with the *t*-butoxy radical case.[12] While the results are rather qualitative,[13] they do show that hydrogen abstraction again occurs more readily from substrates with electron-supplying groups. On the other hand, comparing the rather small difference in reactivity between isopropyl alcohol and cyclohexane with the much more rapid induced chain decomposition in the former indicates that electron-supplying groups enormously increase the rate of radical attack upon the peroxide bond (eq 8). The importance of this step in determining the rate of induced decompositions has been pointed out by Kato and Mashio,[14] and as we have shown elsewhere,[11,15] the attack of simple alkyl radicals on aroyl peroxides is chiefly on the aromatic ring.

Experimental Section

Reagents were commercial materials, purified by standard procedures. Benzoyl peroxide was recrystallized from chloroform–methanol, purity by titration <99%.

Decompositions were carried out in sealed degassed tubes, using 0.0194 *M* peroxide solutions heated in thermostated baths to complete decomposition.

Analyses for CO_2 were carried out by gas chromatography using a silica gel column at 50–70°. By opening the tubes at 0°, and sampling the liquid phase it was found that essentially all the CO_2 remained in solution.

Known concentrations of CO_2 were prepared for calibration by weighing sodium carbonate into 10-ml volumetric flasks, adding 7–8 ml of acetone and then injecting acetic acid through a serum cap to bring the volumn to 10 ml. Calibrations were repeated before each set of analyses, and the method was further checked by comparing our measured CO_2 yields with literature values. Thus in cyclohexane and benzene we obtain 0.90 and 1.62 mol/1 mol of peroxide at 70° compared with 0.93 and 1.61 reported previously.[16]

Registry No.—Carbon tetrachloride, 56-23-5; benzene, 71-43-2; chlorobenzene, 108-90-7; toluene, 108-88-3; *o*-dichlorobenzene, 95-50-1; acetone, 67-64-1; *t*-butyl alcohol, 75-65-0; benzoyl peroxide, 94-36-0; cyclohexane, 110-82-7; isopropyl alcohol, 67-63-0; acetic acid, 64-19-7; diethyl ether, 60-29-7; benzaldehyde, 100-52-7; anisole, 100-66-3; 2,3,4-trimethylpentane, 565-75-3; cumene, 98-82-8.

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[12] Values at 0° are taken from C. Walling and M. J. Mintz, *J. Amer. Chem. Soc.*, **89**, 1515 (1967), and at 40° from C. Walling and B. B. Jacknow, *ibid.*, **82**, 6108 (1960).

[13] With substrates appreciably less reactive than cyclohexane the dependence of CO_2 yield on concentration is too small to determine k_a/k_d.

[14] S. Kato and F. Mashio, *Kogyo Kagaku Zasshi*, **59**, 380 (1956).

[15] C. Walling and Z. Cekovic, *J. Amer. Chem. Soc.*, **89**, 6681 (1967).

[16] P. F. Hartman, H. G. Sellers, and D. Turnbull, *ibid.*, **69**, 2416 (1947).

The Induced Decomposition of Per Esters and Mixed Peroxides in the Presence of Alcohols and Ethers[1]

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Rates and products observed in the fast decomposition of *t*-butyl peracetate and perbenzoate in alcohol and ether solvents confirm an induced chain similar to that recognized with benzoyl peroxide. High yields of *t*-butyl alcohol and only traces of CO_2 implicate the *t*-butoxy radical as the chain carrier, and it is suggested that both steric and polar effects may determine the point of attack by radicals on the peroxide bond. Induced chains are much longer with cyclic than noncyclic ethers. The latter give α-alkoxyalkyl radicals which undergo extensive β scission interfering with the induced chain. With cyclic ethers, β scission is apparently reversible since the fragments cannot separate.

