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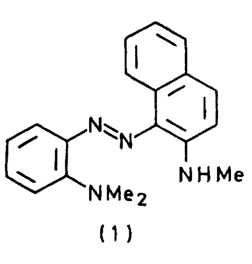
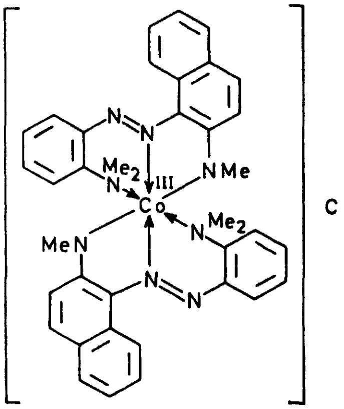
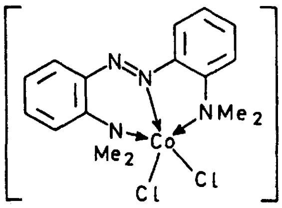
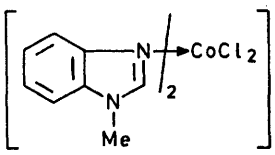
Aerial oxidation of ethanol in the presence of an aromatic azo-compound and CoX_2 (X = F, Cl, O_2CMe, or ClO_4) or iron(III) chloride gives a stoicheiometric amount of acetaldehyde with $CoCl_2$, $Co[O_2CMe]_2$, and $FeCl_3$, but no oxidation occurs with CoF_2 and $Co[ClO_4]_2$. Addition of nitrogen-donor ligands promotes the oxidising activity in CoF_2, and this effect is discussed and a mechanism is proposed for the oxidation. The cobalt(II) chloride–aromatic azo-compound combination effects slow catalytic oxidation of a potassium propionate–propanol mixture. Several rhodium complexes which catalytically oxidise ethanol are reported, and 5% Rh–C dehydrogenates ethanol smoothly at its boiling point.

THIS study was initiated by the observation that, when air was passed through an ethanolic solution of the azo-compound (1) and cobalt(II) chloride during the preparation of the cobalt(III) complex (2),[1] acetaldehyde was evolved from the reaction mixture. No acetaldehyde could be detected on repeating the experiment and omitting the cobalt salt, azo-compound (1), and air in turn. However, when the experiment was repeated quantitatively (air, 200 cm^3 min^{-1}) and the acetaldehyde was trapped as its dimedone (5,5-dimethylcyclohexane-1,3-dione) derivative only 0.92 mol of acetaldehyde per mol of cobalt salt was produced indicating that a stoicheiometric oxidation was occurring. The $CoCl_2$ was replaced with, in turn, cobalt(II) acetate, perchlorate, and fluoride; only in the case of the acetate was any acetaldehyde observed (Table 1), indicating that the anions play a significant part in the reaction. The cobalt complexes were generated *in situ* because of their lability and tendency to decompose on attempted purification.


(1)


(2)


(3)


(4)

The cobalt(II) complex (3) of a closely related azo-compound decomposes in ethanolic solution forming the cobalt(II) complex of 1-methylbenzimidazole (4) and *o*-dimethylaminoaniline. The same products are obtained when the azo-compound reacts with $CoCl_2$ in ethanol.[2] It is not unreasonable therefore to suppose that a related degradation could occur in the case of compound (1). This could then provide an explanation

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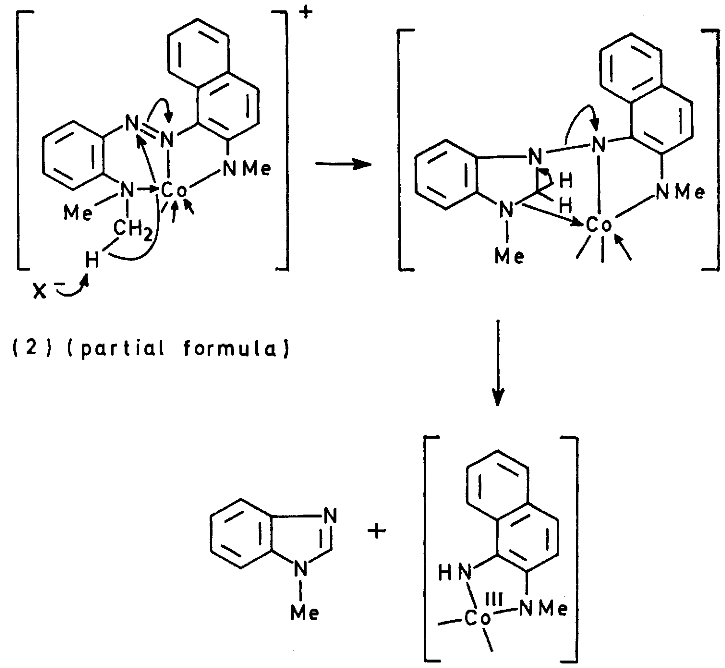
[1] R. Price, *J. Chem. Soc.* (*A*), 1967, 2048.
[2] R. Price, *J. Chem. Soc.* (*A*), 1967, 521.

