**), 1-benzoylamino-4-phenyl-1,2,3-triazole (**189a**), and nickel bisphenyl-2-(5-phenyl-1,3,4-oxadiazolyl) ketone benzoylhydrazone (**190a**). Similarly, 4-methoxyphenylglyoxal bisbenzoylhydrazone (**187b**) gives a mixture of triazoles **188b** and **189b** and the corresponding nickel complex **190b** (Scheme XV).[78]

SCHEME XII



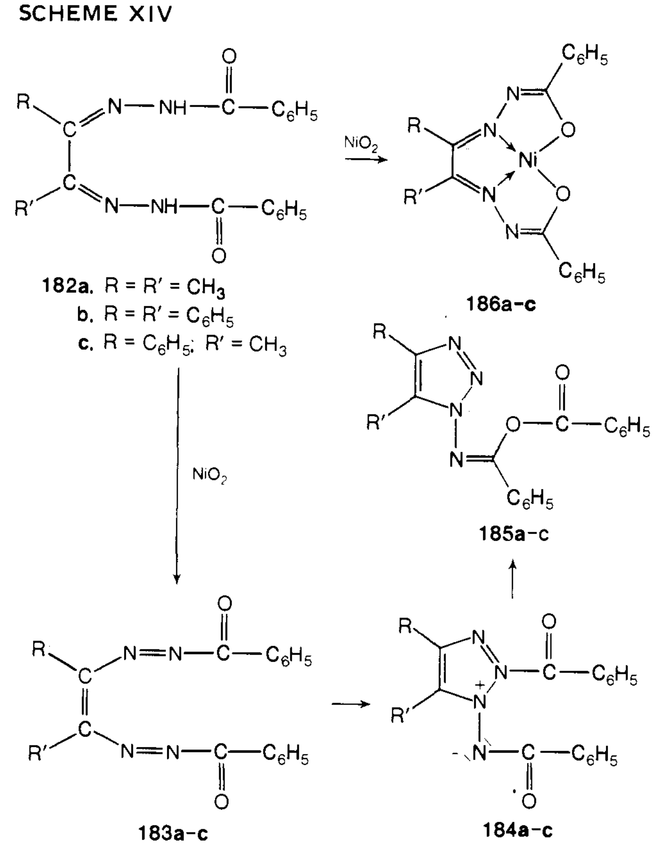
SCHEME XIII



J. Hydroxylamines and Oximes

Aromatic hydroxylamines are oxidized to the corresponding azoxy compounds by nickel peroxide.[77] Table X summarizes the results of the oxidation of several such hydroxylamines. Thus, the oxidation of phenylhydroxylamine (**191**) gives azoxybenzene (**191a**). Similarly, *p*-chlorophenylhydroxylamine (**192**), *p*-methylnaphthylhydroxylamine (**193**), and 2-naphthylhydroxylamine (**194**) give the corresponding azoxy compounds **192a**, **193a**, and **194a**, respectively. It is assumed that the nitroso compounds formed on the surface of the oxidant react further with hydroxylamine leading to the formation of azoxy compounds. Oxidation of *N*-benzylhydroxylamine (**195**) gives a trace of the corresponding azoxy compound **195a**, whereas the major product in this reaction is α-nitrosotoluene (**195b**). The oxidation of benzohydroxamic acid (**196**) gives *N,O*-dibenzoylhydroxylamine (**196a**) as the major product, whereas *N*-benzoyl-*N*-phenylhydroxylamine (**197**)