Since the classic work of Cass[2] and Bartlett and Nozaki[3] over 20 years ago, the fast decomposition of benzoyl peroxide in the presence of ethers and alcohols has been recognized as an induced radical chain process, involving the propagation steps[4] in eq 1 and 2. Subsequently O^{18} tracer experiments[5] in ether systems have shown that eq 2 occurs by radical displacement on peroxide rather than carbonyl oxygen, while kinetics that are first order in peroxide in both ethers[3] and alcohols[6] imply that chains end by cross-termination between the two types of chain carrying radicals.

$$C_6H_5COO\cdot + R_2CH{-}OR(H) \longrightarrow C_6H_5COOH + R_2\dot{C}OR(H) \quad (1)$$

$$R_2\dot{C}OR(H) + C_6H_5COOOCOC_6H_5 \longrightarrow R_2C(OCOC_6H_5)OR(H) + C_6H_5COO\cdot \quad (2)$$

Other peroxides also show rapid decomposition in these solvents. With several classes including per esters,[7] per acids[8] and per sulfate,[9] retardation by radical traps indicates a chain sequence, presumably similar to eq 1 and 2. In contrast, Huyser and Bredeweg[10] have reported that di-*t*-butyl peroxide undergoes a short-chain-induced decomposition in alcohols, but not ethers, for which they suggest eq 3 as an alternative to eq 2, and Tobolsky and Matlack[11] have shown that the fast decomposition of tertiary hydroperoxides in benzyl alcohol reflects an actual increase in the rate of homolytic scission.

$$R_2\dot{C}OH + BuOOBu \longrightarrow R_2CO + BuOH + BuO\cdot \quad (3)$$

Previous results on per esters have been limited to kinetic measurements,[7] although Bartlett[12] has re-

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[1] Taken from the Ph.D. Thesis of J. C. A., Columbia University, 1966. Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

[2] W. E. Cass, *J. Amer. Chem. Soc.*, **69**, 500 (1947).

[3] P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947).

[4] Since some decarboxylation of the benzoyloxy radical occurs, propagation also occurs in part through phenyl radicals.

[5] D. B. Denney and G. Feig, *ibid.*, **81**, 5322 (1959).

[6] S. Kato and F. Mashio, *Kogyo Kagaku Zasshi*, **59**, 380 (1956).

[7] A. T. Blomquist and A. F. Ferris, *J. Amer. Chem. Soc.*, **73**, 3412 (1951).

[8] K. Tokamaro, O. Simamura, and M. Fukuyama, *Bull. Chem. Soc. Jap.*, **35**, 1673 (1962); K. Tokumaro and O. Simamura, *ibid.*, **35**, 1955 (1962).

[9] P. D. Bartlett and J. D. Cotman, Jr., *J. Amer. Chem. Soc.*, **71**, 1419 (1949); I. M. Koltoff, E. J. Meehan, and E. M. Carr, *ibid.*, **75**, 1439 (1953).

[10] E. S. Huyser and C. J. Bredeweg, *ibid.*, **86**, 2401 (1964).

[11] A. V. Tobolsky and L. R. Matlack, *J. Polym. Sci.*, **55**, 49 (1961).

[12] P. D. Bartlett, E. D. Benzing, and R. E. Pincock, *J. Amer. Chem. Soc.*, **82**, 1762 (1960).

ported that di-*t*-butyl peroxalate decomposes rapidly at 0° in diisopropyl ether to yield, as a rather unusual product, isopropyl isopropenyl ether. In the study reported here, our objectives have been to determine the manner of cleavage of asymmetric peroxide bonds and the products formed in the induced process.

Per Ester Decomposition in Alcohols.—Rates of decomposition of *t*-butyl peracetate and perbenzoate were determined in several alcohols as listed in Table I.

