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THE ORGANIC COMPOUNDS OF COBALT(III)

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CONTENTS

INTRODUCTION

Prior to 1955, the field of organocobalt chemistry was limited to a group of ill-defined aryl- and alkyl-cobalt compounds formed during the reaction of Grignard and other organometallic reagents with cobalt halides[1]. However, with the great expansion of organometallic chemistry in the late 1950's and aided by the knowledge that carbon to transition metal bonds might be stabilised by certain ligands, there was also some progress in the preparation of compounds containing carbon–cobalt bonds. The first major group to be prepared and characterised were the alkylcobalt(I) carbonyls[2] along with only infrequent examples of organocobalt(III) compounds[3,4]. Then, in 1962 came one of the most interesting of the developments that have so far occurred in organometallic chemistry; this was the discovery, following the elegant X-ray crystallographic study of vitamin B_{12}, that a naturally occurring molecule, vitamin B_{12} coenzyme (I), contained a carbon–cobalt σ-bond[5]. Moreover, contemporary chemical studies showed that this bond was unaffected by a number of reagents which cleaved bonds elsewhere in the molecule[6]. The realisation that this compound was formally a complex of cobalt(III) and that the corrin ring might be an important factor in the stabilisation of the carbon–cobalt bond, led to wide consideration of the possibility that other carbon–cobalt(III) compounds might be formed with the same ligand and perhaps also with analogous ligands.

Progress since that time has been considerable, and the number of organocobalt(III) compounds that have now been described is more than one thousand; these are catalogued in Table 1. One of the reasons for this rapid development has been the wide interest which these compounds provoke. This ranges from their role as inorganic complexes, through their interest as organic derivatives and in organic synthesis, and especially to their biochemical function and potential. Consequently, the literature on these compounds is scattered over a wide range of journals, is couched in a variety of styles, and reflects a variety

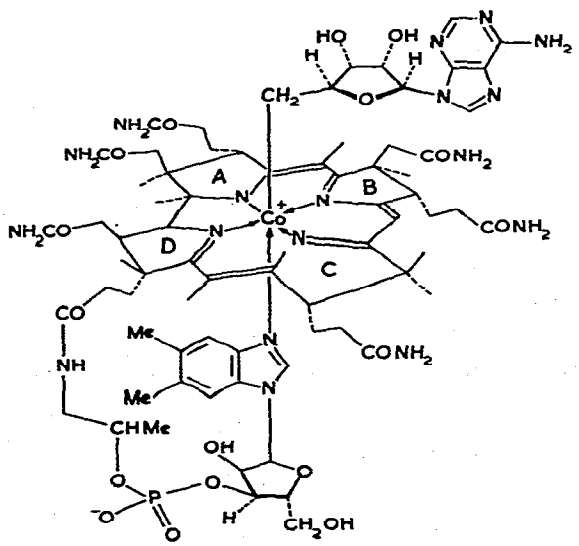
of depth of understanding of the several fields concerned.

This review is an attempt to explore the scope of the whole field with special emphasis on the mechanism of the reactions concerned, thereby to deduce the common features of what are apparently widely different compounds. In such a rapidly growing field covering so wide a range of chemical and biological interest, there are more than the usual number of uncertain results which later prove to be erroneous or incorrect in detail. One of the reasons for this, and indeed for the interesting chemistry of these compounds, is the fact that cobalt(III), cobalt(II), and cobalt(I), and even cobalt(IV) species are all relatively accessible, such that it is often difficult to know precisely with which species one is concerned, without much careful and detailed work.

The organocobalt(III) compounds with which we shall be concerned fall into two main classes. The smaller class, which has not been studied in much detail, and which includes the hexaacetylides[3], some *cis*-dialkylcobalt(III) complexes[7], and the π-cyclopentadienylcobalt(III) compounds[8,9], are merely classified and listed in Table 1. By far the larger class have a variety of nitrogen and oxygen donor ligands attached to the cobalt, besides the organic group, and these are listed in Table 1, and discussed in detail in subsequent chapters.