SCHEME XIV



SCHEME XV

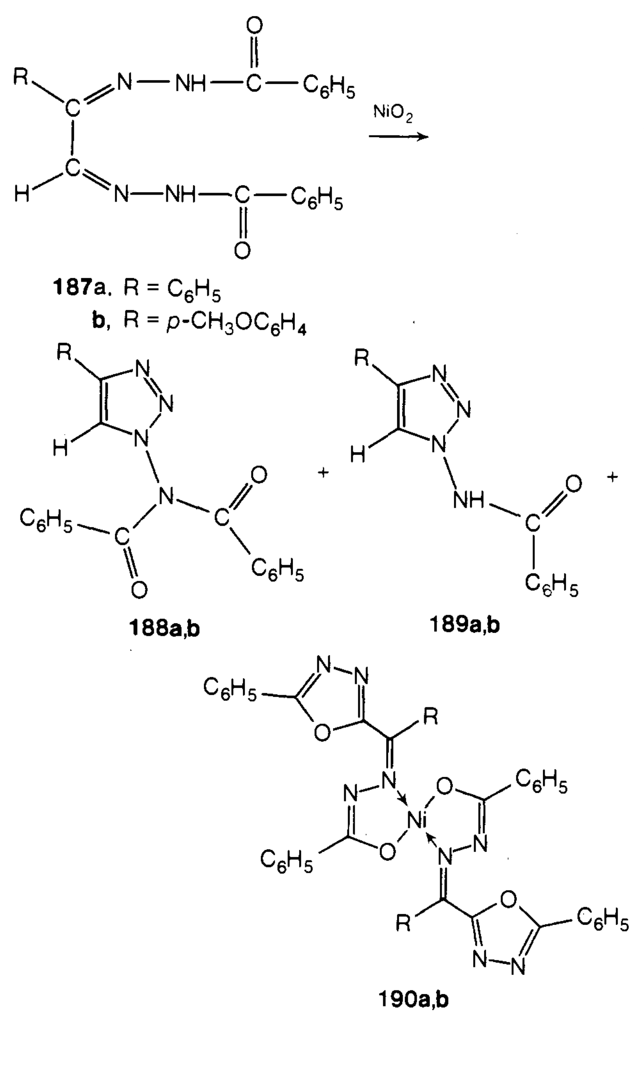


TABLE X. Oxidation of Hydroxylamines and Oximes

Substrate	Ratio of substrate: NiO_2	Solvent	Temp, °C	Time, hr	Product	Yield, %	Ref
C_6H_5NHOH (**191**)					$C_6H_5\overset{+}{N}(O^-)=NC_6H_5$ (**191a**)	90	77
p-ClC_6H_4NHOH (**192**)					p-$ClC_6H_4\overset{+}{N}(O^-)=NC_6H_4Cl$-$p$ (**192a**)	97	77
p-$CH_3C_6H_4NHOH$ (**193**)					p-$CH_3C_6H_4\overset{+}{N}(O^-)=NC_6H_4CH_3$-$p$ (**193a**)	92	77
2-Naphthylhydroxylamine (**194**)					$C_{10}H_7\overset{+}{N}(O^-)=NC_{10}H_7$ (**194a**)	37	77
$C_6H_5CH_2NHOH$ (**195**)					$C_6H_5CH_2\overset{+}{N}(O^-)=NCH_2C_6H_5$ (**195a**)	Trace	
					+ $C_6H_5CH_2N=O$ (**195b**)	35	77
$C_6H_5C(=O)NHOH$ (**196**)					$C_6H_5C(=O)NHOC(=O)C_6H_5$ (**196a**) + $C_6H_5CO_2H$	58	77
$C_6H_5C(=O)-N(OH)C_6H_5$ (**197**)					$C_6H_5CONHC_6H_5$ (**197a**)	29	77
					+ $(C_6H_5CO)(C_6H_5)NOCOC_6H_5$ (**197b**)		
$(R)(H)C=NOH$ (**198**)					$(R)(H)C=\overset{+}{N}(O^-)-\overset{+}{N}(O^-)=C(R)(H)$ (**198a**)		4

gives benzanilide (**197a**) together with a small amount of *N,O*-dibenzoyl-*N*-phenylhydroxylamine (**197b**) (Table X).[77] Aurich and Baer[8] have studied the oxidation of *N*-acyl-*N*-phenylhydroxylamines and have shown through ESR studies that acyl phenylnitroxides are formed in these cases. They have suggested a free radical pathway for these oxidations. The oxidation of aromatic aldoximes (**198**) with nickel peroxide gives aldazine bis-*N*-oxides (**198a**) as major products (Table X).[4]

K. Miscellaneous Reactions

1. Aminotriazoles

The oxidation of 1-aminobenzotriazole (**199**) with nickel peroxide[78,79] gives a mixture of products consisting of bisphenylene (**201**), azobenzene (**202**), and 1-phenylbenzotriazole (**203**), whereas, in presence of manganese dioxide,[78] dibenzopyridazine (**204**) is the major product (Scheme XVI). It has been suggested that this oxidation proceeds through a nitrene intermediate **200** which fragments further, leading to various products. In contrast, the oxidation of 1-aminonaphtho[1,8-*d,e*]triazine (**205**) with nickel peroxide gives a mixture of 1-phenylnaphthalene (**206**), 6b,10a-dihydrofluoranthene (**207**), and fluoranthene (**208**).[80] Under analogous conditions only traces of **206** and **208** are formed in the manganese dioxide oxidation of **205** (Scheme XVI).[80]