TABLE I

DECOMPOSITIONS OF *t*-BUTYL PER ESTERS[a] IN ALCOHOL SOLVENTS

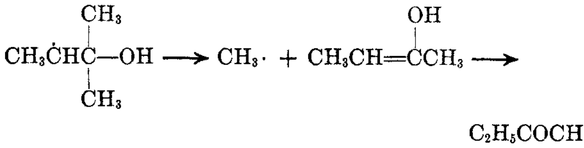
Alcohol	Temp, °C	$k \times 10^5$, sec^{-1}
sec-Butyl[b]	75	12.3
sec-Butyl[c]	75	11.3
sec-Butyl[d]	75	5.3
sec-Butyl[e]	75	0.040
sec-Butyl	85	28.8
sec-Butyl[f]	85	30.2
n-Butyl	75	2.65
Isopropyl	75	13.0
Isopropyl	85	(50)
t-Amyl	75	0.28
Benzene	75[f,g]	0.045
Benzene	85	0.120

[a] *t*-Butyl peracetate, 0.2–0.4 *M* in absence of air unless noted. [b] 0.225 *M*. [c] 0.040 *M*. [d] Air present. [e] 0.266 *M* plus 0.084 *M* methyl methacrylate. [f] *t*-Butyl perbenzoate. [g] Extrapolated from ref 7.

The data in general give good first-order plots, and in *sec*-butyl alcohol, which was studied in most detail, a fivefold change in initial peroxide concentration produced no significant change in the calculated first-order rate constant. Oxygen notably slows the decomposition rate, while 0.084 *M* methyl methacrylate reduces it to the rate in benzene, indicating that the fast decomposition is entirely the result of an induced chain, with no effect of alcohol on the unimolecular homolysis. On this basis the approximate kinetic chain lengths for the induced process are 250–300 in secondary alcohols and about 58 in *n*-butyl alcohol. Apparent chain lengths in *t*-amyl alcohol are only about 6, and these variations of rate with structure are considered further below.

A partial analysis of the products of the per ester–alcohol reactions are given in Table II. The most significant feature is the high yield of *t*-butyl alcohol and low yield of CO_2 from both per esters. (Acids and their derivatives were not determined, but presumably account for the balance of the acyloxy groups.) Since the acetoxy radical would be certain to undergo extensive decarboxylation if it had been formed, we conclude that the *t*-butoxy radical must be the major chain carrier. If so, since decompositions are also rapid in ethers, we assume that α-hydroxyalkyl radical attack occurs by displacement on the acylperoxy oxygen as in the benzoyl peroxide case.

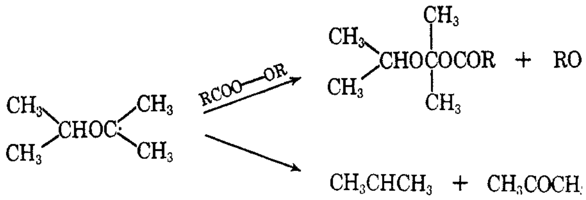
Minor products are also consistent with this direction of cleavage. In such a reactive solvent little β scission of the *t*-butoxy radical would be expected, and only small amounts of acetone are formed. However, dilution of *sec*-butyl alcohol with *o*-dichlorobenzene, which prolongs the life of the *t*-butoxy radicals, almost triples acetone yield. Secondary alcohols give the expected ketone in high yield, but aldehyde yields from 1-butanol are low as has been noted in other systems,[13] in part because of further oxidation.[14] Although, as expected, little induced decomposition occurs in *t*-amyl alcohol, the products are interesting in that they indicate some cleavage of the molecule to yield 2-butanone and acetone (from a material balance, not more than one-third of the acetone produced could come from *t*-butoxy radical decompositions). Such cleavage of tertiary alcohols has been noted previously,[13] and apparently has a path other than *via* RO–H exchange to give an alkoxy radical followed by β scission, since the amyloxy radical cleaves essentially exclusively to ethyl and acetone.[15] The most plausible path[13] seems to be *t*-butoxy radical attack on a β-C–H bond, followed by elimination, *e.g.*, eq 4.



$$CH_3\dot{C}HC(CH_3)_2{-}OH \longrightarrow CH_3\cdot + CH_3CH{=}C(OH)CH_3 \longrightarrow C_2H_5COCH_3 \quad (4)$$

Per Ester Decomposition in Ethers.—Decomposition rates in several ethers are given in Table III. Rates are in interesting contrast to those in alcoholic solvents, since decompositions are slowest in isopropyl ether, next in *n*-butyl ether, and comparable to rates in alcohols only with cyclic ethers.

