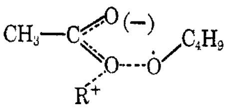
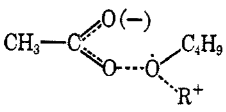
of attack which would liberate the resonance stabilized acyloxy radical. Since fast-induced decompositions of this sort are limited to radicals with strongly electron supplying groups, polar contributions are evidently very important in the transition state.[19] It could also be argued that A is a transition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

[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**, 296 (1963).

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

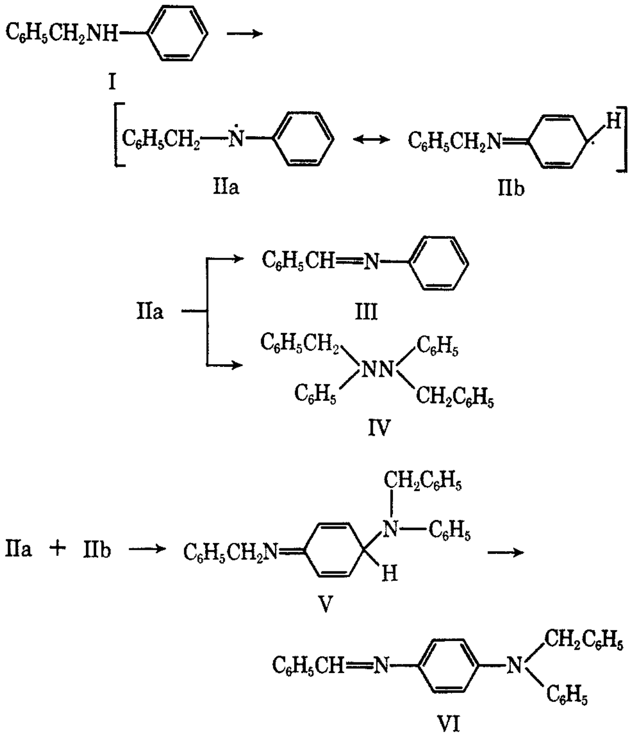
[8] K. Nakagawa, H. Onoue, and K. Minami, *Chem. Commun.*, 17 (1966).

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

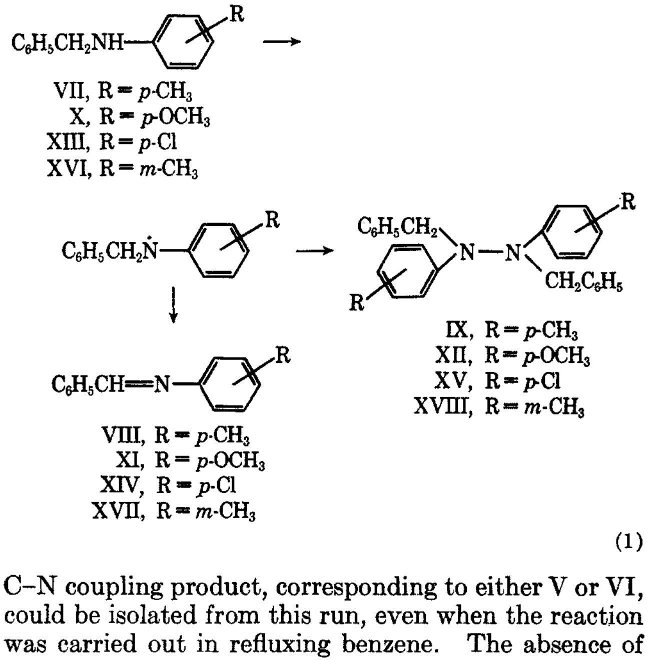
[10] K. Nakagawa, H. Onoue, and K. Minami, *Chem. Commun.*, 730 (1966).

of several organic compounds with nickel peroxide with a view to studying the nature of the products formed from these reactions. Thus, the oxidation of N-benzylanilines, dibenzylamine, diphenylmethane, fluorene, 2,6-di-*t*-butylphenol, aldehyde and ketone phenylhydrazones, benzil osazone, chalcone phenylhydrazones, and pyrazolines have been carried out using nickel peroxide in a suitable solvent like benzene.

