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OXIDATION WITH METAL OXIDES—VI
OXIDATION OF BENZOYLHYDRAZONES OF ALDEHYDES, KETONES AND 1,2-DIKETONES WITH NICKEL PEROXIDE

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Abstract – Benzaldehyde benzoylhydrazone on oxidation with nickel peroxide gives a mixture of 2,5-diphenyl-1,3,4-oxadiazole and nickel-bis-benzaldehyde benzoylhydrazone. Similarly, *p*-tolualdehyde benzoylhydrazone, *o*-methoxybenzaldehyde benzoylhydrazone and anisaldehyde benzoylhydrazone give the corresponding 1,3,4-oxadiazole derivatives and nickel complexes. Acetophenone benzoylhydrazone, on the other hand, gives a mixture of acetophenone and methylbenzylidene-∝-dibenzoylamino-∝-methylbenzylamine. Similarly, propiophenone benzoylhydrazone and benzophenone benzoylhydrazone give the corresponding ketones and Schiff's bases. Biacetyl bisbenzoylhydrazone and benzil bisbenzoylhydrazone on oxidation with nickel peroxide in chloroform give the corresponding enol-benzoates and nickel complexes. In contrast, phenylmethylglyoxal bisbenzoylhydrazone gives only the enolbenzoate under analogous conditions. Phenylglyoxal bisbenzoylhydrazone on oxidation with nickel peroxide gives a mixture of products consisting of 1-dibenzoylamino-4-phenyl-1,2,3-triazole, 1-benzoylamino-4-phenyl-1,2,3-triazole and nickel-bis-phenyl-2-(5-phenyl-1,3,4-oxadiazolyl)-ketone benzoylhydrazone. Similarly, 4-methoxyphenylglyoxal bisbenzoylhydrazone gives a mixture of triazoles and the corresponding nickel complex.

RESULTS AND DISCUSSION

In continuation of our work on the oxidation of bisphenylhydrazones of 1,2-diketones,[1] we have examined the oxidation of benzoylhydrazones of aldehydes, ketones and 1,2-diketones with nickel peroxide to study the nature of the products formed in these cases.

Aldehyde benzoylhydrazones have been oxidized by several reagents like alkaline potassium ferricyanide,[2] amyl nitrite,[2] chlorine[3] and iodine[2] and the major products in these oxidations have been characterized as 1,3,4-oxadiazole derivatives. In the present studies, we have examined the reaction of several aldehyde benzoylhydrazones with nickel peroxide. Benzaldehyde benzoylhydrazone (**1a**), for example, on treatment with nickel peroxide in refluxing chloroform gives a 30% yield of 2,5-diphenyl-1,3,4-oxadiazole (**6a**) and a 47% yield of a nickel complex, melting at 306–307° and identified as trans-nickel-bis-benzaldehyde benzoylhydrazone (**7a**). The structure of **7a** has been established on the basis of elemental analysis and spectral data. The IR spectrum of **7a** does not show the presence of either N—H or C=O bands but shows the presence of a C=N band at 1625 cm^{-1}. Magnetic moment measurements indicate that the nickel complex is diamagnetic and has a square planar configuration.

The formation of both **6a** and **7a** in the oxidation of **1a** can be explained in terms of the pathway shown in Scheme 1. In this scheme, we assume that nickel peroxide abstracts an H atom from benzaldehyde benzoylhydrazone (**1a**) giving rise to a resonance stabilised radical intermediate **2**, which can be represented by any one of the canonical forms like **3** or **4**. The radical intermediate **4** can undergo an intramolecular cyclization to **5**, which on further loss of an H atom will lead to the oxadiazole **6a**.

The actual mode of formation of **7a** is not very clear. A probable route would involve the reaction of the radical intermediate **4** with nickel hydroxide, a possible constituent of the oxide that is used for oxidation. Alternatively, an ionic pathway could also be suggested for the formation of **7a**.

Similarly, the oxidation of *p*-tolualdehyde benzoylhydrazone (**1b**), *o*-methoxybenzaldehyde benzoylhydrazone (**1c**) and anisaldehyde benzoylhydrazone (**1d**) with nickel peroxide in chloroform give the corresponding 1,3,4-oxadiazole derivatives **6b–d** in yields ranging between 20–35% and the nickel complexes **7b–d** in 23–41% yields. In the case of *o*-methoxybenzaldehyde benzoylhydrazone, however, in addition to the oxadiazole derivative **6c** and the nickel complex **7c**, a 20% yield of *o*-methoxybenzaldehyde (**9c**) is also formed, which is isolated through its 2,4-dinitrophenylhydrazone. The formation of **9c** in this reaction may be explained through the hydroxy intermediate **8c** formed from **3**, which can subsequently undergo oxidative fragmentation as shown in Scheme 1.