2. Hydrazines

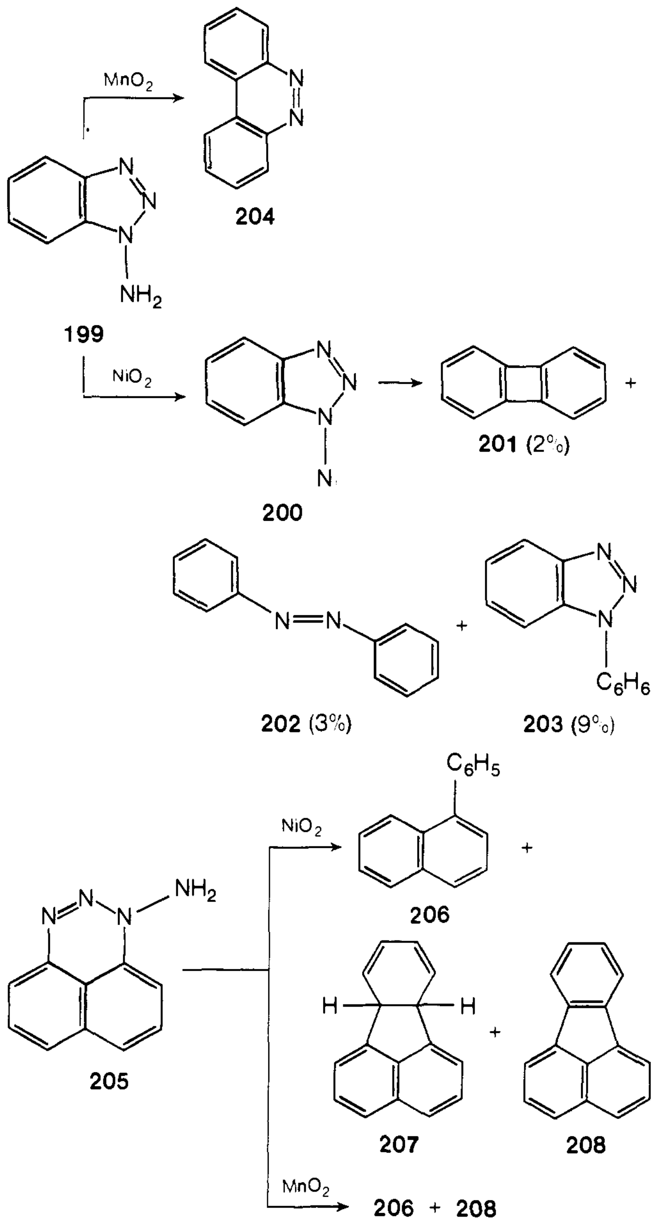
Phenylhydrazine has been oxidized with nickel peroxide to give different products depending on the nature of the solvent employed.[81] Thus, the oxidation of phenylhydrazine in cyclohexane gives benzene and biphenyl, whereas chlorobenzene, benzene, biphenyl, and hexachloroethane are the products isolated when carbon tetrachloride is used as the solvent. In benzene medium, the products of oxidation are biphenyl, traces of phenol, and 1,4-dihydrobiphenyl. In contrast, the oxidation of phenylhydrazine with manganese dioxide, in benzene, gives biphenyl and azobenzene.[36] Manganese dioxide oxidation of 1,2-disubstituted hydrazines gives azobenzene,[82] whereas tetrazenes are formed from unsymmetrical *N,N*-disubstituted hydrazines.[36]

In a recent study, it has been shown that a hydrazine derivative such as 2-hydrazinobenzothiazole (**209**) is oxidized by nickel peroxide in benzene medium to give a mixture of 2-phenylbenzothiazole (**210**) and benzothiazole (**211**).[83] The products formed in toluene medium have been benzothiazole (**211**) and 2,2′-benzothiazolyl (**212**), whereas in chloroform solution both benzothiazole (**211**) and 2,2′-azodibenzothiazole (**213**) are formed (Scheme XVII).[83]

3. Schiff's Bases

Schiff's bases, prepared from substituted o-aminophenols and benzaldehyde, undergo oxidative cyclization with nickel peroxide[84] to form 2-phenylbenzoxazole derivatives in good yields. Table XI summarizes the results of these studies using several Schiff's bases (**214–237**). Similarly, the oxidation of *N*-benzylidene-o-phenylenediamines (**238–241**) has been

SCHEME XVI



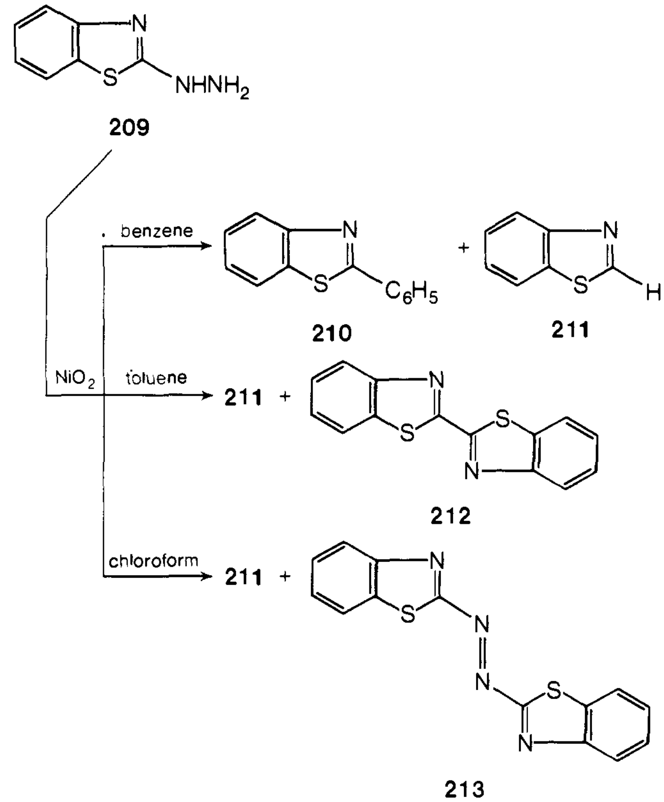
shown to yield 2-substituted benzimidazoles (**238**a–**241**a) (Table XI).[83]