In view of the wide range of compounds within this major group, it is important first to outline the types of ligands that are commonly involved, not only for the purposes of the classification in Table 1, but also in order to become familiar with the terminology and to understand something of the role of those ligands in determining the stability and reactivity of the compounds.

Table 1 starts at the end of the article on page 121.

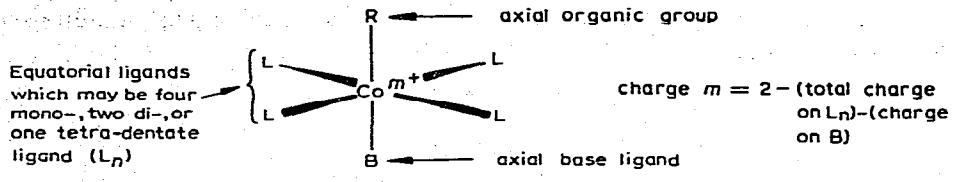


(I)

Classification of ligands

With the exception of the minor group of compounds, the organocobalt(III) compounds discussed in this review are generally square pyramidal or octahedral five- and six-coordinate complexes (II) in which the metal is coordinated to the organic group and to various combinations of mono-, di-, tetra-, and penta-dentate ligands.

Though a variety of monodentate ligands are involved, particularly as axial bases *trans* to the organic group, it is inconvenient to use them for our primary classification. We therefore restrict our nomenclature to an initial consideration of those ligands in the equatorial plane *cis* to the organic group. These are subdivided, for the purposes of Table 1, into the groups shown in Table 2. Since different authors have used different symbols for what, it will be apparent, are a complicated series of molecules some of which are tedious to name systematically, we have attempted to revise the symbolism uniformly. Where more than one symbol has previously been used, we have selected the one that seems most appropriate, except in one case where the symbolism seemed inappropriate and we have provided an alternative. In general we have preferred the symbolism which may be suitably modified to indicate the formation of conjugate acids or conjugate bases of the ligands where appropriate. Some alternatives that may be found in the literature are shown as footnotes to Table 2. The nomenclature of the cobalamins and derivatives is as standardised elsewhere[10].



(II)

In addition to the abbreviations shown in Table 2, the following are also frequently encountered:

Vitamin B_{12} coenzyme = DBCC = 5′-deoxyadenosylcobalamin(III).

B_{12} = cyanocobalamin(III).

B_{12a} = aquo- or hydroxo-cobalamin(III).

B_{12r} = aquo- or hydroxo-cobalamin(II).

B_{12s} = aquo- or hydroxo-cobalamin(I).

The organobis(dioximato)cobalt(III) complexes are also frequently referred to as organocobaloximes.

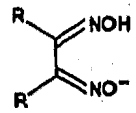
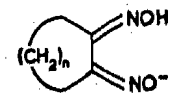
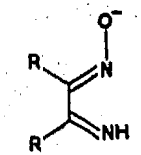
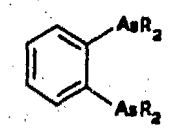
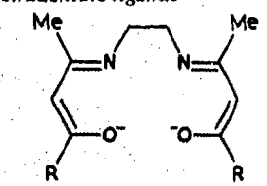
METHODS OF PREPARATION

The methods of preparation of the organocobalt(III) compounds are conveniently classified according to whether the effective cobalt-containing reagent is formally cobalt(III),

(continued on p. 10)