Scheme I



Manganese dioxide oxidation of N-benzylanilines has been reported to give rise to the corresponding benzylideneanilines, in good yields.[11] In the present investigation, we have examined the oxidation of several N-benzylanilines with nickel peroxide. N-Benzylaniline (I), for example in benzene medium at room temperature, gave a 5% yield of the expected benzylideneaniline (III) and a 45% yield of a product, mp 136°, which was identified as N-benzyl-N-phenyl-N′-benzylidene-*p*-phenylenediamine (VI). The structure of VI was established on the basis of elemental analysis, molecular weight, and spectroscopic evidences. The ir spectrum of VI did not show the presence of any NH absorption bands. The uv spectrum of VI was characterized by the presence of strong absorption bands at 365 mμ (ϵ 13,000), 380 (14,000), and 403 (8200), respectively. The spectrum of VI was very similar to that of N-phenyl-N′-benzylidene-*p*-phenylenediamine,[12] which absorbs at 360 (12,590), 378 (13,490), and 404 (7940), respectively. The nmr spectrum of VI showed a sharp singlet at τ 1.9 (1 H) due to the —CH═N— proton.[13] In addition, the spectrum showed a singlet at 5.0 (2 H) due to the methylene protons and a multiplet centered around 3 (19 H) due to aromatic protons. When the oxidation of I was carried out in refluxing benzene, a 29% yield of III and a 35% yield of VI were formed. A probable route to the formation of products like III and VI is shown in Scheme I. In this scheme, we assume that a hydrogen atom is removed from I by nickel peroxide giving rise to a radical intermediate, which may be represented by its mesomeric forms, IIa and IIb.[14] Further abstraction of a hydrogen atom from II by nickel peroxide will lead to the Schiff base III. A second mode of reaction is the dimerization of II through an N–N coupling reaction to give the tetrasubstituted hydrazine IV. However, from the reaction of I with nickel peroxide, we could not isolate this hydrazine.[15] The radical intermediate II can also combine with itself through a C–N coupling process to give the intermediate V which can then undergo oxidation to give N-benzyl-N-phenyl-N′-benzylidene-*p*-phenylenediamine (VI). If a dimerization of the two mesomeric forms of the intermediate, IIa and IIb, is involved, then such a reaction will not be favored if there is a *para* substituent in the phenyl ring. In this connection, we have examined the oxidation of N-benzyl-*p*-toluidine (VII). Treatment of VII with nickel peroxide in benzene at room temperature gave a 24% yield of benzylidene-*p*-toluidine (VIII) and a 64% yield of N,N′-dibenzyl-N,N′-di-*p*-tolylhydrazine (IX). None of the C–N coupling product, corresponding to either V or VI, could be isolated from this run. When the oxidation of VII was carried out for 6 hr at room temperature, a 32% yield of VIII and 54% yield of IX were obtained. Similarly, the oxidation of N-benzyl-*p*-anisidine and N-benzyl-*p*-chloroaniline gave 37 and 17% yields of the corresponding Schiff bases, XI and XIV, and 20% each of the hydrazines XII and XV, respectively. Under similar conditions, N-benzyl-*m*-toluidine (XVI) gave a 28% yield of benzylidene-*m*-toluidine (XVII) and a 39% yield of N,N′-dibenzyl-N,-N′-di-*m*-tolylhydrazine (XVIII, eq 1). None of the C–N coupling product, corresponding to either V or VI, could be isolated from this run, even when the reaction was carried out in refluxing benzene. The absence of any C–N coupling product may be explained on the



(1)

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[11] E. F. Pratt and T. P. McGovern, *J. Org. Chem.*, **29**, 1540 (1964).

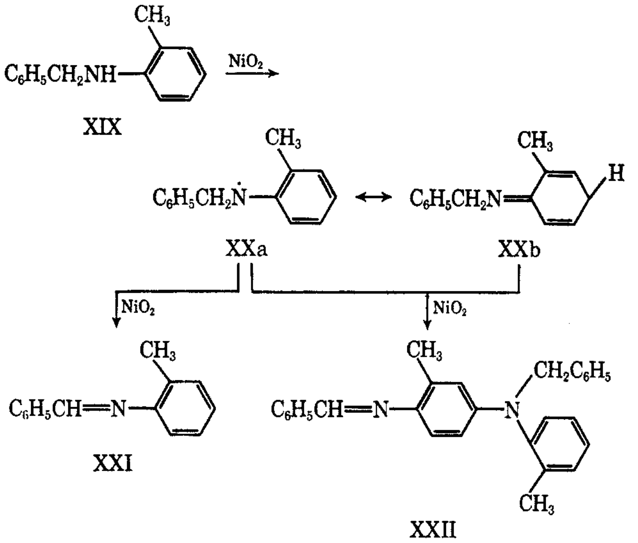
[12] P. Heücke, *Ann.*, **255**, 189 (1889).