4. Sulfur Compounds

Thiophenol (**242**) and ethyl mercaptan (**243**) are easily oxidized to their corresponding disulfides in good yields on treatment with nickel peroxide (Table XII).[85] Oxidation of sulfides to sulfones, however, appears to proceed very slowly. Diphenyl sulfide (**244**), for example, on oxidation under drastic conditions gives the corresponding sulfone (**244a**).[85] On the other hand, dibenzothiophene (**245**) is unaffected on treatment with nickel peroxide. In contrast, manganese dioxide oxidizes mercaptans to disulfides and sulfides to sulfoxides.[86,87]

Phenothiazine (**246**) is oxidized to give 3,10′-biphenothiazine (**246a**) and a polymeric material.[88] Similarly, 2-chloro- and 4-chlorophenothiazines (**247** and **248**) give polymeric products. In contrast, 10-methylphenothiazine (**249**) gives a mixture of 10-methylphenothiazine 5-oxide (**249a**), 10-methylphenothiazine 5,5-dioxide (**249b**), 3*H*-phenothiazin-3-one (**249c**), and a polymeric product.[88] Similarly, 2-chloro-10-methylphenothiazine (**250**) has been reported to give the 5-oxide (**250a**), 5,5-dioxide (**250b**), 2-chloro-3*H*-phenothiazin-3-one (**250c**), and an isomer of **250c**. Analogous products

SCHEME XVII



were obtained in the oxidation of 4-chloro-10-methylphenothiazine (**251**) also (Table XII).[88]

III. Mechanism of Oxidations

Most of the nickel peroxide oxidations of organic compounds are presumed to involve free radical intermediates. In recent years, there have been several attempts to detect the presence of some of these radical intermediates and also to elucidate the mechanism of nickel peroxide oxidations.

In a fairly detailed study of the mechanism of nickel peroxide oxidations using ESR techniques, Konaka and coworkers[5] have shown that radical intermediates are actually involved in the oxidation of several substances like phenols, phenothiazine, hydrocarbons containing active methylene and methine groups, and alcohols. Thus, in the oxidation of 2,6-di-*tert*-butyl-4-methylphenol (**40**) in benzene, the presence of 2,6-di-*tert*-butyl-4-methylphenoxy radical (**252**), a_p^H = 11.15 G and a_m^H = 1.69 G, has been detected through ESR studies. Similarly, the oxidation of 2,6-di-*tert*-butylphenol (**36**) has been shown to proceed through 2,6-di-*tert*-butylphenoxy radical (**253**), a_p^H = 9.58 G and a_m^H = 1.93 G (Scheme XVIII). The oxidation of phenothiazine (**246**), likewise has been shown to proceed through 10-phenothiazinyl radical (**254**), with hyperfine splitting constants, a^N = 7.04 G, $a^H_{3,7}$ = 3.67 G, $a^H_{1,9}$ = 2.85 G, and $a^H_{2,8}$ = $a^H_{4,6}$ = 0.95 G. It has been observed that nearly 72% of the radical species **254** is formed at 2.4 min after mixing **246** with nickel peroxide as evidenced by the ESR spectrum. The rate of decay of **254** has been estimated as $k = 1.2 \times 10^{-2}$ mol^{-1} sec^{-1}.

In a recent investigation on the mechanism of the nickel peroxide oxidation of phenols, ESR spin trapping technique using nitrosobenzene has been employed to show the involvement of phenoxy radicals in these reactions.[9,10] Thus, in the oxidation of phenol (**30**) with nickel peroxide in the presence of nitrosobenzene, the formation of the phenoxazine-*N*-oxyl radical (**259**) has been detected through its ESR spectrum. In addition, they have been able to isolate *N*-4-oxocy-