The oxidation of only very few ketone benzoyl-

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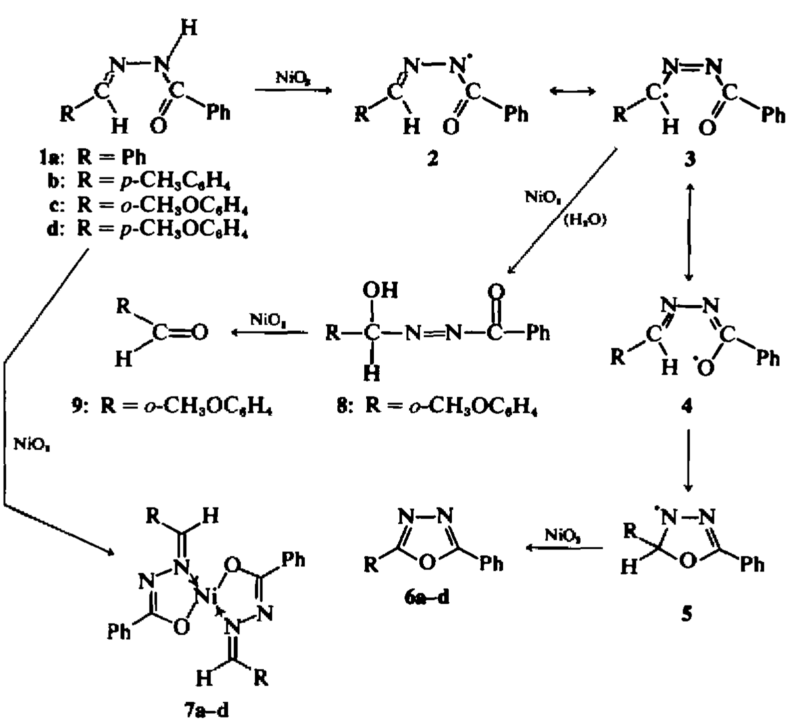
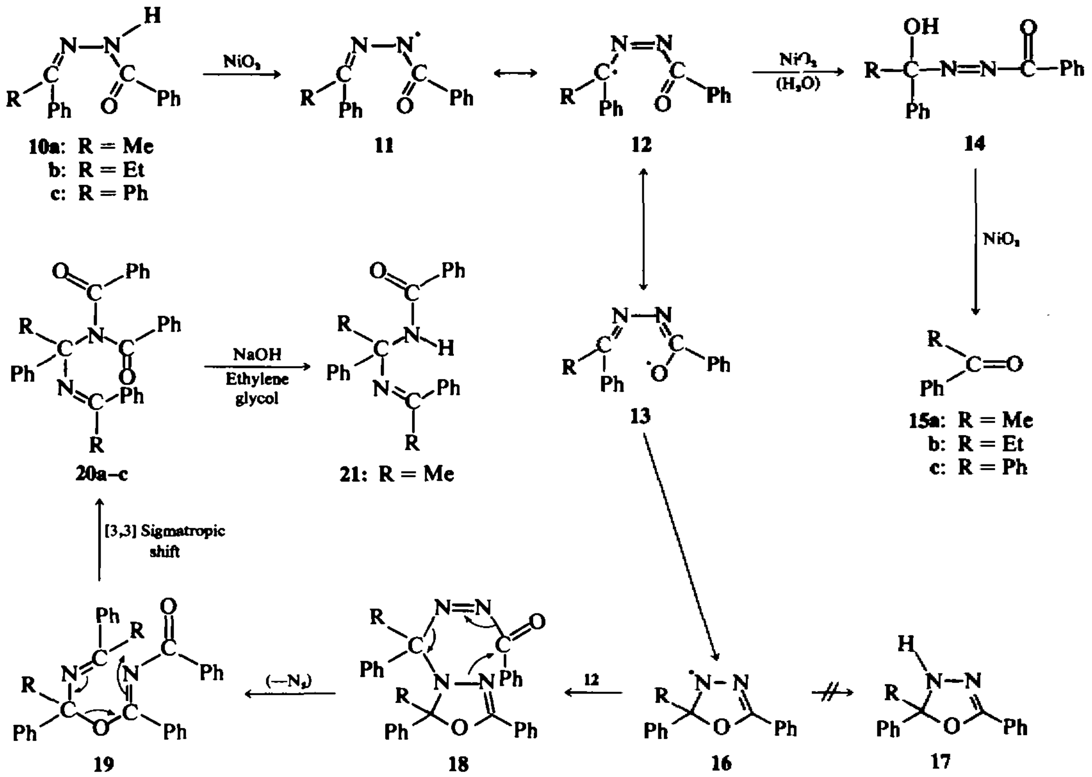


SCHEME 1

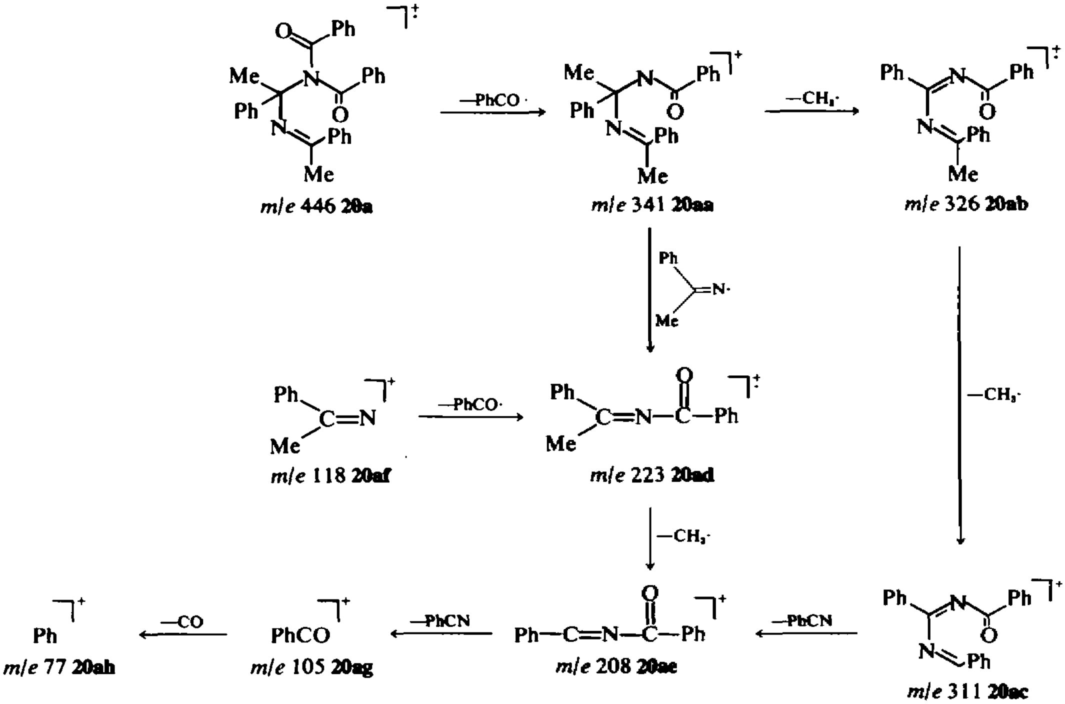
hydrazones has been reported in the literature. The mercury complex of benzophenone benzoylhydrazone, for example, has been oxidised with iodine in ether, to give 2,2,5-triphenyl-3-benzoyl-2,3-dihydro-1,3,4-oxadiazole.[2] In the present studies, we have examined the oxidation of a few ketone benzoylhydrazones with nickel peroxide with a view to studying the nature of the products formed in these reactions. Acetophenone benzoylhydrazone (**10a**), for example, on treatment with nickel peroxide in refluxing benzene, gives a 36% yield of acetophenone (**15a**), identified through its 2,4-dinitrophenylhydrazone. In addition, a 11% yield of a colourless solid, m.p. 249–250° and analyzing for $C_{30}H_{26}N_2O_2$ has also been isolated. The structure of this product has been assigned as methylbenzylidene-α-dibenzoylamino-α-methylbenzylamine (**20a**), on the basis of spectral data and chemical evidences (Scheme 2). The IR spectrum of **20a** shows the presence of two C=O groups at 1665 and 1660 cm^{-1}, respectively and a C=N group at 1640 cm^{-1}. The UV spectrum of **20a** shows absorption bands at 230 nm (ε, 17,900), 280 (14,000) and 292 (12,400) similar to the UV characteristics of a mixture of methylbenzylidene-α-methylbenzylamine[4] and dibenzamide.[5] The NMR spectrum of **20a** in deuterochloroform shows chemical shifts at 1·73 δ (3H, singlet), 1·87 δ (3H, singlet) and between 7·0–8·2 δ (20H, multiplet). The appearance of the Me groups as two separate signals at 1·73 δ and 1·87 δ indicate that they are magnetically non-equivalent. Treatment of **20a** with 2,4-dinitrophenylhydrazine did not give rise to any 2,4-dinitrophenylhydrazone derivative, thereby indicating the absence of a keto CO group.