[13] High Resolution NMR Spectra Catalog, Vol. 2, Varian Associates, Palo Alto, Calif., Spectra No. 663 and 673.

[14] The exact nature of this hydrogen abstraction is not clear, but appears to be analogous to the oxidation of *o*-phenylenediamine, using nickel peroxide.[7]

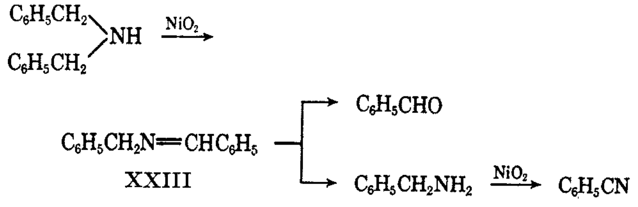
[15] An authentic sample of IV, mp 127°, was prepared by a reported procedure [J. W. B. Reesor and G. F. Wright, *J. Org. Chem.*, **22**, 375 (1957)] for comparison purposes.

basis of a steric effect due to the presence of the methyl group in the intermediate II, *ortho* to the carbon atom undergoing the coupling reaction. If this explanation is valid, then one would infer that such an effect should not be operating in the case of a compound like N-benzyl-*o*-toluidine (XIX). Oxidation of XIX with nickel peroxide gave a 3% yield of the Schiff base, benzylidene-*o*-toluidine (XXI), and a 45% yield of N-benzyl-N-*o*-tolyl-N′-benzylidene-2-methyl-1,4-diaminobenzene (XXII). None of the tetrasubstituted hydrazine could be isolated. The formation of XXII, arising because of a C–N coupling of radical intermediates like XX, fully supports the view that substituent groups in the phenyl ring significantly alter the course of these oxidations (eq 2).



(2)

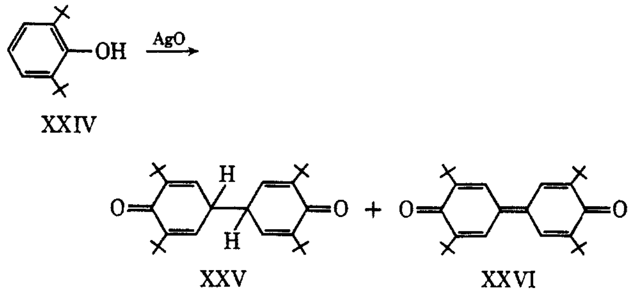
In continuation with our studies, we have attempted the oxidation of both N-benzyl-α-naphthylamine and dibenzylamine with nickel peroxide. N-Benzyl-α-naphthylamine was quite resistant to oxidation, both at room temperature and also in refluxing benzene. The exact reason for this inertness is not very clear. Oxidation of dibenzylamine, on the other hand, gave a mixture of products consisting of 43% N-benzylidenebenzylamine (XXIII), 48% benzaldehyde, and 40% benzonitrile. Both benzaldehyde and benzonitrile may arise through an oxidative fragmentation of XXIII. In this connection, it might be mentioned that the oxidation of dibenzylamine with manganese dioxide gives exclusively XXIII.[11] (See eq 3.)



(3)

Diarylmethanes have been oxidized to the corresponding ketones using manganese dioxide.[16] We find that nickel peroxide is also an excellent reagent for converting diarylmethanes to the corresponding ketones. Thus, when diphenylmethane was treated with nickel peroxide, in the absence of any solvent around 110°, a 79% yield of benzophenone was formed. Similarly, the oxidation of fluorene gave a 66% yield of fluorenone.