TABLE XI. Oxidation of Schiff's Bases

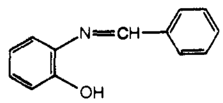
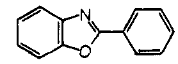
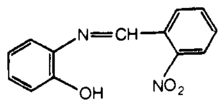
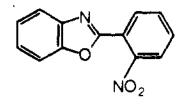
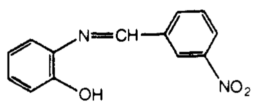
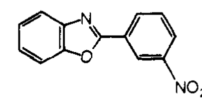
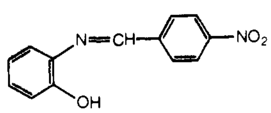
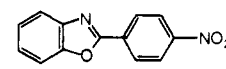
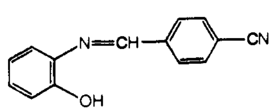
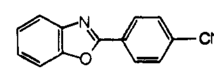
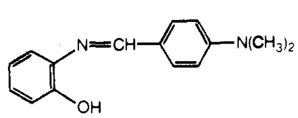
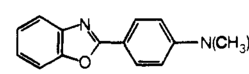
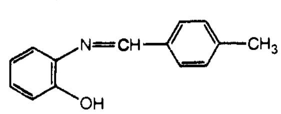
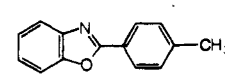
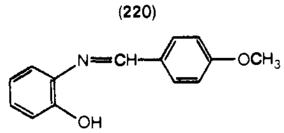
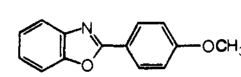
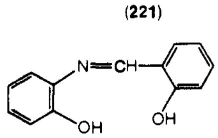
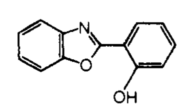
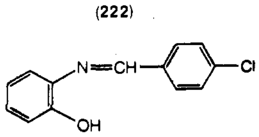
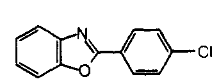
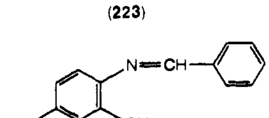
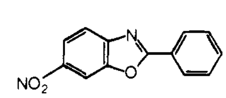
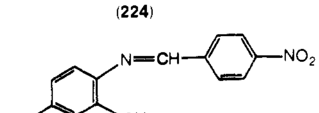
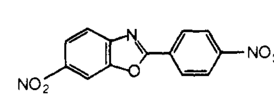
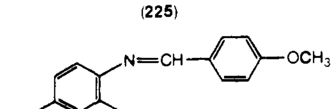
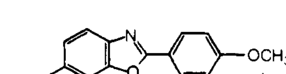
Substrate	Ratio of substrate: NiO_2	Solvent	Temp, °C	Time, hr	Product	Yield, %	Ref
 (214)		C_6H_6	15	1		72	84
 (215)		C_6H_6	15	1		61	84
 (216)		C_6H_6	15	1		77	84
 (217)		C_6H_6	15	1		73	84
 (218)		C_6H_6	15	1		69	84
 (219)		C_6H_6	15	1		66	84
 (220)		C_6H_6	15	1		73	84
 (221)		C_6H_6	15	1		72	84
 (222)		C_6H_6	15	1		20	84
 (223)		C_6H_6	15	1		71	84
 (224)		C_6H_6	15	1		72	84
 (225)		C_6H_6	15	1		73	84
 (228)		C_6H_6	15	1		73	84

TABLE XI (Continued)

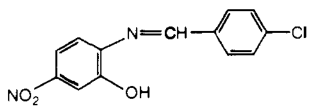
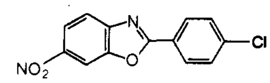
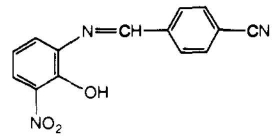
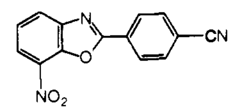
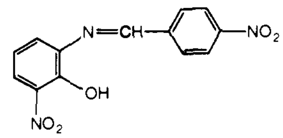
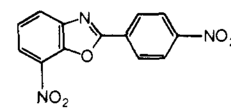
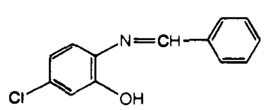
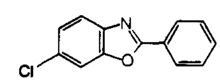
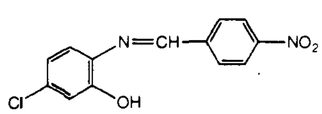
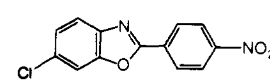
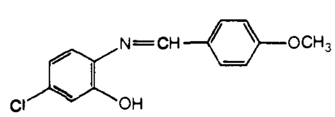
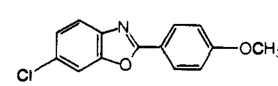
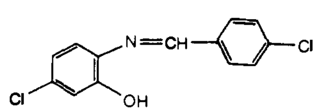
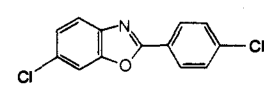
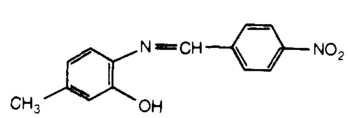
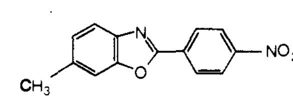
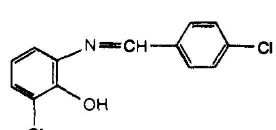
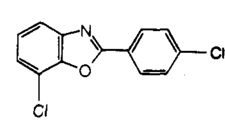
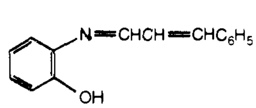
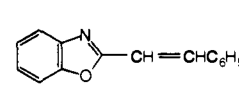
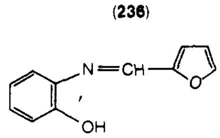
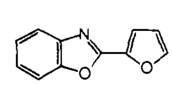
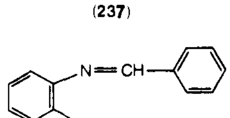
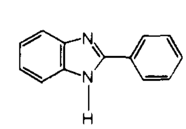
Substrate	Ratio of substrate: NiO_2	Solvent	Temp, °C	Time, hr	Product	Yield, %	Ref
 (227)		C_6H_6	15	1		65	84
 (228)		C_6H_6	15	1		66	84
 (229)		C_6H_6	15	1		78	84
 (230)		C_6H_6	15	1		70	84
 (231)		C_6H_6	15	1		64	84
 (232)		C_6H_6	15	1		62	84
 (233)		C_6H_6	15	1		74	84
 (234)		C_6H_6	15	1		76	84
 (235)		C_6H_6	15	1		48	84
 (236)		C_6H_6	15	1		61	84
 (237)		C_6H_6	15	1		28	84
 (238)		C_6H_6	30	3	 (238a)	71	83