Further evidence concerning the structure **20a** has been derived from its mass spectral data. The mass spectrum of **20a** shows the molecular ion peak at *m/e* 446 (98%). Other peaks are observed at *m/e* 341 (19), 326 (6), 311 (81), 223 (81), 208 (13), 194 (11), 178 (12), 118 (91), 105 (100), 91 (23) and 77 (100) which may be due to some of the fragments shown in Scheme 3. The species at *m/e* 341 is formulated as the ion corresponding to **20aa**, formed by the loss of a benzoyl group from the molecular ion. Successive loss of two Me groups from **20aa** leads to the ions **20ab** (*m/e* 326) and **20ac** (*m/e* 311), respectively. The peak at *m/e* 223 has been assigned to **20ad**, formed by the loss of acetophenoneimine from **20ac**. Similarly, the loss of benzonitrile from **20ac** leads to the ion **20ae** at *m/e* 208 which is also formed from **20ad** by the loss of a Me group. Loss of a benzoyl group from **20ad** leads to the fragment **20af** at *m/e* 118. The fragment at *m/e* 105, corresponding to **20ag** is formed by the loss of a second molecule of benzonitrile from **20ae**. Loss of carbon monoxide from **20ag** leads to the fragment **20ah** at *m/e* 77.

Additional evidence concerning the structure of **20a** is derived from degradative studies. Alkaline



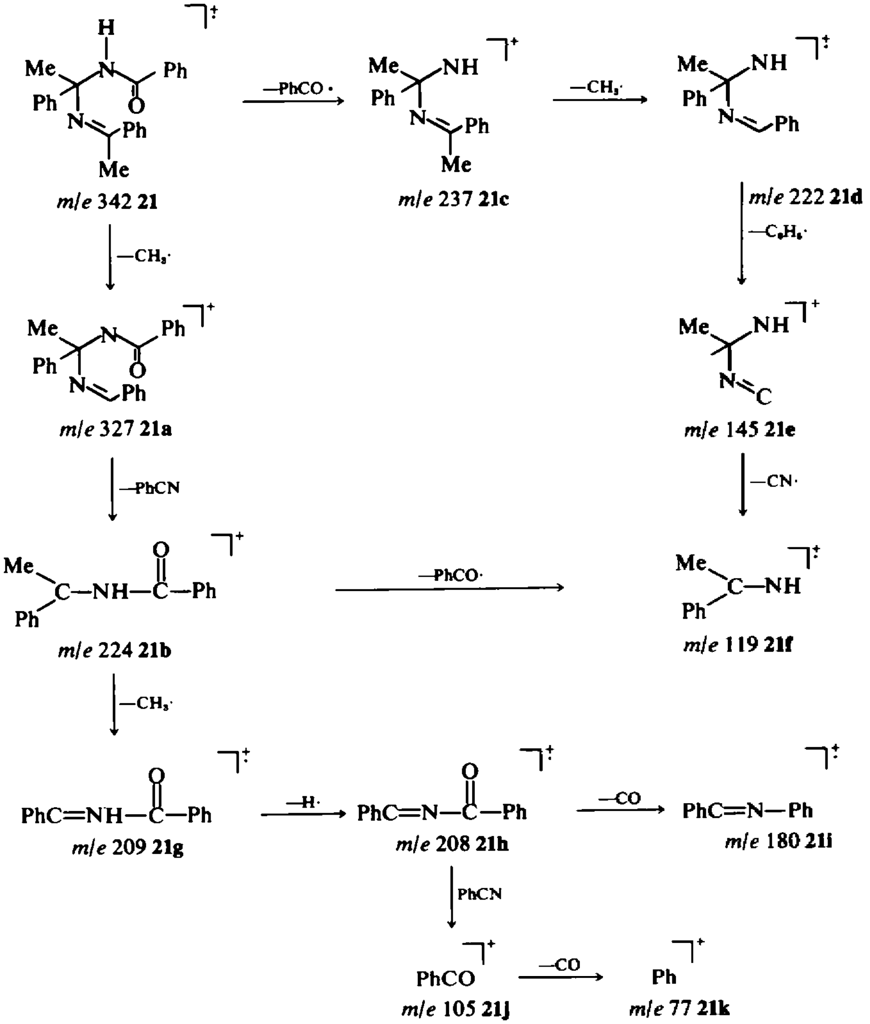
SCHEME 2



SCHEME 3

hydrolysis of **20a** by refluxing it with sodium hydroxide in ethylene glycol for 8 hr gives a solid, melting at 164–165° and identified as methylbenzylidene-α-benzoylamino-α-methylbenzylamine (**21**), on the basis of analytical data and spectral evidences. Compound **21** analyses for $C_{23}H_{22}N_2O$ and its molecular weight is found to be 342 (mass spectrometry). Its IR spectrum shows an N—H absorption band at 3200 cm^{-1} and an amide CO band at 1645 cm^{-1}. The UV spectrum of **21** is characterized by the presence of an absorption maximum at 286 nm (ϵ, 11,700).

Further confirmation of the structure of **21** is derived from its mass spectral data. The mass spectrum of **21** showed the molecular ion peak at *m*/*e* 342 (71%). Other peaks are observed at *m*/*e* 327 (18), 237 (28), 224 (100), 222 (61), 209 (11), 208 (12), 193 (17), 180 (83), 161 (25), 145 (69), 121 (79), 119 (70), 105 (85), 91 (40) and 77 (62), which could be assigned to some of the fragments shown in Scheme 4. The species at *m*/*e* 327 is formulated as the ion corresponding to **21a** formed by the loss of a Me group from the molecular ion. Further loss of a molecule of benzonitrile from **21a** would lead to the ion **21b** at *m*/*e* 224 which is the base peak in the spectrum. Another mode of fragmentation of the molecular ion is by the loss of a benzoyl group leading to the ion **21c** at *m*/*e* 237. Successive loss of Me and Ph groups from **21c** would lead to ions **21d** and **21e** at *m*/*e* 222 and 145, respectively. Further loss of a CN group from **21e** would lead to the ion **21f** at *m*/*e* 119. The same ion can also be formed by the loss of a benzoyl group from **21b**. The peak at *m*/*e* 209 is assigned to the fragment **21g** formed by the loss of a Me group from **21b**, which can then lose a proton giving rise to the fragment **21h** at *m*/*e*



SCHEME 4

208. Loss of a molecule of carbon monoxide from **21h** leads to the fragment **21i** at *m/e* 180. The peaks at *m/e* 105 and 77 have been assigned to fragments **21j** and **21ak**, respectively.