Several reagents have been used in the oxidation of phenols.[17] 2,6-Di-*t*-butylphenol (XXIV), for example, has been oxidized by different reagents such as lead dioxide,[18] silver oxide[19] and potassium ferricyanide[20] to give 2,6,2′,6′-tetra-*t*-butyldiphenoquinone (XXVI) as the major product. Besides the diphenoquinone XXVI other products are also formed in these reactions. Thus, in the oxidation of XXIV with lead dioxide, a mixture of XXVI and 2,6-di-*t*-butylbenzoquinone is formed, whereas oxidation of XXIV in the presence of silver oxide gives a mixture of XXVI and the dihydro intermediate XXV (eq 4). In this investigation, we have studied the oxidation of XXIV using nickel peroxide.



(4)

Treatment of XXIV in benzene for 2 hr gave a 87% yield of the diphenoquinone XXVI. No other product could be isolated from this run.

In earlier communications, we have reported the oxidation of several organic compounds such as aldehyde and ketone phenylhydrazones,[21] benzil osazone,[21] chalcone phenylhydrazones,[22] and pyrazolines[22] with manganese dioxide. Oxidation of benzaldehyde phenylhydrazone, for example, gives several products such as 1,2-(bisphenylazo)-1,2-diphenylethane (XXVII), N$^{\alpha}$,N$^{\beta'}$-diphenyl-N$^{\beta}$-benzalbenzhydrazidine (XXVIII), benzil osazone (XXIX), 2,4,5-triphenyl-1,2,3-triazole (XXX), and 2,3-diphenyl-1,4-dibenzaltetrazene (XXXI, eq 5). Benzophenone phenylhydrazone, on the other hand, gives a mixture of benzophenone and biphenyl. We have studied the reaction of few aldehyde and ketone phenylhydrazones with nickel peroxide. In contrast to the oxidation of aldehyde phenylhydrazones with manganese dioxide, only bisazoalkanes were formed during the oxidation of these compounds with nickel peroxide. Thus, the oxidation of benzaldehyde phenylhydrazone, *p*-tolualdehyde phenylhydrazone, and *p*-anisaldehyde phenylhydrazone gave 1,2-diphenyl-1,2-(bisphenylazo)ethane (65%), 1,2-di-*p*-tolyl-1,2-(bisphenylazo)ethane (80%), and 1,2-di-*p*-anisyl-1,2-(bisphenylazo)ethane (84%), respectively. Oxidation of benzophenone phenylhydrazone gave a mixture of biphenyl (10%) and benzophenone (60%), as in the case of manganese dioxide oxidation.

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(16) E. F. Pratt and S. P. Suskind, *J. Org. Chem.*, **28**, 638 (1963).

(17) For a recent review on the oxidative coupling of phenols, see A. I. Scott, *Quart. Rev.* (London), **19**, 1 (1965).

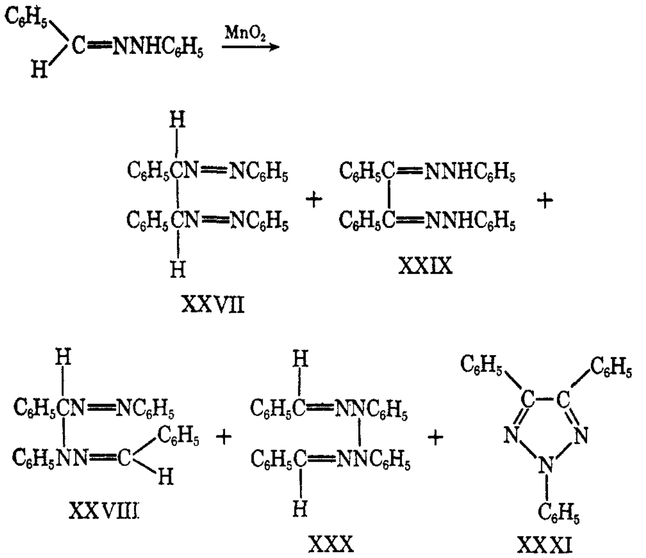
(18) C. D. Cook and E. S. English, *J. Org. Chem.*, **23**, 755 (1958).

(19) H. S. Blanchard, *ibid.*, **25**, 264 (1960).

(20) M. S. Kharasch and B. S. Joshi, *ibid.*, **22**, 1439 (1957).

(21) I. Bhatnagar and M. V. George, *ibid.*, **32**, 2252 (1967).

(22) I. Bhatnagar and M. V. George, *Tetrahedron*, **24**, 1293 (1968).