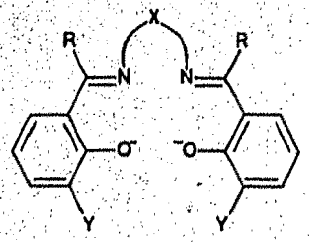
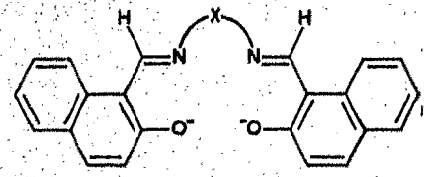
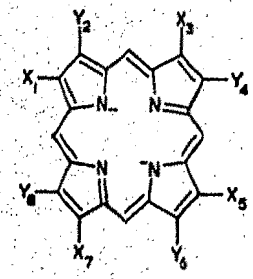
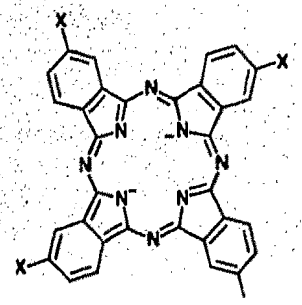
TABLE 2

Equatorial ligands and symbolism in organocobalt(III) chemistry

Ligand		*Typical formula*[a]
Monodentate ligands		
CN^-		$RCo(CN)_4B^{2-}$
Bidentate ligands		
	R = H	$RCo(gH)_2B$
	R = Me	$RCo(dmgH)_2B$ [b]
	R = Ph	$RCo(dpgH)_2B$
	R = *p*-$MeOC_6H_4$	$RCo(MeO\text{-}dpgH)_2B$
	R = *p*-$O_2NC_6H_4$	$RCo(O_2N\text{-}dpgH)_2B$
	*n* = 3	$RCo(c\text{-}pgH)_2B$
	n = 4	$RCo(c\text{-}hgH)_2B$[c]
	R = Me	$RCo(dmimoxH)_2B$
	R = Me	$RCo(diars)_2B$
Tetradentate ligands		
	R = Me	RCo(acacen)B[d]
	R = CF_3	RCo(F-acacen)B
	R = $PhCH_2$	RCo(bzacen)B

(continued next page)

TABLE 2 (continued)

Ligand	*Typical formula*[a]
	
R = H, Y = H, X = $(CH_2)_2$	RCo(salen)B
R = H, Y = H, X = $(CH_2)_3$	RCo(saltn)B
R = H, Y = H, X = CH_2CHMe	RCo(salpn)B
R = H, Y = H, X = $(CH_2CH_2CH_2)_2NH$	RCo(salpr)B[e,f]
R = H, Y = H, X = *o*-phenylene	RCo(salphen)B[g]
R = H, Y = H, X = 4-Cl-*o*-phenylene	RCo(Cl-salphen)B
R = H, Y = OMe, X = $(CH_2)_2$	RCo(3,3'-MeO-salen)B
R = Me, Y = H, X = $(CH_2)_2$	RCo(7,7'-Me-salen)B[h]
	
X = $(CH_2)_2$	RCo(napsalen)B
X = *o*-phenylene	RCo(napsalphen)B
	
X = Me, Y = Et (aetioporphyrin I)	RCo(aetpor)B
X = Y = Et (octaethylporphin)	RCo(octetpor)B
X, Y = *o*-phenylene (tetraphenylporphin)	RCo(tetphpor)B
$X_1 = X_3 = X_5 = Y_8$ = Me; $Y_2 = Y_4$ = H; $Y_6 = X_7 = CH_2CH_2CO_2Me$ (deuteroporphyrin IX dimethyl ester) (phthalocyanine)	RCo(Me-deutpor)B
	
X = H	RCo(pc)B
X = SO_3H	RCo(tspc)B

RCo(ambpn)B[i]

RCo(doenH)B[j]
RCo(dotnH)B[k]