We believe that the difference arises from the importance of β scission in the reaction of the α-alkoxyalkyl radicals involved in the ether reactions and resulting competition, *e.g.*, eq 5, since the alkyl radicals formed by β scission show little tendency to propagate the induced chain. Such β scissions have long been known in high temperature reactions, and we have recently shown that they occur even at 0° when they result in the formation of a relatively stable radical.[14] On this basis, β scission of the radical from isopropyl ether, yielding the isopropyl radical, should be faster than that of the radical from *n*-butyl ether yielding *n*-butyl radicals. Product analyses support this conclusion. In addition to almost quantitative yields of *t*-butyl alcohol and only traces of CO_2 in all of the systems, the reaction in isopropyl ether at 100° yielded 4.1 mol of acetone/mol of peroxide indicating that here a short-chain-induced decomposition of ether occurs presumably *via* the sequence in eq 6 and 7 competing with the peroxide chain. Similarly, decomposition of di-*t*-butyl peroxide in isopropyl ether at



(5)

$$(CH_3)_2CHO\dot{C}(CH_3)_2 \longrightarrow (CH_3)_2\dot{C}H + CH_3COCH_3 \quad (6)$$

$$(CH_3)_2\dot{C}H + (CH_3)_2CHOCH(CH_3)_2 \longrightarrow C_3H_8 + (CH_3)_2CHO\dot{C}(CH_3)_2 \quad (7)$$

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(13) M. S. Kharasch, J. L. Rowe, and W. H. Urry, *J. Org. Chem.*, **16**, 905 (1951).

(14) Acetaldehyde is some five times as reactive as ethanol toward *t*-butoxy radicals derived from *t*-butyl hypochlorite: C. Walling and M. J. Mintz, *J. Amer. Chem. Soc.*, **89**, 1515 (1967).

(15) C. Walling and A. Padwa, *ibid.*, **85**, 1593 (1963).

TABLE II

PRODUCTS OF PER ESTER–ALCOHOL REACTIONS

Per Ester	Alcohol	Temp, °C	t-Butyl[a] alcohol	Acetone[a]	Benzene[a]	Aldehyde[a] or ketone	CO_2[a]
Per benzoate	*sec*-Butyl	100	0.95	0.05	0.05	1.41[c]	0.04
Per benzoate	*sec*-Butyl[b]	100	0.82	0.14	0.05	0.86[c]	0.12
Per benzoate	*sec*-Butyl	85	0.94	0.06	0.04	1.42[c]	
Per acetate	*sec*-Butyl	100	0.61	0.03		0.81[c]	0.07
Per acetate	*sec*-Butyl[b]	100	0.89	0.12		0.90[c]	
Per acetate	*sec*-Butyl	85	0.64	0.04		0.84[c]	
Per benzoate	*n*-Butyl	100	0.89	0.07	0.05	0.06[d]	
Per benzoate	*n*-Butyl	85	0.96	0.04	0.03	0.13[d]	0.06
Per benzoate	*sec*-Octyl	100	0.95		0.18	0.98[e]	
Per benzoate	*sec*-Octyl	85	1.00		0.13	0.97[e]	
Per benzoate	*sec*-Octyl	75	0.98		0.16	0.96[e]	
Per acetate	*t*-Amyl	75	0.89	0.33		0.09[c]	

[a] In moles/mole of per ester. [b] 0.2 *M* in *o*-dichlorobenzene. [c] 2-Butanone. [d] *n*-Butyraldehyde. [e] 2-Octanone.