TABLE XI (Continued)

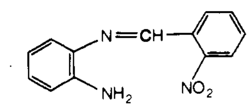
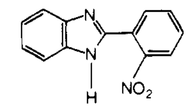
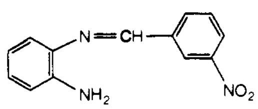
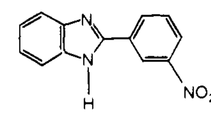
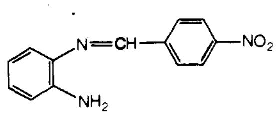
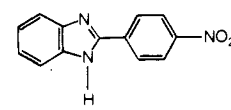
Substrate	Ratio of substrate: NiO_2	Solvent	Temp, °C	Time, hr	Product	Yield, %	Ref
 (239)		C_6H_6	30	3	 (239a)	41	83
 (240)		C_6H_6	30	4	 (240a)	49	83
 (241)		C_6H_6	30	4	 (241a)	57	83

TABLE XII. Oxidation of Sulfur Compounds

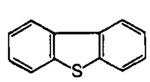
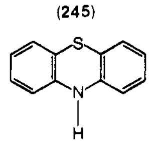
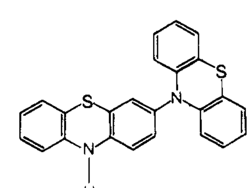
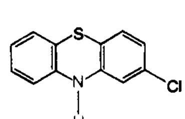
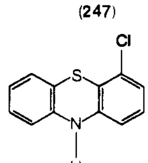
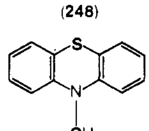
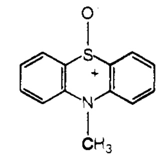
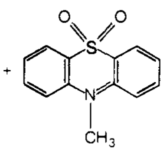
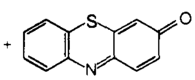
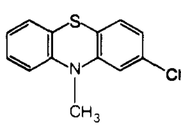
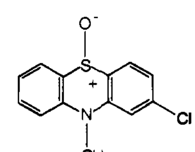
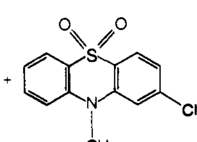
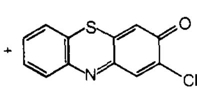
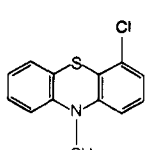
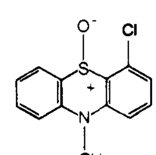
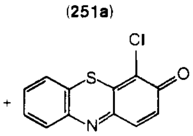
Substrate	Ratio of substrate: NiO_2	Solvent	Temp, °C	Time, hr	Product	Yield, %	Ref
C_6H_5SH (**242**)				1	$C_6H_5SSC_6H_5$	95	85
CH_3CH_2SH (**243**)			30	2	$CH_3CH_2SSCH_2CH_3$	87	85
$C_6H_5SC_6H_5$ (**244**)			80	10	$C_6H_5-\overset{O}{\underset{O}{\overset{\parallel}{\underset{\parallel}{S}}}}-C_6H_5$ (**244a**)	48	85
 (245)					No reaction		85
 (246)		C_6H_6	30		Polymer		88
246		Ether	25		 (246a) + polymer	2	88
 (247)					Polymer		88
 (248)					Polymer		88
 (249)		Ether			No reaction		88

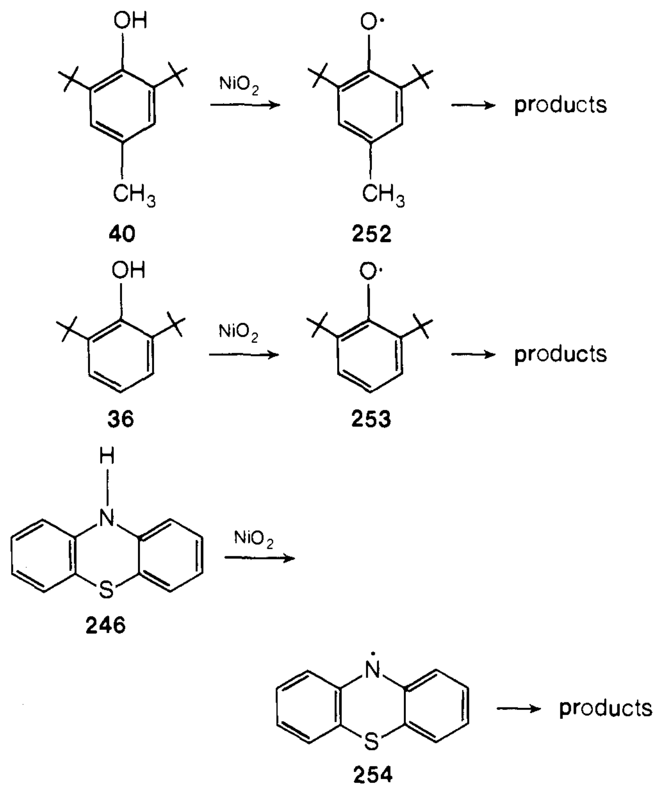
TABLE XII (Continued)