for the variation of acetaldehyde yield with change of anion (Scheme 1).



(2) (partial formula)

SCHEME 1

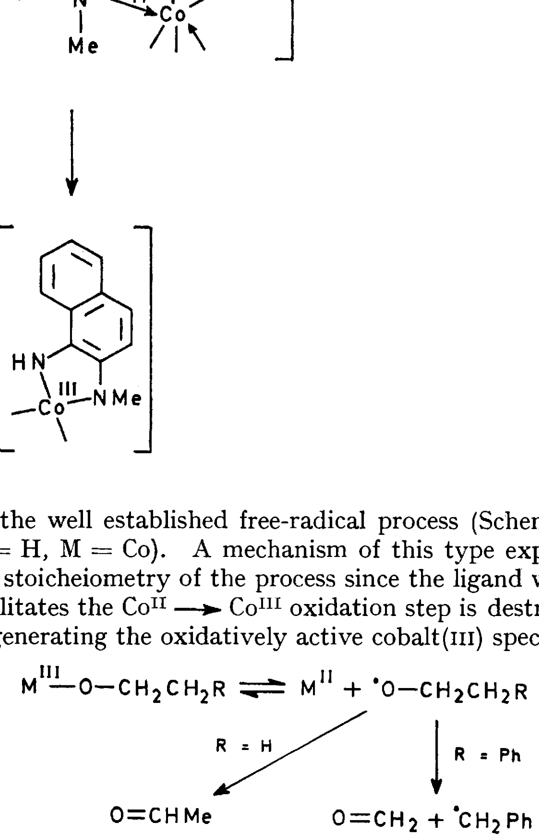
Thus co-ordination of the azo-compound promotes aerial oxidation of the cobalt to Co^{III}. The cobalt(III) ion co-ordinated to the tertiary amine function [Scheme 1; (2)] might then sufficiently activate the *N*-methyl group to permit deprotonation by the acetate and chloride ions but not by the much weaker bases fluoride and perchlorate. A similar gradation in basicity of anions in the deprotonation of methyl groups has been observed by us in the thermal rearrangement of nickel 1,19-dialkyltetradehydrocorrin salts to nickel porphines.[3] The new ligands generated by decomposition of compound (1) are postulated to be incapable of stabilising the oxidation state III of cobalt. The cobalt(III) species present in solution then effects oxidation of the ethanol by the well established free-radical process (Scheme 2; R = H, M = Co). A mechanism of this type explains the stoicheiometry of the process since the ligand which facilitates the $Co^{II} \longrightarrow Co^{III}$ oxidation step is destroyed in generating the oxidatively active cobalt(III) species.

TABLE 1

Acetaldehyde yield (mol per mol complex) from various ligand–metal salt (2 : 1) combinations

Metal salt	Ligand	Reaction time (t/h)	Yield of MeCHO
$CoCl_2$	(1)	24	0.92
CoF_2	(1)	24	
CoF_2	Benzimidazole	24	
$Co[ClO_4]_2$	(1)	24	
$Co[O_2CMe]_2$	(1)	24	0.90
$FeCl_3$	(1)	72	1.20
$FeCl_3$		72	
$RhCl_3$	(1)	120	1.60
$RhCl_3$		72 [a]	85.2
$[Rh_2(CO)_4Cl_2]$	(1)	48	11.4
$[Rh_2(CO)_4Cl_2]$		288	227.5
$[Rh_2(CO)_4Cl_2]$	PPh_3 (4 mol)	384	276.2
$[Rh(CO)_2(pd)]$ [b]		96	40.5
Rhodium(III) aetioporphyrin I		48	6.42
Iron(III) aetioporphyrin I		48	
$Rh[O_2CMe]_2$		48	6.2
5% Rh–C		240 [a]	1 954

[a] Oxidation still occurring. [b] pd = Pentane-2,4-dionate.