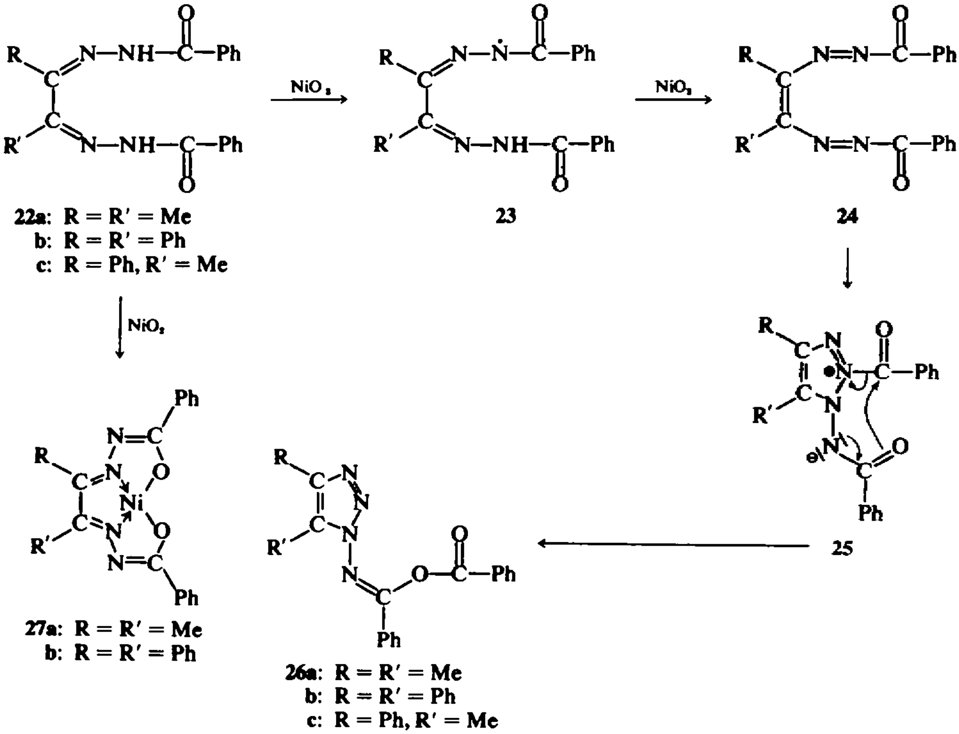
The formation of both **15a** and **20a** in the oxidation of acetophenone benzoylhydrazone (**10a**) can be rationalized in terms of a reaction mechanism shown in Scheme 2. In this scheme, we assume that the initial removal of an H atom from **10a** by nickel peroxide can give rise to the radical intermediate **11**, which can be represented by other canonical forms **12** or **13**. Hydroxylation of the radical intermediate **12**, followed by oxidative fragmentation in presence of nickel peroxide leads to the formation of acetophenone (**15a**). Another possible mode of reaction is the cyclization of the radical intermediate **13** giving rise to a new radical intermediate **16** which can then abstract an H atom from the solvent giving rise to the 2,3-dihydro-1,3,4-oxadiazole derivative **17**. Interestingly enough, this mode of reaction has not been observed under these conditions. On the other hand, a coupling reaction of the radical intermediates **12** and **16** would lead to the intermediate **18** which can then lose a molecule of nitrogen giving rise to **20a** through the intermediate **19**. Thermal isomerization of **19** through a symmetry allowed, [3,3]-sigmatropic shift would lead to **20**.

1,2-Diketone bisbenzoylhydrazones have been oxidized by several reagents like alkaline potassium ferricyanide,[6–12] a mixture of mercuric oxide and iodine,[8–10] silver oxide[9] and iodine.[2] It has been observed that the products formed in these reactions vary considerably with the nature of the oxidizing agent. Glyoxal bisbenzoylhydrazone, for example, on oxidation with alkaline potassium ferricyanide[7] gives 2-benzoylamino-1,2,3-triazole, whereas 5,5′-diphenyl-2,2′-bis-1,3,4-oxadiazolyl is obtained when the mercury complex of glyoxal bisbenzoylhydrazone is oxidized with iodine.[2] Similarly, the oxidation of biacetyl bisbenzoylhydrazone[8] and benzil bisbenzoylhydrazone[8] with alkaline potassium ferricyanide has been reported to give 1-benzoyloxybenzylideneamino-4,5-dimethyl-1,2,3-triazole and 1-benzoyloxybenzylideneamino-4,5-diphenyl-1,2,3-triazole, respectively. Considerable controversy exists in the literature concerning the structure of the oxidation products of 1,2-diketone bisbenzoylhydrazones. It has been assumed earlier that these oxidation products are essentially dihydro-1,2,3,4-tetrazine derivatives.[2,6,7,10] Petersen and Heitzer,[13] on the other hand, have suggested a mesionic structure for the oxidation product obtained from biacetyl bisbenzoylhydrazone. However, recent studies[14,15] have shown that the oxidation products of 1,2-diketone bisbenzoylhydrazones are correctly represented as triazole derivatives containing enolbenzoate side chains. It has been reported that the oxidation of biacetyl bismesitoylhydrazone with either a mixture of mercuric oxide and iodine or alkaline potassium ferricyanide proceeds with oxidative fragmentation leading to the formation of acetonitrile and azodimesitoyl.[9] In contrast, the oxidation of benzil bismesitoylhydrazone with mercuric oxide and iodine gives 1-mesitoylamino-4,5-diphenyl-1,2,3-triazole.[9] It has been reported that the oxidation of benzil bismesitoylhydrazone with silver oxide in ether gives rise to a disilver salt which on treatment with iodine in carbon disulfide gives 1-amino-4,5-diphenyl-1,2,3-triazole. However, the formation of the unstable bisbenzoylazostilbene is observed during shorter reaction periods and at lower temperatures.[9]

In the present investigation, we find that the oxidation of biacetyl bisbenzoylhydrazone (**22a**) with nickel peroxide in refluxing chloroform gives rise to a 7% yield of 1-α-benzoyloxybenzylideneamino-4,5-dimethyl-1,2,3-triazole (**26a**) and a 24% yield of nickel-biacetyl bisbenzoylhydrazone (**27a**) (Scheme 5). Similarly, the oxidation of benzil bisbenzoylhydrazone (**22b**) gives a 26% yield of the enol-benzoate **26b** and a 22% yield of the nickel complex **27b**. In contrast, the oxidation of phenylmethylglyoxal bisbenzoylhydrazone (**22c**) gives only the enolbenzoate **26c**. No nickel complex could be isolated from this reaction.