Substrate	Ratio of substrate: NiO_2	Solvent	Temp, °C	Time, hr	Product	Yield, %	Ref
		C_6H_6			 (249a) +  (249b) +  (249c) + polymer		88
 (250)					 (250a) +  (250b) +  (250c)		88
 (251)					 (251a) +  (251b) + isomer of **251b**		88

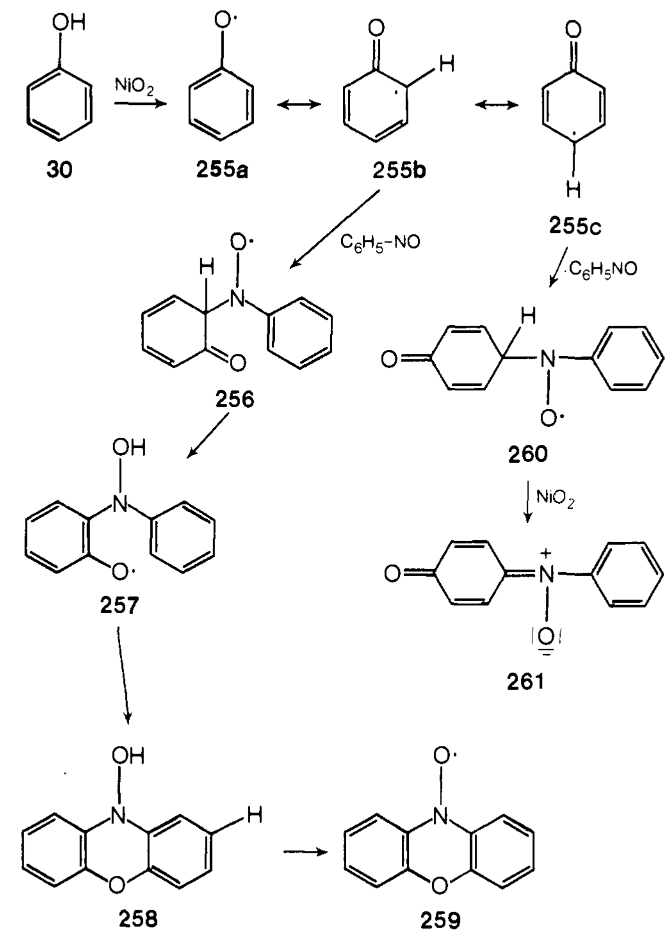
clohexa-2,5-dienylideneaniline *N*-oxide (**261**), a product formed through the initially formed phenoxy radical (**255**) with nitrosobenzene as shown in Scheme XIX.

Nickel peroxide oxidation of hydrocarbons containing active methylene and methine groups gives oxygenated products. Thus, toluene derivatives and diphenylmethane are oxidized to benzoic acid derivatives and benzophenone, respectively.[5] The oxidation of triphenylmethane, on the other hand, gives triphenylcarbinol, though in poor yields. It has been shown that a sample of nickel peroxide, prepared by the sodium hypochlorite oxidation, has the formula $NiO_{2.77}H_{2.85}$ on analysis. Hence, in the oxygenation reactions, the participation of species like OH radicals has to be invoked. These OH radicals could either be present in the starting nickel peroxide or may arise through a hydrogen abstraction process from the substrate by the oxidant. It might be pointed out in this connection that the thermal decomposition of phenylazotriphenylethane, in benzene, in the presence of nickel peroxide, gives a mixture of triphenylcarbinol, triphenylmethane, and biphenyl, whereas the thermal decomposition in benzene in the