SCHEME 2

The sensitivity of the reaction to the structure of the azo-compound is illustrated by the failure both of 2,2′-bis(dimethylamino)azobenzene to form a cobalt(III) complex (with aeration of the solution) and of the mixture 2,2′-bis(dimethylamino)azobenzene–cobalt(II) chloride–ethanol to produce any acetaldehyde. The involvement of substituents *ortho* to an azo-linkage, of aromatic azo-compounds, in heterocyclic ring formation has been long known. The oxidative cyclisation of *o*-aminoazo-compounds to triazoles [(5) ⟶ (6)] under the influence of copper salts,[4] and other formally similar examples,[5] are part of a more general class of cyclisation

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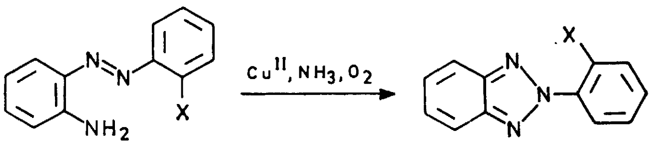
[3] R. Grigg, A. W. Johnson, K. Richardson, and K. W. Shelton, *J. Chem. Soc.* (*C*), 1969, 655.

[4] M. M. Jones, ' Ligand Reactivity and Catalysis,' Academic Press, New York, 1968, p. 111.

[5] O. Meth-Cohen and H. Suschitzky, *Adv. Heterocyclic Chem.*, 1972, **14**, 211.

reactions in which, however, the mechanisms of the cyclisations may vary widely. The thin-layer chromatographic (t.l.c.) detection of complex (4) in a standard $CoCl_2$–(1)–EtOH mixture, together with the foregoing speculations, prompted a study of the reactivity of CoF_2 in the presence of both (1) and of added coordinating bases (Table 2).



(5) (6)

TABLE 2

Acetaldehyde yields (mol) obtained with various nitrogenous ligands added to CoF_2 and ligand (1)

Base (amount/mol)	pK_a of conjugate acid of base [a]	Yield of MeCHO [b]
Imidazole (2)	6.93	0.08
(1)	6.93	
1-Methylbenzimidazole (2)	5.54	0.52
Benzimidazole (2)	5.53	0.88
(1)	5.53	0.99
Pyridine (2)	5.21	0.64
Pyrazole (2)	2.48	0.32
(1)	2.48	0.32
Pyrimidin-2-ol (2)	2.15	0.08
Trimethylisoxazole (2)	−1	0.20

[a] Taken from D. D. Perrin, 'Dissociation Constants of Organic Bases in Aqueous Solution,' Butterworths, London, 1965. [b] All the reactions were carried out for 24 h with an air flow rate of 200 cm^3 min^{-1}.

RESULTS AND DISCUSSION

On addition of 2 mol of 1-methylbenzimidazole per mol of CoF_2 under conditions otherwise identical to those employed in the original reaction [*i.e.* in the presence of (1) and with air blowing], a yield of 0.52 mol of acetaldehyde was obtained. Variation of the added nitrogen-donor ligand resulted in a wide variation in the yield of acetaldehyde (Table 2), with benzimidazole (0.99 mol) giving the highest yield and imidazole and pyrimidin-2-ol the lowest yield (0.08 mol). A control experiment, in the absence of (1), using CoF_2 and benzimidazole in a 1 : 2 mol ratio failed to produce any acetaldehyde, showing that the active species was not merely a complex of the cobalt salt with this base. Apart from the result with trimethylisoxazole, the acetaldehyde yields recorded in Table 2 increase with increasing basicity up to benzimidazole and then decrease when the basicity of the added nitrogen ligand is further increased. The lack of oxidation of ethanol by the cobalt(II) fluoride–benzimidazole mixture in the absence of (1) suggests these added bases may be functioning by triggering decomposition of complex (2) as outlined in Scheme 1 (X = added base). The present data are insufficient to warrant further speculation on these results. The ability of metalloporphyrins and metallophthalocyanines to catalyse the oxidation of organic substrates is well known.[6] However, cobalt(II) aetioporphyrin I in the presence of benzimidazole (2 mol) failed to promote the aerial oxidation of ethanol.