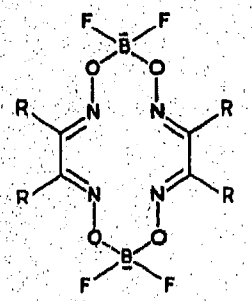
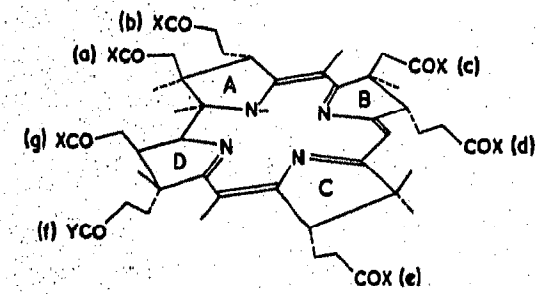
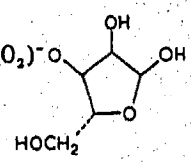
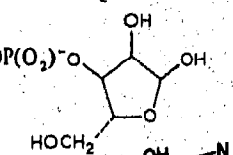
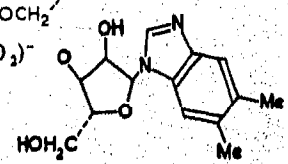
X = $(CH_2)_2$
X = $(CH_2)_3$

RCo(cr)B[3+l]

RCo(tim)B[2+]

(continued next page)

TABLE 2 (continued)

Ligand		*Typical formula*[a]
	R = Me	$RCo(dmgBF_2)_2B$
	$X = NH_2$, $Y = OH$	Rcobyric acid[n]
	$X = OH$, $Y = OH$	Rcobyrinic acid[n]
	$X = NH_2$, $Y = NH \cdot CH_2CHMe \cdot OH$	Rcobinamide[n]
	$X = OH$, $Y = NH \cdot CH_2CHMe \cdot OH$	Rcobinic acid[n]
	$X = NH_2$, $Y = NH \cdot CH_2CHMe \cdot OP(O_2)^- O$ 	Rcobamide[n]
	$X = OH$, $Y = NH \cdot CH_2CHMe \cdot OP(O_2)^- O$ 	Rcobamic acid[n]
	$X = NH_2$, $Y = NH \cdot CH_2CHMe \cdot OP(O_2)^-$ 	Rcobalamin[m,n]

[a] The ligand B is considered to be neutral in these formulae; for anionic ligands the charge should be increased accordingly. In some cases the ligand B may be absent.
[b] Also referred to as $RCo(DH)_2B$, $RCo(DMG)_2B$.
[c] Also referred to as $RCo(nioxime)_2B$, $RCo(nioxH)_2B$.
[d] Also referred to as RCo(BAE)B.
[e] This ligand may also behave as a pentadentate.
[f] Also referred to as RCo(saldpt)B.
[g] Also referred to as RCo(saloph)B.
[h] Also referred to as RCo(oiaphen)B.
[i] Also referred to as RCo(abpn)B.
[j] Also referred to as $RCo(dmed)B^+$, $RCo[(DOH)(DO)en]B^+$.
[k] Also referred to as $RCo(tmed)B^+$, $RCo[(DOH)(DO)pn]B^+$.
[l] Also referred to as RCo(cyp)B.
[m] This ligand usually behaves as a pentadentate, except when the fifth nitrogen (on the benziminazole group) is alkylated or protonated, or in the presence of a strongly coordinating monodentate base, or when the group R is very bulky (cf. I).
[n] A variety of derivatives of these species are also known. See Table 1.

cobalt(II), cobalt(I) or a hydridocobalt species. For clarity, the methods of preparation have been arranged as follows: (I) A discussion of the methods of preparation of the organocobalt(III) compounds from their immediate cobalt precursors and organic reagents. (II) A brief discussion of the methods of preparation of those cobalt-containing precursors and (III) a detailed discussion of the mechanisms of the preparative reactions. The methods are summarised in Table 3 and those used for each individual compound are included in Table 1, in which the abbreviations under the heading 'method' refer to the headings of the following sub-sections.