(5)

In continuation of our work, we have studied the oxidation of benzil osazone, chalcone phenylhydrazones, and pyrazolines with nickel peroxide. Thus, the oxidation of benzil osazone gave chiefly 1,3,4-triphenyltriazole (39%), along with a small amount of azobenzene. The oxidation of *m*-nitrochalcone phenylhydrazone, on the other hand, gave a 53% yield of 1,3-diphenyl-5-*m*-nitrophenylpyrazole. Nickel peroxide oxidations of 1,5-diphenyl-3-styrylpyrazoline, 1,5-diphenyl-3-(*p*-bromophenyl)pyrazoline, and 1,3-diphenyl-3-thienylpyrazoline afforded the corresponding pyrazoles in 76, 95, and 93% yields, respectively. Thus, nickel peroxide and manganese dioxide behave more or less similarly in these oxidations.

Experimental Section

All melting points are uncorrected. Ir spectra were determined on a Perkin-Elmer, Model 137, Infracord spectrometer, and uv spectra were determined on a Cary 14-R spectrophotometer. Nmr traces were recorded on a Varian HR-100 spectrometer.

Starting Materials.—Nickel peroxide (65 g) was prepared by the treatment of nickel sulfate (130 g) with a mixture of sodium hypochlorite (6% solution, 300 ml) and sodium hydroxide (42 g), as per a reported procedure.[3] The oxygen content of this sample was found to be of the order of 2.8×10^{-3} g-atom per gram of nickel peroxide.[23] N-Benzyl-*o*-toluidine, N-benzyl-*m*-toluidine, N-benzyl-*p*-toluidine, N-benzyl-*p*-anisidine, N-benzyl-*p*-chloroaniline, and N-benzyl-α-naphthylamine were prepared by the reaction between benzyl alcohol and the corresponding amines.[24] All the starting materials, excepting 2,6-di-*t*-butylphenol, were prepared by standard procedures. 2,6-Di-*t*-butylphenol was obtained from the Aldrich Chemical Co.

Oxidation of Benzylaniline (I).—A mixture of I (1 g, 0.005 mol) and nickel peroxide (3 g) was stirred in dry benzene (75 ml) at room temperature (22°) for 4 hr. Removal of the solvent and inorganic material gave a red viscous liquid which on treatment with ethanol gave 0.65 g (65%) of crude N-benzyl-N-phenyl-N′-benzylidene-*p*-phenylenediamine (VI), mp 125–130°. Recrystallization from cyclohexane gave 0.45 g (45%) of a pure sample of VI, mp 136°.

Anal. Calcd for $C_{26}H_{22}N_2$: C, 86.1; H, 6.08; N, 7.7; mol wt, 362. Found: C, 86.28; H, 6.1; N, 7.56; mol wt (mass spectrometry), 362.

The ir spectrum (KBr) of VI did not show any NH absorption band.

The uv spectrum of VI in cyclohexane was characterized by the following absorption maxima: 255 mμ (ε 21,300), 365 sh (13,000), 380 (14,100), and 403 (8200).

The nmr spectrum of VI ($CDCl_3$) showed a singlet at τ 5.0 (2 H) due to methylene protons, a multiplet centered around 3.0 (19 H) due to aromatic protons, and a sharp singlet at 1.9 (1 H) due to the —CH=N— proton.

Work-up of the mother liquor, after removal of VI, gave 0.15 g (15%) of unchanged benzylaniline, mp and mmp 37°, and 0.05 g (5%) of benzylideneaniline (III), mp and mmp 65°.

In a repeat experiment, a mixture of 1 g (0.005 mol) of I and 3 g of nickel peroxide was refluxed in benzene (75 ml) for 6 hr. Work-up of the mixture gave 0.35 g (35%) of VI and 0.3 g (29%) of III.

In another run, a mixture of 1 g (0.005 mol) of I and 3 g of nickel peroxide, having a slightly higher activity (active oxygen content, 3.3×10^{-3} g-atom per gram of nickel peroxide), was stirred in benzene (75 ml) at room temperature for 4 hr. Work-up of the mixture yielded 0.43 g (43%) of VI and 0.17 g (17%) of III.