The oxidation of n-propanol containing *ca.* 10% (w/w) potassium propionate was studied using the cobalt(II) chloride–compound (1) system. Carbon dioxide was evolved and a mixture of acetaldehyde and propionaldehyde (ratio *ca.* 1 : 19) was produced, from the propionate and propanol respectively, showing that both substrates were undergoing oxidation. The reaction was slow but catalytic and *ca.* 12 mol of aldehydes per mol of cobalt(II) salt were produced after 15 d. No aldehydes were detected when the reaction was repeated in the absence of the azo-compound. The formation of acetaldehyde from potassium propionate suggests the usual free-radical mechanism [*i.e.* (7) ⟶ (8)] is operating,[7,8] followed by oxidation of ethanol to acetaldehyde. The difference between the stoicheiometric oxidation of ethanol and the, albeit, sluggishly catalytic oxidation of the propanol–propionate mixture may be due to the formation of anionic carboxylatocobalt(III) species[8] such as $[Co(O_2CEt)_4]^-$.

$$\underset{(7)}{EtCO_2^{\bullet}} \longrightarrow Et^{\bullet} \longrightarrow \underset{(8)}{EtOH}$$

The reactivity of iron(III) chloride as a potential catalyst was studied briefly (Table 1) under the standard conditions. Oxidation of ethanol was only observed in the presence of the compound (1), and iron(III) aetioporphyrin I was found to be inactive.

The study was then extended to rhodium trichloride and in this case compound (1) was found to inhibit the oxidation (Table 1). Rhodium chloride in the presence of (1) under standard conditions gave only 1.6 mol of acetaldehyde, whilst in the absence of (1) the reaction produced 85.2 mol of acetaldehyde over 3 d. The reactivity of $RhCl_3$ prompted a study of (9) and the related pentane-2,4-dionate (10). Once again compound (1) strongly inhibited the catalytic activity of (9), whereas addition of triphenylphosphine resulted in a slower rate of oxidation but an increased production of acetaldehyde (Table 1). Complex (10) and the rhodium porphyrin (11) were much less active catalysts (Table 1).

The rhodium complex (9) was also studied as a catalyst for oxidation of the n-propanol–10% (w/w) potassium propionate mixture and was operating at an undiminished rate after 35 d when >4 000 mol of aldehydes per mol of (9) had been produced. However, during the rhodium-catalysed reaction a grey deposit appeared on the side of the reaction vessel, presumably

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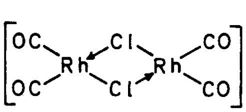
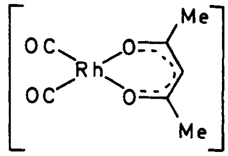
[6] C. F. Cullis and D. L. Trimm, *Discuss. Faraday Soc.*, 1968, **46**, 144; H. Inoue, Y. Kida, and E. Imoto, *Bull. Chem. Soc. Japan*, 1968, **41**, 692; E. Ochiai, *Tetrahedron*, 1964, **20**, 1819; Y. Kamiya, *Kogyo Kagaku Zasshi*, 1969, **72**, 1693; H. Kropf and W. Knabjohann, *Annalen*, 1970, **739**, 95; H. Kropf, W. Gebert, and K. Franke, *Tetrahedron Letters*, 1968, 5527; A. H. Cook, *J. Chem. Soc.*, 1938, 1774.

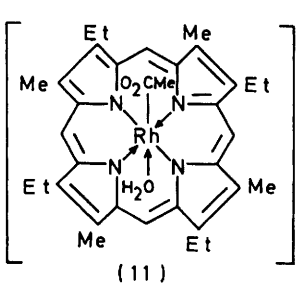
[7] D. G. Hoare and W. A. Waters, *J. Chem. Soc.*, 1964, 2561; A. A. Clifford and W. A. Waters, *ibid.*, 1965, 2796.

[8] S. S. Lande and J. K. Kochi, *J. Amer. Chem. Soc.*, 1968, **90**, 5196.