TABLE III

REACTIONS OF BENZOYL PEROXIDE WITH OTHER SUBSTRATES (70°)

Substrate	Solvent	k_a/k_d	Rel reactivity	t-$C_4H_9O\cdot$[a]
Diethyl ether	CCl_4	1.96	20	2.0
Benzaldehyde	Benzene	0.50	3.5	3.43
Isopropyl alcohol		*b*	1.45[c]	
Cyclohexane (std)		*b*	1.00	1.00
Anisole	Benzene	0.12	0.83	0.125
2,3,4-Trimethylpentane	Benzene	*d*	<0.1	0.53[e]
Cumene	Benzene	*d*	<0.1	0.47[e]

[a] At 0° unless noted. [b] *Cf.* Tables I and II. [c] Average of values in CCl_4, benzene, and chlorobenzene. [d] Indistinguishable from zero. [e] At 40°.

100° was found to give 9.5 mol of acetone per mole of peroxide decomposed, but here no acceleration in decomposition rate over that in inert solvents.

The relatively long chain reactions occurring with cyclic ethers we attribute to reversibility of the β scission in the cyclic case, *e.g.*, eq 8, since here the fragments cannot separate after scission has occurred.

(8)

Many such radical additions to carbonyl groups are now known, of which the conversion of ω-chlorobutyrophenone into 2-phenyltetrahydrofuran by tributyltin hydride[16] is perhaps the closest parallel, and we have noted a similar phenomena in the *t*-butyl hypochlorite chlorination of cyclic ethers, which also show relatively little scission.[14]

Except for this complication, the ether reaction appears to involve the same direction of peroxide cleavage as in the alcohol case. Mixed acylals should be the products from the cyclic ethers, and we have examined the higher boiling products from tetrahydropyran and *t*-butyl peracetate. Actually, acetic acid and 2-*t*-butoxytetrahydropyran were detected, but Sosnovsky[17] has shown that 2-acyloxy ethers of this structure readily exchange with *t*-butyl alcohol to give such products.

Mixed Diacyl Peroxides.—The decomposition of acetyl benzoyl peroxide in isopropyl alcohol has been studied by Rasuvaev and Latiaeva[18] who reported a rapid first-order reaction with benzoic acid, CO_2, acetone, and methane as major products. Since we had the peroxides available we have examined briefly the products of decomposition of acetyl benzoyl and acetyl *p*-chlorobenzoyl peroxides in several alcohol and ether solvents (Table IV). Qualitatively, our results confirm the earlier report.[18] Substantial yields of CO_2 and methane and low and zero yields of benzene and chlorobenzene respectively indicate that most of the chain is propagated *via* acetoxy and methyl radicals.

TABLE IV

REACTION PRODUCTS OF ACETYL BENZOYL PEROXIDES WITH ALCOHOLS AND ETHERS[a]

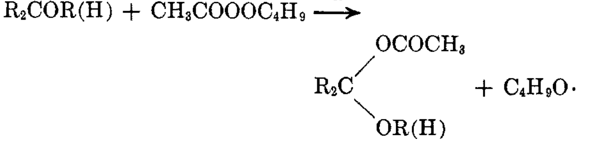
Solvent	Carbonyl compds	Benzene	CO_2	Other
sec-Butyl alcohol	1.40[c]	0.11	0.50	*e*
sec-Butyl alcohol[b]	1.36[c]			*e*
Isopropyl alcohol[b]	1.24[d]		0.42	*e*
Isopropyl ether	0.86[d]			*e, f*
Isopropyl ether	0.81[d]			*e, f*

[a] Acetyl benzoyl peroxide unless indicated at 60–70°. [b] Acetyl *p*-chlorobenzoyl peroxide. No chlorobenzene detected in products. [c] 2-Butanone. [d] Acetone. [e] Methane detected. [f] Propane detected.