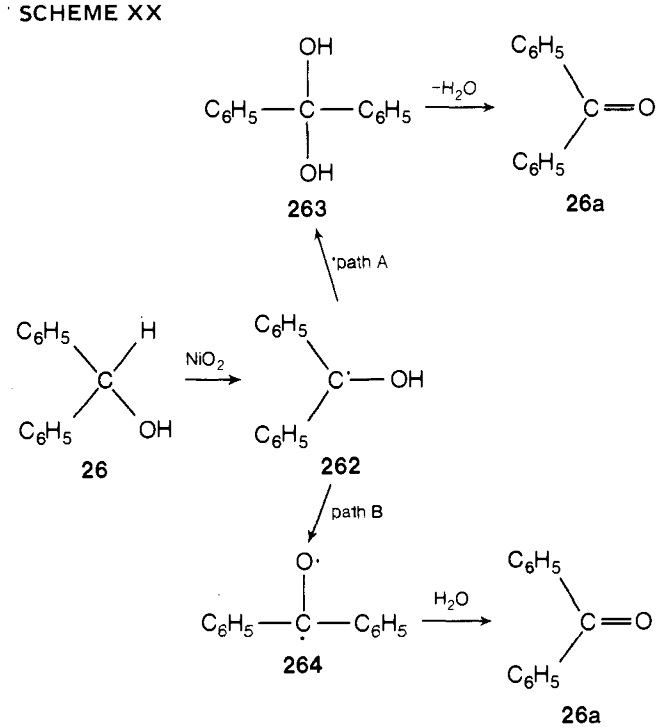
SCHEME XVIII



SCHEME XIX



SCHEME XX

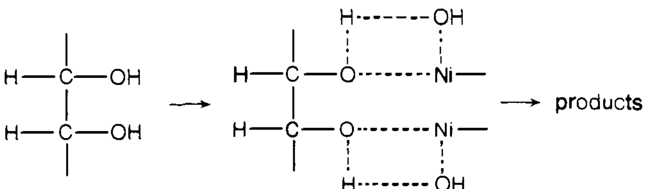


absence of nickel peroxide gives only triphenylmethane and biphenyl. It has, therefore, been inferred that the formation of triphenylcarbinol in presence of nickel peroxide is through the reaction of triphenylmethyl radicals with the hydroxyl radicals present in the oxidant. Similarly, it has been shown that hexaphenylethane is converted to triphenylcarbinol in nearly quantitative yields on treatment with nickel peroxide in benzene.[5] Since 1 mol of triphenylcarbinol is produced from 1 mol of triphenylmethyl radical and about 0.5 equiv of nickel peroxide, we can conclude that 1 equiv of available oxygen in nickel peroxide corresponds to two OH radicals. The formation of benzylic radicals in the nickel peroxide oxidation of aromatic hydrocarbons like $ArCHR_2$ and Ar_2CHR, has been recently demonstrated through esr spin trapping techniques, using nitrosobenzene and 2-methyl-2-nitrosopropane as spin traps.[10]

Konaka and coworkers[5] have suggested that the nickel peroxide oxidation of alcohols involves the initial abstraction of the α-hydrogen atom, followed by the hydrogen atom abstraction from the OH group, as against the alternative possibility of an initial hydrogen atom abstraction from the OH group. The appreciable difference in the rates of oxidation of $(C_6H_5)_2CHOH$ and $(C_6H_5)_2CDOH$ (k_H/k_D = 7.4) has been cited in support of this view. However, it may be pointed out that the observance of a kinetic effect in this reaction does not necessarily signify that the CH bond cleavage is the initial process. Two mechanistic possibilities are to be considered for the formation of benzophenone from the radical species **262** formed after the initial abstraction of a hydrogen atom from diphenylcarbinol (**26**) as shown in Scheme XX. The radical **262** can combine with a hydroxyl radical from nickel peroxide to give the dihydroxy intermediate **263** which can lead to the formation of benzophenone through the loss of a molecule of water (path A). An alternative pathway (path B) involves the formation of an intermediate **264** which can lead to benzophenone. Using diphenylcarbinol with ^{18}O label, it has been shown that path B is actually being followed in the oxidation of diphenylcarbinol.[5]

The oxidation of 1,2-diols with nickel peroxide gives rise to 1,2-dicarbonyl compounds, as well as oxidative fragmentation products.[26] Thus, the oxidation of *meso*-hydrobenzoin with nickel peroxide gives mainly benzaldehyde and a small amount of benzil, whereas pinacol gives chiefly acetone. These studies are indicative of the fact that the elimination of the hydrogen atom of the α position of 1,2-glycols need not necessarily be taking place in the oxidative cleavage of these compounds. It is interesting to note that there is an apparent

SCHEME XXI



1,2-glycol

inverse isotope effect in the rates of oxidation of *meso*-1,2-diphenylethane-1,2-diol and *meso*-1,2-diphenyl-1,2-dideuterioethane-1,2-diol ($k_H/k_D = 0.8$). A similar observation has been made in the oxidations of *meso*-butane-2,3-diol and *meso*-2,3-dideuteriobutane-2,3-diol ($k_H/k_D = 0.75$). It has been suggested that the oxidation of 1,2-glycols by nickel peroxide may be taking place through a concerted process of hydrogen atom abstractions, taking place on the surface of the oxidant (Scheme XXI). However, the formation of any cyclic complex, as in the case of lead tetraacetate oxidation,[90] has been ruled out, since no appreciable difference in the rates of oxidations of *cis*- and *trans*-cyclopentane-1,2-diols has been observed ($k_{cis}/k_{trans} = 2.1$).

In conclusion, it might be stated that the actual mechanistic details of the oxidation of organic compounds employing a nonstoichiometric oxide like nickel peroxide are yet to be clarified, on the basis of more definitive studies.

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IV. References

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