TABLE 3

Summary of methods of preparation of organocobalt(III)[a] compounds

Inorganic reagent	*Organic reagent*	*Products*	*Section*
Electrophilic reactions of cobalt(III) species			
Y(Co)B, Y = Hal, etc.	RM, M = metal	R(Co)B + YM	IA
B(Co)$^+$	R^-	R(Co)B	IB
B(Co)$^+$	CH_2=CR(OH)	$RCOCH_2$(Co)B + H^+	IB
B(Co)$^+$	ROH + CO	ROCO(Co)B + H^+	IC
Free radical reactions of cobalt(II) species			
2 (Co)B	RX, X = Hal, etc.	R(Co)B + X(Co)B	IIA, B
2 (Co)B	RH + H_2O_2	R(Co)B + HO(Co)B	IIA
2 (Co)B	$X_2C=CX_2$	B(Co)CX_2CX_2(Co)B	IIC
2 (Co)B	RC≡CR	B(Co)CR=CR(Co)B	IIC
n (Co)B	ArN_2^+	Ar(Co)B	IID
n (Co)B	R_2TlX	R(Co)B + ?	IIE
Nucleophilic reactions of cobalt(I) species			
B(Co)$^-$	RX, X = Hal, tosylate etc.	R(Co)B + X^-	IIIA
B(Co)$^-$/ROH	epoxides	Hydroxyethyl (Co)B	IIIA
B(Co)$^-$/ROH	$XCH=CH_2$, X = CN, etc.	XCH_2CH_2(Co)B + OR^-	IIIB
B(Co)$^-$/ROH	XC≡CH, X = CN^-, aryl, etc.	XCH=CH(Co)B + OR^-	IIIB
B(Co)$^-$/ROH	$CH_2=C=CH_2$	CH_2=CMe(Co)B + OR^-	IIIB
Additions of hydridocobalt species			
H(Co)B	$RCH=CH_2$	CH_3CHR(Co)B	IIIC
H(Co)B	RC≡CH	CH_2=CR(Co)B	IIIC
H(Co)B	$RCHN_2$	RCH_2(Co)B	IIIC

[a] (Co) refers to the metal together with its equatorial ligands, charge unspecified.

(I) Preparation from cobalt(III) reagents

(A) The earliest attempts made to prepare organocobalt compounds involved the reaction of Grignard reagents with cobalt(II) halides. Apart from the formation of a few acetylides[3], these failed because of the absence of the requisite stabilising ligands on the metal (Table 2) and probably also because of the greater instability of organocobalt(II) than of organocobalt(III) compounds. However, a variety of stable covalent halocobalt(III) compounds are now available, and many of these react smoothly with aryl- and alkyl-Grignard reagents and with other organometallic reagents such as the alkali metal alkyls, in ethereal solvents, to give the corresponding alkyl-or aryl-cobalt(III) compound in good yield. Several equivalents of the organometallic reagent are often necessary in order to allow for the reaction with acidic sites on equatorial and axial ligands and with axial ligands (*e.g.* as in eq. 1).

$$PhLi + BrCo(aetpor)py \xrightarrow{(MeOCH_2)_2} PhCo(aetpor) + LiBr \quad (1)^{11}$$

$$PhC{\equiv}CMgX + XCo(dmgH)_2py \xrightarrow{THF} PhC{\equiv}CCo(dmgH)_2py + MgX_2 \quad (2)^{12}$$

$$C_6F_5MgBr + ICo(salen) \xrightarrow{THF} C_6F_5Co(salen) + MgBrI \quad (3)^{13}$$

(B) In principle, coordinatively unsaturated cobalt(III) species are mildly electrophilic reagents. Since cobalt(III) complexes are usually substitution inert, they are generally insufficiently reactive to promote bimolecular displacement reactions, but some are sufficiently reactive to capture appropriate stabilised carbanions and to react with enols, even in aqueous solution. For example:

$$CH_2(CN)_2 + B \rightleftharpoons {}^-CH(CN)_2 + BH^+ \quad (4)^{14}$$

$${}^-CH(CN)_2 + Co(ambpn)(H_2O)^+ \xrightarrow{aq} (NC)_2CHCo(ambpn) \quad (5)^{15}$$

$$CH_2{=}C(OH)Me + Co(salen)(MeOH)^+ \longrightarrow MeCOCH_2Co(salen)(MeOH) + H^+ \quad (6)^{16}$$