The formation of the enol-benzoates **26a–c** in the oxidation of the bisbenzoylhydrazones of biacetyl, benzil and phenylmethylglyoxal can be rationalised in terms of the reaction sequences shown in Scheme 5. In this scheme, we assume that nickel peroxide abstracts a proton from **22** giving rise to the radical intermediate **23** which on further oxidation gives rise to the bisazobenzoylolefin **24**. The bisazoolefin **24** can, through the zwitterionic intermediate **25**, rearrange to the enolbenzoate **26**. The exact mode of formation of the nickel complexes **27a,b** in these oxidations is not very clear. They could arise through an analogous pathway indicated for the formation of the nickel complexes from aldehyde benzoylhydrazones **1a–d**.

Oxidation of phenylglyoxal bisbenzoylhydrazone (**28a**) with nickel peroxide in refluxing chloroform gives a mixture of products consisting of 1-dibenzoylamino-4-phenyl-1,2,3-triazole (**33a**) and 1-benzoylamino-4-phenyl-1,2,3-triazole (**34**). In addition, a pink coloured nickel complex, melting at 321–322° and analyzing for $C_{44}H_{30}N_8O_4Ni$ is also isolated from this reaction (Scheme 6). The IR spectrum of this complex does not show the presence of either NH or C=O groups. The UV spectrum of the product in chloroform shows two intense absorption maxima at 288 nm (ε, 33,600) and 426 (87,900). Magnetic moment measurements indicate that the complex is diamagnetic and hence has a square planar configuration. On the basis of these evidences, we have assigned structure **38a** representing nickel-bis-phenyl-2-(5-phenyl-1,3,4-oxadiazolyl)-ketone benzoylhydrazone for this



SCHEME 5

product. Similarly, the oxidation of 4-methoxyphenylglyoxal bisbenzoylhydrazone with nickel peroxide gives a 7% yield of 1-dibenzoylamino-4-(4-methoxyphenyl)-1,2,3-triazole (**33b**), a 9% yield of 1-benzoylamino-4-(4-methoxyphenyl)-1,2,3-triazole (**34b**) and a 6% yield of the nickel complex **38b**.

The formation of the various products such as **33**, **34** and **38** in the oxidation of phenylglyoxal bisbenzoylhydrazone (**28a**) and 4-methoxyphenylglyoxal bisbenzoylhydrazone (**28b**) may be rationalised in terms of the reaction sequences shown in Scheme 6. In this scheme, we assume that the initial oxidation product of **28** is the radical intermediate **29** which on further oxidation goes to the bisbenzoylazoolefin **30**. Intramolecular cyclization of **30** leads to the zwitterionic intermediate **31** which subsequently rearranges to the enolbenzoate **32** and finally to the dibenzoylaminotriazole **33**. The formation of the 1-benzoylamino-1,2,3-triazole derivative **34** may be rationalized in terms of the hydrolysis of the dibenzoyl derivative **33**, under the reaction conditions. Another mode of oxidation of **28** is through the radical intermediate **35**, which then cyclizes to give the intermediate **36**. Subsequent oxidation of **36** would result in the formation of 1,3,4-oxadiazolyl ketone benzoylhydrazone **37**. Two molecules of **37** can later react with nickel peroxide giving rise to the nickel complex **38**.

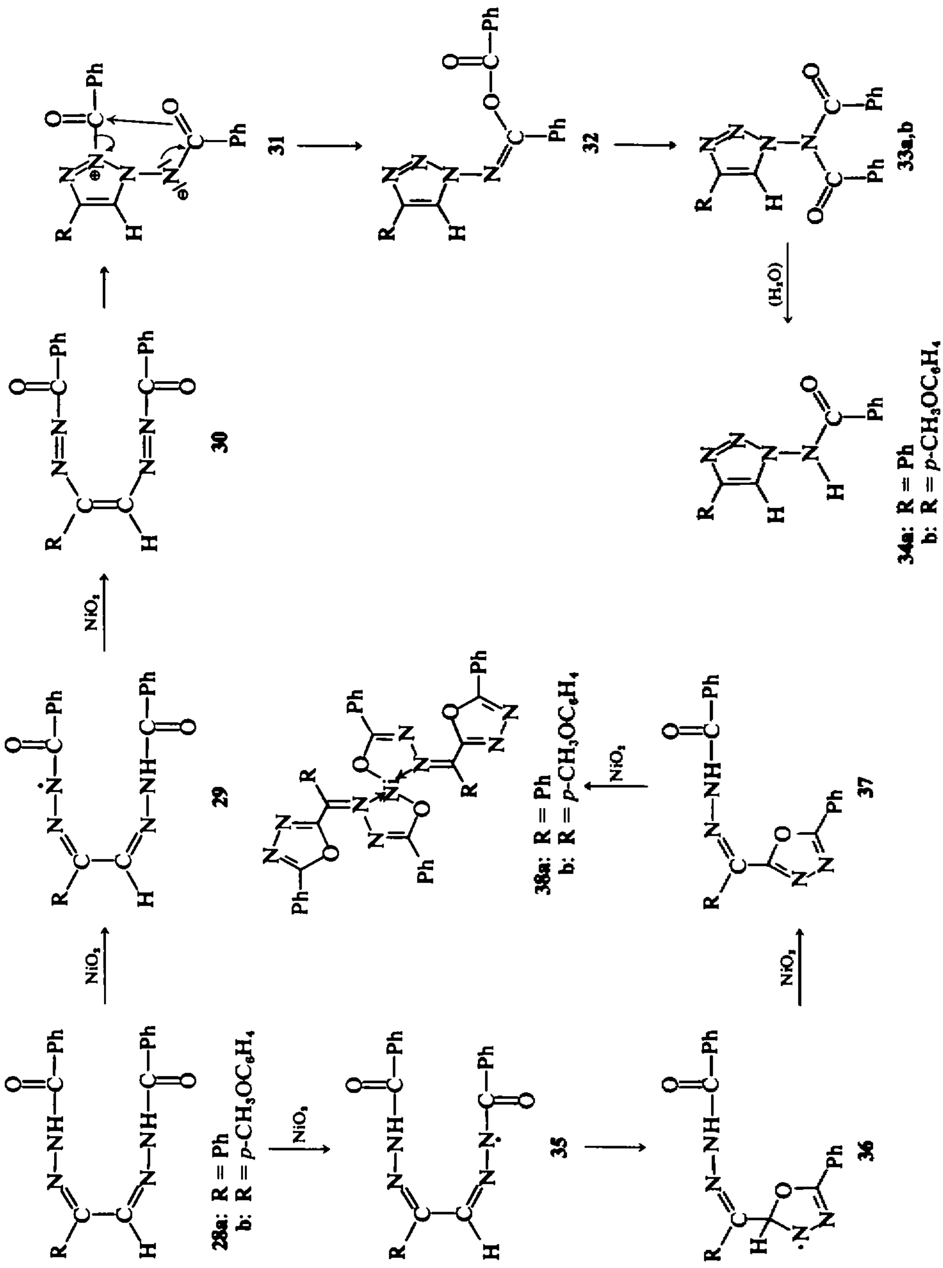
EXPERIMENTAL

Magnetic moment measurements were carried out on a Gouy balance by the standard procedure.