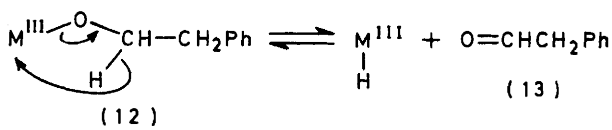
of rhodium metal,[9] and this proved to be the active catalyst. Thus filtration of the mixture gave a green filtrate devoid of oxidising properties, whilst the grey deposit was an active catalyst. The green colour of the filtrate suggested the presence of a rhodium(II) species [10] and prompted the screening of rhodium(II) acetate as a catalyst. The acetate was an inefficient catalyst (Table 1) but no rhodium metal was deposited. Rhodium metal on a suitable carrier is known to effect dehydrogenation of alcohols to the corresponding carbonyl compounds,[11] although usually at >150 °C. However, we found that 5% Rh–C catalysed the aerial oxidation of boiling ethanol (Table 1) and this heterogeneous system was by far the most efficient of the catalysts we studied.

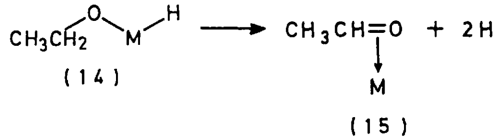

(9)


(10)


(11)

The rhodium trichloride-catalysed dehydrogenation of isopropyl alcohol to acetone in acidic media has been reported [9] and the results interpreted in terms of an intermediate rhodium(III) hydride. However, the reduction of rhodium(III) to rhodium(I) species by alcohols has been reported by several groups.[12] There are also many reports of rhodium(I) complexes catalysing allylic oxidation [13,14] or oxidative cleavage of double bonds [15] in which radical species are clearly implicated. The deactivating effect of compound (1) on the catalytic properties of the rhodium complexes may be due to the ability of (1) or its breakdown products to stabilise the rhodium(III) oxidation state and so prevent the redox reaction occurring. In an attempt to gain information on the rhodium-catalysed oxidations of alcohols, the oxidation of 2-phenylethanol was studied. A free-radical mechanism (Scheme 2) should give rise to formaldehyde and a benzyl radical.[16] Further reaction of the benzyl radical could then give rise to benzaldehyde or benzoic acid. An alternative hydrogen-transfer reaction would yield phenylacetaldehyde and a metal hydride [(12) ⟶ (13)]. Both cobalt(II) chloride–compound (1) and complex (9) promoted the aerial oxidation of 2-phenylethanol producing mixtures of formaldehyde and benzaldehyde which were isolated as their dimedone derivatives and identified by comparison with authentic samples. The yield of mixed aldehydes was too low to merit discussion in the cobalt case, but was sufficient in the rhodium case to implicate a free-radical process. However, the observation that 5% Rh–C is an efficient catalyst for the oxidation of ethanol to acetaldehyde urges caution in interpreting our results for complex (9) since small amounts of colloidal rhodium metal may be responsible for the observed catalytic activity. Rhodium metal is known to facilitate rapid deuteriation of methanol at low temperatures,[17] and the activation energy for hydroxyl exchange is significantly lower than that for exchange of the methyl hydrogen atoms. These observations are consistent with the sequence (14) ⟶ (15) with the oxygen removing the liberated hydrogen as water.


(12) (13)


(14) (15)

The benzylic oxidation of tetralin (1,2,3,4-tetrahydronaphthalene) to α-tetralone using (9) was briefly investigated. A slow oxidation occurred but was much less efficient than the previously reported chlorotris(triphenylphosphine)rhodium process.[13]

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. Ultraviolet and visible spectra were recorded on a Unicam SP 700 instrument, using chloroform solutions unless otherwise stated. Infrared spectra were determined with a Unicam SP 100 instrument and refer to potassium bromide discs unless otherwise stated. N.m.r. spectra were obtained for deuteriochloroform solutions (except where otherwise stated) on Perkin-Elmer RS 10

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[9] H. B. Charman, *J. Chem. Soc.* (*B*), 1967, 629.

[10] P. Legzdius, G. Rempel, and G. Wilkinson, *Chem. Comm.*, 1969, 825; F. Maspere and H. Taube, *J. Amer. Chem. Soc.*, 1968, **90**, 7361.

[11] M. Hajek, J. C. Duchet, and K. Kochloefl, *Coll. Czech. Chem. Comm.*, 1970, **35**, 2258; P. Tetenyi and K. Schachter, *Acta Chim.* (*Budapest*), 1970, **65**, 253; *Acta Chim. Acad. Sci. Hung.*, 1968, **56**, 141.