Discussion

Our results confirm the induced chain nature of the fast decomposition of per esters in alcohol and ether solvents and provide further evidence of the ease of β scission of α-alkoxyalkyl radicals. More important, they indicate the point of attack of radicals on the per ester bond, showing that the major induced chain sequence is, *e.g.*, eq 9 and 10.

$$C_4H_9O\cdot + R_2CHOR(H) \xrightarrow{k_9} C_4H_9OH + R_2\dot{C}OR(H) \quad (9)$$



$$R_2\dot{C}OR(H) + CH_3COOOC_4H_9 \xrightarrow{k_{10}} R_2C\begin{matrix} \diagup OCOCH_3 \\ \diagdown OR(H) \end{matrix} + C_4H_9O\cdot \quad (10)$$

The most obvious explanation of this point of attack is a steric one, since displacement on the other peroxide oxygen involves the same crowding as in a neopentyl system, and is consistent with the failure of di-*t*-butyl peroxide to undergo this sort of reaction. Energetic considerations actually predict the opposite direction

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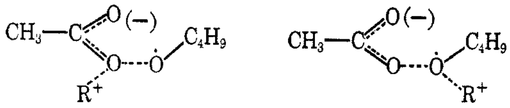
(16) L. W. Menapace and H. G. Kuivila, *J. Amer. Chem. Soc.*, **86**, 3047 (1964).

(17) G. Sosnovsky, *Tetrahedron*, **13**, 241 (1961).

(18) G. A. Rasuvaev and V. N. Latiaeva, *Zh. Obshch. Khim.*, **26**, 1986 (1956).

of attack which would liberate the resonance stabilized acyloxy radical. Since fast-induced decompositions of this sort are limited to radicals with strongly electron supplying groups, polar contributions are evidently very important in the transition state.[19] It could also be argued that A is a transition state involving more bonding and less charge separation than B,



A B

and it may be pertinent that the same direction of cleavage is observed in the redox reaction between metal ions, *e.g.*, Cu(I), and per esters.[20] In comparing induced decompositions with those of diacyl peroxides or interpreting rates in different solvents, over-all rates are not immediately illuminating since they involve the composite rate expression

$$-\mathrm{d}[\text{peroxide}]/\mathrm{d}t = (k_9k_{10}k_df/k_t)^{1/2}[\text{peroxide}][\text{RH}]^{1/2}$$

where k_9 and k_{10} are rate constants for the chain propagation steps, k_df is the rate constant for homolytic scission multiplied by the fraction of radicals starting chains, and k_t the rate constant for cross-termination, although Kato and Mashio[6] have argued that changes in k_{10} account for the major difference between solvents. Since β scission of α-alkoxyalkyl radicals from ethers is significantly more important with per esters than with benzoyl peroxide, we conclude that eq 10 is appreciably slower than eq 2 as might be expected on energetic grounds.

Finally, looking briefly at other unsymmetric peroxides, our results with acetyl benzoyl peroxide are consistent with either the "steric" or "polar" explanation. The induced decomposition of perbenzoic acid has been examined in both alcohols and ethers.[8] The authors conclude that the benzoyloxy radical is the chief chain carrier, but they obtain almost quantitative yields of benzoic acid and only traces of CO_2, much less than is found in benzoyl peroxide decompositions, so their interpretation (which would favor the "steric" explanation) seems in doubt.

Experimental Section

Materials. Solvents were commercial materials purified by conventional techniques. Per esters were also commercial samples purity checked by titration. Acetyl benzoyl peroxides were samples supplied by Dr. Z. Cekovic.

Kinetic experiments were run in sealed degassed tubes in suitable thermostats and reactions were followed either by iodimetry or ir spectrometry using the per ester carbonyl peak at 1773 cm^{-1}.

Products.—Product analyses were carried out by gas–liquid partition chromatography, calibrated by internal standards and peaks identified by retention time and actual collection. In examination of the product formed, *t*-butyl peracetate and tetrahydropyran, two high boiling peaks were collected. One was identified as acetic acid, but the other could not be obtained entirely pure. It was tentatively identified as 2-butoxytetrahyropyran on the basis of ir (ether and *t*-butyl absorption) and mass spectra (parent peak at *m/e* 158, strong peak at *m/e* 85 corresponding to cleavage of a *t*-butoxy group).