Starting materials. Benzaldehyde benzoylhydrazone, m.p. 204–205°,[16] *p*-tolualdehyde benzoylhydrazone, m.p. 155°,[2] *o*-methoxybenzaldehyde benzoylhydrazone, m.p. 179°,[17] anisaldehyde benzoylhydrazone, m.p. 147°,[17] acetophenone benzoylhydrazone, m.p. 153°,[16] benzophenone benzoylhydrazone, m.p. 116–117°,[2] biacetyl bisbenzoylhydrazone, m.p. 286°,[7] phenylglyoxal bisbenzoylhydrazone, m.p. 240–241°,[15] and benzil bisbenzoylhydrazone, m.p. 206°,[16] were prepared as per reported procedures.

Propiophenone benzoylhydrazone (**10b**) was prepared by heating a mixture of propiophenone (2·68 g, 20 mmol) and benzhydrazide (2·72 g, 20 mmol) in an oil bath, around 125°, for 10 hr. The solid product was filtered off and recrystallized from EtOH to give 4·5 g (89%) of **10b**, m.p. 155°. (Found: C, 76·25; H, 6·41; N, 10·94. $C_{16}H_{16}N_2O$ requires: C, 76·19; H, 6·35; N, 11·11%); IR spectrum (KBr): ν_{max} 1660 cm^{-1} (C=O, amide), UV spectrum (EtOH): 286 nm (ε, 24,700).

Compound **28b** was prepared by heating a mixture of 4-methoxyphenylglyoxal (0·82 g, 5 mmol) and benzhydrazide (1·53 g, 11·3 mmol) in EtOH (20 ml) containing AcOH (1 ml) for 1 hr, on a water-bath. The solid which separated out on cooling was filtered and then recrystallized from a mixture (1 : 1) of EtOH and benzene to give 1·7 g (85%) of **28b**, m.p. 261–262°. (Found: C, 69·33; H, 4·89; N, 13·68. $C_{23}H_{20}N_4O_3$ requires: C, 69·00; H, 5·00; N, 14·00%); IR spectrum (KBr): ν_{max} 1650 cm^{-1} (C=O, amide); UV spectrum (EtOH): 218 (ε, 24,300), 290 (26,200) and 360 nm (24,100).



28a: R = Ph
b: R = p-$CH_3OC_6H_4$

29

30

31

32

33a,b

34a: R = Ph
b: R = p-$CH_3OC_6H_4$

35

36

37

38a: R = Ph
b: R = p-$CH_3OC_6H_4$

SCHEME 6

Compound **22c** was prepared by refluxing a mixture of phenylmethylglyoxal (0·66 g, 4·1 mmol), benzhydrazide (1·4 g, 10·3 mmol) and AcOH (1 ml) in EtOH (10 ml) for 5 hr on a water-bath. The solid which separated out on cooling was filtered off and recrystallized from a mixture (1:1) of EtOH and AcOH to give 1·6 g (87%) of **22c**, m.p. 252–253°. (Found: C, 71·80; H, 5·26; N, 14·51. $C_{23}H_{20}N_4O_2$ requires: C, 71·88; H, 5·21; N, 14·58%); IR spectrum (KBr): ν_{max} 1650 cm^{-1} (C=O, amide); UV spectrum (EtOH): 224 (ϵ, 26,100), 294 (27,000) and 356 nm (24,400).

Oxidation of aldehyde benzoylhydrazones. In a typical run, a mixture of benzaldehyde benzoylhydrazone (1·5 g, 6·7 mmol) and nickel peroxide (2·5 g) was refluxed in chloroform (175 ml) for 4 hr. Removal of the inorganic material and the solvent gave a solid which was treated with benzene. The benzene-soluble portion was worked up separately. Recrystallization of the benzene insoluble portion from chloroform gave 0·8 g (47%) of **7a**, m.p. 306–307°. (Found: C, 66·33; H, 4·41; N, 11·24. $C_{28}H_{22}N_4O_2Ni$ requires: C, 66·58; H, 4·36; N, 11·10%); IR spectrum (KBr): ν_{max} 1572 cm^{-1} (C=N); UV spectrum (chloroform): 250 (ϵ, 40,000), 315 (35,700), 325 (24,000), 341 (20,400), 360 (27,800), 394 (15,400) and 402 nm (15,000). Magnetic moment measurements of **7a** showed that the compound is diamagnetic.

The benzene-soluble portion, after removal of **7a** was chromatographed over alumina. Elution with benzene gave a solid which on recrystallization from light petroleum gave 0·45 g (30%) of **6a**, m.p. 139–140° (lit.[3] m.p. 139–140°), characterized through its IR spectrum.

Refluxing a mixture of **1b** (2 g, 8·4 mmol) and nickel peroxide (4 g) in chloroform (175 ml) for 4 hr and work-up as in the previous cases gave 0·6 g (27%) of **7b** as orange, silky needles, melting 272–273°. (Found: C, 67·34; H, 4·99; N, 10·26. $C_{30}H_{26}N_4O_2Ni$ requires: C, 67·57; H, 4·88; N, 10·52%); IR spectrum (KBr): ν_{max} 1580 cm^{-1} (C=N); UV spectrum (chloroform): 251 (ϵ, 37,600), 315 (37,600), 327 (23,800), 342 (21,200), 358 (21,100), 395 (17,000) and 408 nm (16,100). From the benzene-soluble portion of the initial reaction mixture was isolated 0·7 g (35%) of **6b**, m.p. 115° (lit.[18] m.p. 115°), through chromatography over alumina, followed by recrystallization from light petroleum.

Treatment of 2 g (7·9 mmol) of *o*-methoxybenzaldehyde benzoylhydrazone with 4 g of nickel peroxide in refluxing chloroform (200 ml) for 3 hr and work-up as in the earlier cases gave a product which was extracted with benzene. The benzene-insoluble portion on recrystallization from chloroform gave 0·5 g (23%) of **7c**, m.p. 262–263°. (Found: C, 63·96; H, 4·72; N, 9·52. $C_{30}H_{26}N_4O_2Ni$ requires: C, 63·75; H, 4·60; N, 9·92%); IR spectrum (KBr): ν_{max} 1582 cm^{-1} (C=N); UV spectrum (chloroform): 250 (ϵ, 32,700), 310 (23,900), 317 (24,100), 324 (20,600), 340 (22,100), 355 (22,700), 369 (23,600), 404 (20,600) and 411 nm (20,300). The benzene-soluble portion of the original reaction mixture was chromatographed on alumina. Elution with benzene gave 0·21 g (20%) of **8**, characterized through its 2,4-dinitrophenylhydrazone, m.p. 253° (mixture m.p.). Further elution of the column with a mixture (9:1) of benzene and ethyl acetate gave a solid which on recrystallization from aqueous EtOH gave 0·4 g (20%) of **6c**, m.p. 96–97° (lit.[19] m.p. 96–97°), characterized through its IR spectrum.