(C) Several aquocobalt(III) species also react with carbon monoxide in alcoholic solution to give alkoxycarbonyl derivatives, *i.e.*,

$$ROH + CO + MeOCo(dmgH)_2py \longrightarrow ROCOCo(dmgH)_2py + MeOH \quad (7)^{17,18}$$

(II) Preparation from cobalt(II) reagents

(A) Cobalt(II) species are paramagnetic and hence are capable of inducing and terminating free radical reactions. One of the earliest methods of synthesis involved combination of both of these properties[19,20]. Thus, on addition of an alkyl halide to a solution of the pentacyanocobaltate(II) ion under anaerobic conditions, the cobalt(II) species acts both as a halogen atom abstractor and as a radical trap for the free radical produced, with

the formation of a relatively stable organopentacyanocobaltate(III) ion, *i.e.*:

$$RHal + Co(CN)_5^{3-} \longrightarrow R^{\cdot} + HalCo(CN)_5^{3-} \quad (8)$$

$$R^{\cdot} + Co(CN)_5^{3-} \longrightarrow RCo(CN)_5^{3-} \quad (9)$$

The reaction is also applicable to other cobalt(II) species, but there are few examples of its application, and it may require fairly reactive alkyl halides, *e.g.*:

$$CCl_4 + 2Co(dmgH)_2py \longrightarrow Cl_3CCo(dmgH)_2py + ClCo(dmgH)_2py \quad (10)^{21}$$

Since the second stage of this reaction, *i.e.*, the capture of the organic radical, is highly favourable, any method which may produce organic radicals in the presence of coordinatively unsaturated cobalt(II) species may result in the formation of organocobalt(III) compounds. A possible[22] route might be:

$$H_2O_2 + Co^{II} \longrightarrow HOCo + HO^{\cdot} \quad (11)$$

$$HO^{\cdot} + C_2H_5OC_2H_5 \longrightarrow H_2O + C_2H_5O\dot{C}HCH_3 \quad (12)$$

$$C_2H_5O\dot{C}HCH_3 + Co^{II} \longrightarrow C_2H_5OCHMeCo^{III} \quad (13)$$

(B) Cobalt(II) species are also capable of undergoing electron transfer to certain readily reducible organic substrates. Thus, *p*-nitrobenzyl halides react with some cobalt(II) species to give the corresponding nitrobenzyl radical, which may be captured by the excess of cobalt(II). This method has been investigated in some detail[23], but has only limited preparative scope.

$$ArCH_2Br + Co^{II}(salen)(Meimd)_2 \longrightarrow [ArCH_2Br]^{\cdot-} + Co^{III}(salen)(Meimd)_2^{+} \quad (14)$$

$$[ArCH_2Br]^{\cdot-} \longrightarrow ArCH_2^{\cdot} + Br^{-} \quad (15)$$

$$ArCH_2^{\cdot} + Co^{II}(salen)(Meimd) \longrightarrow ArCH_2Co(salen)(Meimd) \quad (16)$$

(C) One of the first organocobalt(III) compounds to be synthesised[4] was a dicobalt compound formed from acetylene and the pentacyanocobaltate(II) ion. Similar addition of two paramagnetic cobalt(II) species also occurs with mono- and di-substituted acetylenes[24], and with tetrafluoroethylene, to give diamagnetic vinyl- and perfluoroalkyl-dicobalt complexes, respectively.

$$RC{\equiv}CR' + 2Co(CN)_5^{3-} \longrightarrow (NC)_5CoCR{=}CR'Co(CN)_5^{6-} \quad (17)$$

$$F_2C{=}CF_2 + 2Co(CN)_5^{3-} \longrightarrow (NC)_5CoCF_2CF_2Co(CN)_5^{6-} \quad (18)^{25}$$