Registry No.—*sec*-Butyl alcohol, 78-92-2; *n*-butyl alcohol, 71-36-3; isopropyl alcohol, 67-63-0; *t*-amyl alcohol, 75-85-4; benzene, 71-43-2; *t*-butyl perbenzoate ester, 614-45-9; *t*-butyl peracetate ester, 107-71-1; *sec*-octyl alcohol, 123-96-6; isopropyl ether, 108-20-3; acetyl benzoyl peroxide, 644-31-5.

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[19] F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 191 (1950).

[20] J. K. Kochi, *Tetrahedron*, **18**, 483 (1962).

Oxidation by Metal Oxides. IV. Oxidation of Organic Compounds Using Nickel Peroxide

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N-Benzylaniline, on oxidation with nickel peroxide, gave a mixture of N-benzyl-N-phenyl-N′-benzylidene-*p*-phenylenediamine and benzylideneaniline. Similarly, N-benzyl-*o*-toluidine gave N-benzyl-N-*o*-tolyl-N′-benzylidene-2-methyl-1,4-diaminobenzene and benzylidene-*o*-toluidine, respectively. The oxidation of N-benzyl-*p*-toluidine, N-benzyl-*p*-chloroaniline, N-benzyl-*p*-anisidine, and N-benzyl-*m*-toluidine with nickel peroxide, on the other hand, gave a mixture of the corresponding benzylideneanilines and N,N′-dibenzyl-N,N′-diphenylhydrazines, respectively. The oxidation of dibenzylamine gave a mixture of N-benzylidenebenzylamine, benzaldehyde, and benzonitrile. Diphenylmethane and fluorene, under similar conditions, were converted into benzophenone and fluorenone, respectively, in excellent yields. Oxidation of 2,6-di-*t*-butylphenol gave exclusively 2,6,2′,6′-tetra-*t*-butyldiphenoquinone. Aldehyde and ketone phenylhydrazones, benzil osazone, and pyrazolines gave products similar to those obtained from the oxidation of these substances with manganese dioxide.

Nickel peroxide[2] has been used in the oxidation of a variety of organic compounds. Quite recently, the oxidation of several substrates such as alcohols,[3] glycols,[4] hydroxy acids,[4] 4-hydroxytriphenylmethanes,[5] aliphatic and aromatic primary amines,[6,7] aldehydes,[8] Schiff's bases,[9] and hydrazones of aldehydes and ketones[10] have been tried. During the course of the present investigation, we have examined the oxidation

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[1] To whom inquires should be addressed.

[2] Nickel peroxide is the name commonly used to designate the black, hydrous, higher oxides of nickel which are formed by the reaction between a strong oxidizing agent, such as one of the hypochlorites and freshly precipitated nickelous hydroxide. Its structure is not clearly understood.

[3] K. Nakagawa, R. Konaka, and T. Nakata, *J. Org. Chem.*, **27**, 1597 (1962).

[4] K. Nakagawa, K. Igano, and J. Sugita, *Chem. Pharm. Bull.* (Tokyo), **12**, 403 (1964).

[5] H. D. Becker, *J. Org. Chem.*, **32**, 2943 (1967).

[6] K. Nakagawa and T. Tsuji, *Chem. Pharm. Bull.* (Tokyo), **11**, 298 (1963).

[7] K. Nakagawa and H. Onoue, *Tetrahedron Lett.*, 1433 (1965).

[8] K. Nakagawa, H. Onoue, and K. Minami, *Chem. Commun.*, 17 (1966).

[9] K. Nakagawa, H. Onoue, and J. Sugita, *Chem. Pharm. Bull.* (Tokyo), **12**, 1135 (1964).

[10] K. Nakagawa, H. Onoue, and K. Minami, *Chem. Commun.*, 730 (1966).