Oxidation of N-Benzyl-*p*-toluidine (VII).—A mixture of VII (2 g, 0.01 mol) and nickel peroxide (6 g) was stirred in benzene (75 ml) for 2 hr at room temperature. Work-up in the usual manner gave 1.3 g (64%) of a white solid, mp 124° (after recrystallization from ether), which was identified as N,N′-dibenzyl-N,N′-di-*p*-tolylhydrazine (IX).

Anal. Calcd for $C_{28}H_{28}N_2$: C, 85.67; H, 7.19; N, 7.14; mol wt, 392. Found: C, 85.86; H, 7.1; N, 7.17; mol wt (mass spectrometry), 392.

The uv spectrum (cyclohexane) of IX showed the following absorption maxima: 252 mμ (ε 26,000) and 302 (5700).

The nmr spectrum ($CDCl_3$) of IX showed a singlet at τ 7.73 (6 H) due to methyl protons, a singlet around 5.2 (4 H) due to methylene protons, and a multiplet centered around 2.9 (18 H) due to aromatic protons.

Work-up of the mother liquor gave 0.47 g (14%) of benzylidene-*p*-toluidine (VIII), mp and mmp 35°.

In a repeat run, the same quantities of starting materials were refluxed in benzene for 6 hr and worked up in the usual manner to give 1.1 g (54%) of IX, mp 124°, and 0.65 g (32%) of VIII, mp 35°.

Oxidation of N-Benzyl-*p*-anisidine (X).—Treatment of 1 g (0.0047 mol) of X with nickel peroxide (2.5 g) in benzene (50 ml) for 2 hr at room temperature and work-up of the reaction mixture gave 0.2 g (20%) of N,N′-dibenzyl-N,N′-dianisylhydrazine (XII), mp 121°, after recrystallization from ether.

Anal. Calcd for $C_{28}H_{28}O_2N_2$: C, 79.22; H, 6.65; N, 6.6; mol wt, 424. Found: C, 78.83; H, 6.5; N, 6.48; mol wt (mass spectrometry), 424.

The uv spectrum (cyclohexane) of XII showed the following absorption maxima: 250 mμ (ε 28,100) and 310 (8050).

Work-up of the mother liquor gave 0.38 g (37%) of benzylidene-*p*-anisidine (XI), mp and mmp 72°.

Oxidation of N-Benzyl-*p*-chloroaniline (XIII).—A mixture of 1 g (0.0046 g) of XIII and 3 g of nickel peroxide was stirred in benzene (75 ml) for 4 hr at room temperature. Removal of the inorganic material and solvent gave 0.4 g of a crude product, which when recrystallized from ether gave 0.2 g (20%) of N,N′-dibenzyl-N,N′-di-*p*-chlorophenylhydrazine (XV), mp 109°.

Anal. Calcd for $C_{26}H_{22}N_2Cl_2$: C, 72.03; H, 5.8; N, 6.4; mol wt, 432. Found: C, 71.7; H, 5.5; N, 6.4; mol wt (mass spectrometry), 432.

The uv spectrum (cyclohexane) of XV showed the following absorption maxima: 256 mμ (ε 27,200) and 304 (4100).

Work-up of the mother liquor gave 0.2 g (20%) of unchanged starting material, mp and mmp 45°, and 0.18 g (17%) of N-benzylidene-*p*-chloroaniline (XIV), mp and mmp 62°.

Oxidation of N-Benzyl-*m*-toluidine (XVI).—Treatment of 1 g (0.0051 mol) of XVI with 3 g of nickel peroxide in benzene for 4 hr and work-up in the usual manner gave 0.4 g (39%) of N,N′-dibenzyl-N,N′-di-*m*-tolylhydrazine (XVIII), mp 159°, after recrystallization from ether.

Anal. Calcd for $C_{28}H_{28}N_2$: C, 85.67; H, 7.19; N, 7.14; mol wt, 392. Found: C, 85.5; H, 6.98; N, 7.18; mol wt (mass spectrometry), 392.

The uv spectrum (cyclohexane) of XVIII showed the following absorption maxima: 250 mμ (ε 21,300) and 295 (4200).

From the mother liquor, 0.29 g (28%) of benzylidene-*m*-toluidine (XVII) was isolated.

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[23] A considerable portion of the available oxygen in nickel peroxide is lost gradually when it is heated, but if the sample is stored in a desiccator and kept in a cool place, the activity remains unchanged for about 1 month.