[12] J. Chatt and B. L. Shaw, *Chem. and Ind.*, 1960, 931; 1961, 290; J. V. Rund, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 1964, **3**, 658.

[13] J. Blum, H. Rosenman, and E. Bergmann, *Tetrahedron Letters*, 1967, 3665.

[14] J. Blum, J. Y. Becker, and E. D. Bergmann, *J. Chem. Soc.* (*B*), 1969, 1000; A. J. Birch and G. S. R. Subba Rao, *Tetrahedron Letters*, 1968, 2917; J. E. Baldwin and J. C. Swallow, *Angew. Chem. Internat. Edn.*, 1969, **8**, 601.

[15] J. E. Lyons and J. O. Turner, *Tetrahedron Letters*, 1972, 2903.

[16] J. R. Jones and W. A. Waters, *J. Chem. Soc.*, 1960, 2772.

[17] J. R. Anderson and C. Kemball, *Trans. Faraday Soc.*, 1955, **51**, 966.

(60 MHz) or Varian HA 100 instruments using tetramethylsilane as internal reference (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Mass spectra were recorded on an A.E.I. MS 902 instrument.

Oxidation of Ethanol.—In general, a mixture of a metal salt and an azo-ligand was used in the manner described below, in an attempt to oxidise the ethanol solvent. The ethanol was replenished as necessary.

Cobalt(II) *Chloride and* 1-(2-*Dimethylaminophenylazo*)-N-*methyl*-2-*naphthylamine.*—Air was passed through a refluxing solution of cobalt(II) chloride hexahydrate (0.24 g, 1 mmol) and 1-(2-dimethylaminophenylazo)-*N*-methyl-2-naphthylamine (0.6 g, 2 mmol) in dry ethanol (30 cm^3) at a rate of 200 cm^3 min^{-1}. The exit gases from the condenser were passed through a series of bubblers containing concentrated aqueous dimedone solution. After 24 h, when the reaction had terminated, the dimedone derivative was collected (0.28 g, 0.92 mmol), m.p. 140—141 °C (lit.,[18] 141 °C), identical to an authentic sample of acetaldehyde dimedone derivative: τ −2.5 (s, 2 H, 2 OH), 5.85 (q, 1 H, C*H*Me), 7.7 (s, 8 H, ring C*H*$_2$), 8.5 (d, 3 H, CH*Me*), and 8.95 (s, 12 H, 4 Me).

Iron(III) *aetioporphin* I *acetate.* Iron(III) aetioporphin I acetate (0.1 g) was dissolved in a mixture of chloroform (10 cm^3) and dry ethanol (10 cm^3). Air was passed through the refluxing solution at 200 cm^3 min^{-1}, with the exit gases passing through dimedone bubblers. No dimedone derivative had precipitated after 48 h.

Di-μ-*chloro*-*bis*[*dicarbonylrhodium*(I)]. A stream of air was passed through a refluxing solution of the complex (39 mg, 0.1 mmol) in dry ethanol (40 cm^3) at the rate of 200 cm^3 min^{-1}. The exit gases were passed through dimedone bubblers and after 12 d the derivative was collected (6.96 g, 227.5 mmol), m.p. 140—143 °C. Repetition of the experiment with addition of triphenylphosphine gave the dimedone derivative (8.45 g, 276.2 mmol) after 16 d.

The following reactions were carried out similarly: dicarbonyl(pentane-2,4-dionato)rhodium(I) (26 mg, 0.1 mmol), yielding the dimedone derivative (1.24 g, 40.5 mmol), m.p. 141—142 °C, after 4 d; rhodium(II) acetate (53.4 mg, 0.1 mmol), yielding the dimedone derivative (0.19 g, 0.62 mmol), m.p. 140—141 °C, after 48 h; and 5% Rh–C (20 mg) oxidation still occurring (Table 1) after 10 d.

Cobalt(II) *fluoride and* 1-(2-*dimethylaminophenylazo*)-N-*methyl*-2-*naphthylamine with various nitrogenous ligands.* The general procedure is illustrated by the following example.

1-*Methylbenzimidazole.* Air was passed through a refluxing solution of CoF$_2$ (0.1 g, 1 mmol), 1-(2-dimethylaminophenylazo)-*N*-methyl-2-naphthylamine (0.6 g, 2 mmol), and 1-methylbenzimidazole (0.26 g, 2 mmol) in dry ethanol (30 cm^3) at a rate of 200 cm^3 min^{-1}. The exit gases were passed through dimedone bubblers and after 24 h the derivative was collected (0.16 g, 0.52 mmol), m.p. 141—143 °C.