Oxidation of **1d** (1·5 g, 5·9 mmol) with nickel peroxide (3 g) in refluxing chloroform (100 ml) for 2½ hr and work-up in the usual manner gave 0·75 g (41%) of **7d**, m.p. 289–290°. (Found: C, 63·67; H, 4·24; N, 9·66. $C_{30}H_{26}N_4O_4Ni$ requires: C, 63·75; H, 4·60; N, 9·92%); IR spectrum (KBr): ν_{max} 1582 cm^{-1} (C=N); UV spectrum (chloroform): 248 (ϵ, 35,100), 314 (34,600), 320 (37,300), 325 (26,700), 343 (24,700), 353 (27,100), 398 (27,900) and 412 nm (27,100). The benzene-soluble portion after the removal of **7d** from the mixture was worked up as in the earlier cases to give a solid which on recrystallization from a mixture (1:1) of light petroleum and benzene gave 0·4 g (21%) of **6d**, m.p. 151–152° (lit.[19] m.p. 151–152°), characterized through its IR spectrum.

Oxidation of acetophenone benzoylhydrazone (**10a**). A mixture of acetophenone benzoylhydrazone (2 g, 8·4 mmol) and nickel peroxide (4 g) was refluxed in benzene (175 ml) for 4 hr. Work-up of the mixture in the usual manner gave a viscous liquid which was chromatographed over alumina. Elution with a mixture (4:1) of light petroleum and benzene gave 0·36 g (36%) of **15a**, isolated as its 2,4-dinitrophenylhydrazone derivative (0·9 g), m.p. 237° (mixture m.p.). Further elution of the column with the same solvent mixture gave a solid which on recrystallization from a mixture (3:1) of alcohol and benzene gave 0·2 g (11%) of a colourless solid melting at 249–250° and identified as **20a**. (Found: C, 80·83; H, 6·16; N, 6·14; Mol. wt., 446 (mass spectrometry). $C_{30}H_{26}N_2O_2$ requires: C, 80·72; H, 5·80; N, 6·25%, mol. wt., 446); IR spectrum (KBr): ν_{max} 1675 (C=O), 1670 (C=O) and 1640 cm^{-1} (C=N); UV spectrum (EtOH): 230 (ϵ, 17,900), 280 (14,000) and 292 nm (12,400); NMR spectrum ($CDCl_3$): 1·73 δ (3H, s, Me protons), 1·87 δ (3H, s, Me protons) and 7·0–8·2 δ (20H, m, aromatic protons).

Hydrolysis of methylbenzylidene-α-dibenzoylamino-α-methylbenzylamine (**20a**). A mixture of **20a** (0·1 g, 0·022 mmol) and NaOH (0·1 g, 2·5 mmol) was refluxed in ethylene glycol (10 ml) for 8 hr and later poured into ice-cold water. The solid (60 mg) which separated out was filtered and then recrystallized from EtOH to give 50 mg (66%) of **21**, m.p. 164–165°. (Found: C, 80·94; H, 6·27; N, 8·32; Mol. wt., 342 (mass spectrometry). $C_{23}H_{22}N_2O$ requires: C, 80·70; H, 6·43; N, 8·18%; (Mol. wt., 342); IR spectrum (KBr): ν_{max} 3308 (N—H), 1640 (C=O, amide) and 1633 cm^{-1} (C=N); UV spectrum (EtOH): 286 nm (ϵ, 11,700); NMR spectrum ($CDCl_3$): 1·33 δ (3H, s, Me protons), 1·66 δ (3H, s, Me protons), 5·23 δ (1H, broad s, N—H proton) and 7·65 δ (15H, m, aromatic protons).

Oxidation of propiophenone benzoylhydrazone (**10b**). A mixture of propiophenone benzoylhydrazone (2 g, 7·94 mmol) and nickel peroxide (3·5 g) was refluxed in benzene (175 ml) for 4 hr. Removal of the inorganic material and the solvent in the usual manner gave a viscous liquid which was chromatographed over alumina. Elution with a mixture (4:1) of light petroleum and benzene gave 0·45 g (40%) of **15b** isolated through its 2,4-dinitrophenylhydrazone derivative (1 g), m.p. 187–189° (mixture m.p.). Further elution of the column with a mixture (1:1) of light petroleum and benzene gave a solid which on recrystallization from a mixture (3:1) of EtOH and benzene gave 0·15 g (8%) of **20b**, m.p. 262–263°. (Found: C, 80·68; H, 6·52; N, 5·85; Mol. wt., 474 (mass spectrometry). $C_{32}H_{30}N_2O_2$ requires: C, 81·00; H, 6·33; N, 5·91%; Mol. wt., 474); IR spectrum (KBr): ν_{max} 1660 (C=O) and 1635 cm^{-1} (C=N); UV spectrum (cyclohexane): 223 (ϵ, 33,300), 286 (14,400) and 295 nm (14,200); NMR spectrum ($CDCl_3$): 0·54 δ (3H, t, Me protons), 0·99 δ (3H, t, Me protons), 2·17 δ (2H, q, methylene/protons), 2·23 δ (2H, q, methylene protons) and 7·49 δ (20H, m, aromatic protons).

Oxidation of benzophenone benzoylhydrazone (**10c**). Refluxing a mixture of benzophenone benzoylhydrazone (1·5 g, 5·0 mmol) and nickel peroxide (3 g) in benzene (175 ml) for 4 hr and work-up in the usual manner gave a viscous liquid which was chromatographed over alumina. Elution with a mixture (4 : 1) of light petroleum and benzene gave 0·45 g (50%) of **15c** isolated as its 2,4-dinitrophenylhydrazone derivative, m.p. 238° (mixture m.p.). Further elution of the column with a mixture (1 : 1) of light petroleum and benzene gave 0·15 g (16%) of **20c**, m.p. 168–169°. (Found: C, 84·26; H, 5·38; N, 5·03; Mol. wt., 570 (mass spectrometry). $C_{40}H_{30}N_2O_2$ requires: C, 84·21; H, 5·26; N, 4·91; Mol. wt., 570); IR spectrum (KBr): ν_{max} 1655 (C=O) and 1600 cm^{-1} (C=N); UV spectrum (cyclohexane): 230 (ϵ, 33,100) and 313 nm (7,000); NMR spectrum ($CDCl_3$): m centred at 7·39 δ (30H) due to the aromatic protons.