[24] Y. Sprinzak, *J. Amer. Chem. Soc.*, **79**, 3207 (1957).

In a repeat experiment, 1 g (0.0051 mol) of XVI and 3 g of nickel peroxide was stirred in benzene (75 ml) for 6 hr at room temperature. Work-up of the mixture gave 0.49 g (48%) of XVIII and 0.37 g (36%) of XVII.

Oxidation of N-Benzyl-*o*-toluidine (XIX).—A mixture of 1 g (0.0051 mol) of XIX and 3 g of nickel peroxide was stirred in benzene for 5 hr at room temperature. Work-up as in the previous cases gave 0.45 g (45%) of N-benzyl-N-*o*-tolyl-N′-benzylidene-2-methyl-1,4-diaminobenzene (XXII), mp 103–104°, after recrystallization from *n*-hexane.

Anal. Calcd for $C_{28}H_{26}N_2$: C, 86.1; H, 6.6; N, 7.1; mol wt, 390. Found: C, 86.21; H, 6.5; N, 7.01; mol wt (mass spectrometry), 390.

The uv spectrum (cyclohexane) of XXII showed the following absorption maxima: 255 mμ (ϵ 22,450), 365 (13,900), 385 (16,300), 404 (11,800).

The nmr spectrum ($CDCl_3$) of XXII showed two singlets at τ 7.81 (3 H) and 7.66 (3 H) corresponding to two methyl groups. In addition, the spectrum showed a singlet at 5.1 (2 H) due to the methylene group, a multiplet centered around 2.9 (17 H) due to aromatic protons, and a singlet at 1.7 (1 H) due to the —CH=N— proton.

Work-up of the mother liquor gave 0.03 g (3%) of benzylidene-*o*-toluidine (XXI), bp 176° (15 mm), identified by comparison of its ir spectrum with that of an authentic sample. In addition, 0.15 g (15%) of unchanged starting material (XIX), mp and mmp 56°, could also be isolated.

Oxidation of N-Benzyl-α-naphthylamine.—A mixture of N-benzyl-α-naphthylamine (1 g, 0.004 mol) and 3 g of nickel peroxide was stirred in benzene (75 ml) at room temperature for 4 hr. Work-up of the mixture gave 0.9 g (90%) of the unchanged starting material, mp and mmp 66°.

In a repeat run, the same quantities of the starting materials were refluxed in benzene for 6 hr. Work-up in the usual manner resulted in the recovery of 0.9 g (90%) of unchanged N-benzyl-α-naphthylamine.

Oxidation of Dibenzylamine.—Dibenzylamine (3 g, 0.015 mol) and nickel peroxide (9 g) were refluxed in dry benzene for 6 hr. Removal of the inorganic material and the solvent gave a yellow liquid, which was fractionally distilled to give 1.3 g (43%) of benzylidenebenzylamine (XXIII), bp 200° (10 mm), 0.78 g (48%) of benzaldehyde, bp 62° (10 mm), and 0.61 g (40%) of benzonitrile, bp 71° (10 mm). Identities of these products were confirmed, through a comparison of their infrared spectra with those of authentic samples.

Oxidation of Diphenylmethane. A. In Refluxing Xylene.—A mixture of 1 g (0.006 mol) of diphenylmethane and 10 g of nickel peroxide was refluxed in 100 ml of xylene for 5 hr. Removal of the solvent and the inorganic material gave a viscous liquid which on treatment with petroleum ether (bp 60–80°) gave 0.5 g (45%) of benzophenone, mp and mmp 48°.

B. Without Solvent.—Diphenylmethane (1 g, 0.006 mol) and nickel peroxide (10 g) were heated together for 5 hr in an oil bath around 110°. Repeated extraction of the mixture with benzene and fractional crystallization of the product from petroleum ether (bp 60–80°) gave 0.85 g (79%) of benzophenone, mp and mmp 48°.

Oxidation of Fluorene.—Heating a mixture of fluorene (1 g, 0.006 mol) and nickel peroxide (6 g) for 5 hr around 110° and work-up as in the previous case gave 0.7 g (66%) of fluorenone, identified through its 2,4-dinitrophenylhydrazone, mp and mmp 302°.