Cobalt(II) *aetioporphin* I *and benzimidazole.* A mixture of cobalt(II) aetioporphin I (0.54 g, 1 mmol) and benzimidazole (0.24 g, 2 mmol) in chloroform (10 cm^3) and dry ethanol (20 cm^3) was heated under reflux with air bubbling (200 cm^3 min^{-1}). No dimedone derivative had been produced after 24 h. The absorption spectrum of the reaction solution showed a high-intensity (Soret) band at 426 nm corresponding to the cobalt(III) complex. A similar result was obtained using imidazole in place of benzimidazole.

Cobalt(II) *chloride and potassium propionate–n-propanol.* Air (200 cm^3 min^{-1}) was passed through a solution of CoCl$_2$·6H$_2$O (0.24 g, 1 mmol), 1-(2-dimethylaminophenylazo)-*N*-methyl-2-naphthylamine (0.60 g, 2 mmol), and potassium propionate monohydrate (6.5 g, 50 mmol) in n-propanol (50 cm^3). After 15 d the dimedone derivative was collected (3.83 g) and was shown by t.l.c. to be a mixture of one main component with a small amount (*ca.* 5% from n.m.r.) of a second (the acetaldehyde derivative). Crystallisation from aqueous methanol yielded pure propionaldehyde dimedone derivative (3.45 g), m.p. 155—157 °C (lit.,[18] 155 °C) identical to an authentic sample.

Di-μ-*chloro*-*bis*[*dicarbonylrhodium*(I)] *and potassium propionate–n-propanol.* Air was passed through a refluxing solution of the complex (39 mg, 0.1 mmol) and potassium propionate (6.5 g, 50 mmol) in n-propanol (70 cm^3). The reaction was stopped after 5 weeks and the dimedone derivative was collected (148.72 g). As in the above case this was a mixture of the acetaldehyde (5%) and the propionaldehyde (m.p. 156—158 °C) derivatives.

Oxidation of 2-*Phenylethanol.*—*Cobalt*(II) *chloride and* 1-(2-*dimethylaminophenylazo*)-N-*methyl*-2-*naphthylamine.* Air (200 cm^3 min^{-1}) was passed through a solution of CoCl$_2$·6H$_2$O (0.24 g, 1 mmol) and 1-(2-dimethylaminophenylazo)-*N*-methyl-2-naphthylamine (0.60 g, 2 mmol) in 2-phenylethanol (300 cm^3), heated on a steam-bath. After 24 h the dimedone derivative was collected (0.07 g), m.p. 162—165 °C [lit.,[18] 189 (formaldehyde derivative), 195 °C (benzaldehyde derivative)]. T.l.c. comparison with authentic samples showed the derivative to be a mixture of the formaldehyde and benzaldehyde derivatives. The n.m.r. spectra also showed this, giving signals at τ 2.80 (m, aromatic protons), 4.44 (s, C*H*), 7.62 (s, ring-methylene protons), and 8.84 (s, ring Me) corresponding to the benzaldehyde derivative and 6.85 (s, C*H*$_2$), 7.75 (s, ring-methylene protons), and 8.97 (s, ring Me) corresponding to the formaldehyde derivative.

Di-μ-*chloro*-*bis*[*dicarbonylrhodium*(I)]. This reaction was carried out as above using the complex (39 mg), and yielded the dimedone derivative (0.45 g). Again this was shown to be a mixture of the formaldehyde and benzaldehyde derivatives by t.l.c. and n.m.r. comparison with authentic samples.

Oxidation of Tetralin.—Air (200 cm^3 min^{-1}) was passed through a solution of [Rh$_2$(CO)$_4$(μ-Cl)$_2$] (39 mg, 0.1 mmol) in tetralin (50 cm^3), heated on a steam-bath. After 11 d the reaction mixture was distilled yielding unchanged tetralin (26.8 g), b.p. 80—90 °C (13 mmHg),* and α-tetralone (8.12 g, 51.4 mmol), b.p. 129—132 °C (13 mmHg). The α-tetralone was spectroscopically identical (n.m.r. and i.r.) to an authentic sample.

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[6/1492 *Received*, 30*th July*, 1976]

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

[18] A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 1970.