Oxidation of biacetyl bisbenzoylhydrazone (**22a**). A mixture of biacetyl bisbenzoylhydrazone (1·5 g, 4·7 mmol) and nickel peroxide (5 g) was refluxed in chloroform for 4 hr. Removal of the inorganic material and the solvent as in the previous cases gave a solid which was extracted with a mixture of benzene and chloroform. The residual solid was recrystallized from chloroform to give 0·4 g (24%) of **27a**, m.p. 284–285° (mixture m.p.).[20]

The filtrate after removal of the nickel complex **27a** was chromatographed over alumina. Elution with benzene gave 0·1 g (7%) of **26a**, m.p. 139–140° (mixture m.p.).[8]

Oxidation of benzil bisbenzoylhydrazone (**22b**). A mixture of benzil bisbenzoylhydrazone (2 g, 4·5 mmol) and nickel peroxide (4 g) was refluxed in chloroform (175 ml) for 4 hr. Work-up of the mixture as in the earlier cases gave a product which was extracted with a mixture of benzene and chloroform. The residual solid was recrystallized from chloroform to give 0·5 g (22%) of **27b**, m.p. 300–301°. (Found: C, 66·53; H, 3·58; N, 11·50; Ni, 11·83. $C_{28}H_{0}N_4O_2Ni$ requires: C, 66·83; H, 3·98; N, 11·14; Ni 11·68%); IR spectrum (KBr): ν_{max} 1600 cm^{-1} (C=N); UV spectrum (chloroform): 292 (ϵ, 20,800), 340 (16,800), 358 (17,800), 392 (19,900), 404 (19,200) and 424 nm (15,100). Magnetic moment measurements of **27b** showed it to be diamagnetic.

The benzene-chloroform soluble portion after the removal of **24b** was chromatographed over alumina. Elution with benzene gave 0·5 g (26%) of **26b**, m.p. 188–189° (mixture m.p.).[8] Further elution of the column with the same solvent gave 0·6 g (30%) of the unchanged starting material (**22b**), m.p. 206° (mixture m.p.).

Oxidation of phenylmethylglyoxal bisbenzoylhydrazone (**22c**). Refluxing a mixture of phenylmethylglyoxal bisbenzoylhydrazone (1 g, 2·6 mmol) and nickel peroxide (3 g) in chloroform (150 ml) for 4 hr and work-up in the usual manner gave a product mixture which on subsequent treatment with EtOH gave a colourless solid. Recrystallization of this solid from a mixture (2 : 1) of light petroleum and benzene gave 0·25 g (25%) of **26c**, m.p. 165–166°. (Found: C, 72·30; H, 4·50; N, 14·35. $C_{23}H_{18}N_4O_2$ requires: C, 72·24; H, 4·71; N, 14·66%); IR spectrum (KBr): ν_{max} 1750 (C=O) and 1640 cm^{-1} (C=N); UV spectrum (EtOH): 245 (ϵ, 30,500), 256 (27,300) and 329 nm (3,000).

Oxidation of phenylglyoxal bisbenzoylhydrazone (**28a**). A mixture of phenylglyoxal bisbenzoylhydrazone (1·5 g, 4·1 mmol) and nickel peroxide (4 g) was refluxed in chloroform (200 ml) for 3 hr. Work-up in the usual manner gave a solid which was extracted with cold benzene. The benzene-insoluble portion was recrystallized from benzene to give 0·3 g (19%) of **38a**, m.p. 321–322°. (Found: C, 66·28; H, 3·76; N, 13·73. $C_{44}H_{30}N_8O_4Ni$ requires: C, 66·62; H, 3·78; N, 14·13%); IR spectrum (KBr): ν_{max}: 1595 cm^{-1} (C=N); UV spectrum (chloroform): 288 (ϵ, 33,600) and 426 nm (87,900); Magnetic moment measurements of **38a** showed it to be diamagnetic.

The benzene-soluble portion, after the removal of the nickel complex **38a** was chromatographed over alumina. Elution with a mixture (1 : 4) of light petroleum and benzene gave an additional amount (0·2 g, 12%) of **38a**, m.p. 321–322° (mixture m.p.). Further elution of the column with benzene gave a solid which was recrystallized from a mixture (5 : 1) of benzene and alcohol to give 0·35 g (23%) of **33a**, m.p. 213–214°. (Found: C, 71·78; H, 3·96; N, 15·37. $C_{22}H_{16}N_4O_2$ requires: C, 71·74; H, 4·35; N, 15·22%; IR spectrum (KBr): ν_{max} 1692 cm^{-1} (C=O); UV spectrum (EtOH): 230 (ϵ, 16,900), 284 (16,300) and 336 nm (21,400).

Further elution of the column with EtOH gave a solid which on recrystallization from aqueous MeOH gave 0·1 g (7%) of **34a**, m.p. 217–218° (mixture m.p.).[15]

Oxidation of 4-methoxyphenylglyoxal bisbenzoylhydrazone (**28b**). A mixture of 4-methoxyphenylglyoxal bisbenzoylhydrazone (1·5 g, 3·7 mmol) and nickel peroxide (5 g) was refluxed in chloroform (200 ml) for 3 hr. Removal of the inorganic material and the solvent gave a semi-solid which was chromatographed over alumina. Elution with benzene gave a solid which was recrystallized from benzene to give 0·1 g (6%) of a brown amorphous powder which was characterized as **38b**, m.p. 361–362°(d). (Found: C, 64·43; H, 4·03; N, 12·77. $C_{46}H_{34}N_8O_8Ni$ requires: C, 64·74; H, 4·00; N, 13·13%); IR spectrum (KBr): ν_{max} 1600 cm^{-1} (C=N); UV spectrum (chloroform): 306 (ϵ, 37,600) and 432 nm (54,200). Magnetic moment measurements of **38b** showed it to be diamagnetic.

Further elution of the column with benzene gave a solid which on recrystallization from a mixture (2 : 1) of light petroleum and benzene gave 0·1 g (7%) of **33b**, m.p. 225–226°. (Found: C, 69·67; H, 4·65; N, 14·23. $C_{23}H_{18}N_4O_3$ requires: C, 69·34; H, 4·52; N, 14·07%); IR spectrum (KBr): ν_{max} 1695 cm^{-1} (C=O); UV spectrum (EtOH): 239 (ϵ, 20,850), 295 (19,800) and 348 nm (17,600).

Subsequent elution of the column with EtOH gave a solid which on recrystallization from aqueous EtOH gave 0·1 g (9%) of **34b**, m.p. 200–201°. (Found: C, 65·07; H, 5·06; N, 18·71. $C_{16}H_{14}N_4O_2$ requires: C, 65·31; H, 4·76; N, 19·05%); IR spectrum (KBr): ν_{max} 3250 (N—H) and 1690 cm^{-1} (C=O, amide); UV spectrum (EtOH): 256 nm (ϵ, 27,300).

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