Oxidation of 2,6-Di-*t*-butylphenol.—Treatment of 1.5 g (0.007 mol) of 2,6-di-*t*-butylphenol with 4.5 g of nickel peroxide in benzene (75 ml) for 2 hr and work-up in the usual manner gave 1.3 g (87%) of 2,6,2′,6′-tetra-*t*-butyldiphenoquinone, mp and mmp 246°.[18]

Oxidation of Aldehyde Phenylhydrazones.—The general procedure was to treat 0.051 mol of the aldehyde phenylhydrazone with 2 g of nickel peroxide in dry benzene for 1 hr and to work-up the mixture by removing the inorganic material and the solvent, followed by recrystallization from benzene.

Oxidation of benzaldehyde phenylhydrazone gave 0.6 g (65%) of 1,2-diphenyl-1,2-(bisphenylazo)ethane (XXVII), mp and mmp 184°. From the mother liquor, 0.2 g (20%) of the unchanged starting material was also isolated.

Oxidation of *p*-tolualdehyde phenylhydrazone gave 0.81 g (80%) of 1,2-di-*p*-tolyl-1,2-(bisphenylazo)ethane, mp and mmp 170°.

p-Anisaldehydephenylhydrazone gave 0.85 g (85%) of 1,2-di-*p*-anisyl-1,2-(bisphenylazo)ethane, mp and mmp 164–165°.

Oxidation of Benzophenone Phenylhydrazone.—Refluxing a mixture of benzophenone phenylhydrazone (1 g, 0.004 mol) and nickel peroxide (8 g) with dry benzene (50 ml) for 3 hr and work-up in the usual manner gave a crude mixture which when chromatographed on alumina using petroleum ether (bp 60–80°) yielded 0.1 g (10%) of biphenyl, mp and mmp 70°. Further elution of the column with a mixture of benzene and chloroform gave 0.8 g (60%) of benzophenone, identified through its 2,4-dinitrophenylhydrazone, mp and mmp 239°.

Oxidation of Benzil Osazone.—A mixture of benzil osazone (1 g, 0.0025 mol) and 5 g of nickel peroxide in benzene (75 ml) was stirred at room temperature for 4 hr. Removal of the solvent and inorganic material gave a crude product which was chromatographed on alumina. Elution with petroleum ether (bp 60–80°) gave 0.02 g (5%) of biphenyl, mp and mmp 70°. Further elution with petroleum ether gave a trace of azobenzene, identified on a tlc plate by comparison with an authentic sample. Repeated elution of the alumina column with petroleum ether (bp 60–80°) gave 0.3 g (39%) of 1,3,4-triphenyltriazole, mp and mmp 120°.

Oxidation of *m*-Nitrochalcone Phenylhydrazone.—Treatment of 1.5 g (0.004 mol) of *m*-nitrochalcone phenylhydrazone with 3 g of nickel peroxide in dry benzene (75 ml) for 3 hr at room temperature and work-up in the usual manner, employing chromatography over alumina, gave 0.8 g (53%) of 1,3-diphenyl-5-*m*-nitrophenylpyrazole, mp and mmp 130°.

Oxidation of Pyrazolines.—In a typical run, 1 g (0.003 mol) of the pyrazoline and 2.5 g of nickel peroxide were stirred in refluxing benzene (75 ml) for 3 hr. After removal of the inorganic material, the solvent was removed under vacuum, and the products were recrystallized from a mixture of benzene and ethanol.

Oxidation of 1,5-diphenyl-3-styrylpyrazoline gave a 76% yield of 1,5-diphenyl-3-styrylpyrazole, mp and mmp 139°.

1,5-Diphenyl-3-(*p*-bromophenyl)pyrazoline gave a 95% yield of 1,5-diphenyl-3-(*p*-bromophenyl)pyrazole, mp and mmp 159°.

Oxidation of 1,3-diphenyl-5-thienylpyrazoline gave a 93% yield of a 1,3-diphenyl-5-thienylpyrazole, mp and mmp 112°.

Registry No.—Nickel peroxide, 12035-36-8; VI, 17393-42-9; IX, 17393-43-0; XII, 17414-50-5; XV, 17448-27-0; XVIII, 17393-44-1; XXII, 17393-45-2; XXIII, 780-25-6.

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