(D) The pentacyanocobaltate(II) ion also reacts with the benzenediazonium ion in aqueous solution to give the phenylpentacyanocobaltate(III) ion[20], but the mechanism

and stoechiometry of this reaction have not been studied.

$$PhN_2^+ + nCo(CN)_5^{3-} \longrightarrow PhCo(CN)_5^{3-} \quad (19)$$

(E) Perfluorophenylcobalt(III) diarsine complexes have been prepared by the reaction of bis(pentafluorophenyl)thallium(III) bromide with the bis(diarsine) cobalt(II) bromide[26]. The scope of this type of reaction has not been explored.

$$(C_6F_5)_2TlBr + Co(diars)_2Br_2 \longrightarrow C_6F_5Co(diars)_2Br^+ + ? \quad (20)$$

(III) Preparation from cobalt(I) and hydridocobalt species

(*a*) *Nucleophilic displacements by cobalt(I) species.* The commonest route to organocobalt(III) compounds, and also the most versatile, involves the reaction of nucleophilic cobalt(I) species with organic compounds. A wide range of cobalt(I) species, including vitamin B_{12s}[27,28] (a reduced form of cyanocobalamin and of the coenzyme) and the anionic bis(dimethylglyoximato)pyridinecobaltate(I) ion[12], are amongst the most powerful of known nucleophiles towards saturated carbon; capable of displacing halide, phosphate[27], and tosylate ion from the corresponding alkyl derivatives, and of displacing trimethylamine from benzyltrimethylammonium ion[29], and of opening epoxide and ethyleneimine rings. The species $[Co^I(7,7'\text{-Me-salen})]^-$ is apparently so nucleophilic that it is capable of displacing bromide ion from bromobenzene, though the mechanism of this reaction has not been confirmed.

$$^{14}CH_3I + B_{12s} \longrightarrow {}^{14}CH_3\text{cobalamin} + I^- \quad (21)^{31}$$

$$CHBr_3 + [Co(dmgH)_2py]^- \longrightarrow Br_2CHCo(dmgH)_2py + Br^- \quad (22)^{21,32}$$

$$MeCHCH_2O + [Co(dmgH)_2py]^- \xrightarrow{MeOH} MeCH(OH)CH_2Co(dmgH)_2py \quad (23)^{33}$$

$$PhBr + [Co(7,7'\text{-Me-salen})]^- \longrightarrow PhCo(7,7'\text{-Me-salen}) + Br^- \quad (24)^{16}$$

$$CH_2{=}CHCl + [Co(acacen)]^- \longrightarrow CH_2{=}CHCo(acacen) + Cl^- \quad (25)^{34}$$

$$p\text{-}C_6H_4(CH_2Br)_2 + 2Co(dmgH)_2py^- \longrightarrow p\text{-}C_6H_4[CH_2Co(dmgH)_2py]_2 + 2Br^- \quad (26)^{35}$$

This method is usually unsuccessful with vicinal dihalides, and unexpected products may be obtained with bromohydrins, *e.g.*:

$$ClCH{=}CHCl + [Co(dmgH)_2py]^- \longrightarrow HC{\equiv}CH + ClCo(dmgH)_2py + Cl^- \quad (27)^{36}$$

$$HOCH_2CHMeBr + [Co(aetpor)]^- \longrightarrow HOCHMeCH_2Co(aetpor) + Br^- \quad (28)^{11}$$

(*b*) *Preparation via nucleophilic addition of cobalt(I) species to unsaturated organic molecules.* Cobalt(I) species are also capable of undergoing nucleophilic addition to a

variety of olefins in protic solvents. In the few cases studied in detail, the reaction with acetylenes has been shown to be a *trans*-addition of the metal ion and the proton from the solvent[37,38]. Suitable activated olefins include acrylonitrile and dimethylmaleate.

$$CH_2{=}CHCO_2Et + [Co(dmgH)_2py]^- \xrightarrow{EtOH} EtOCOCH_2CH_2Co(dmgH)_2py + EtO^- \quad (29)^{39}$$

$$HC{\equiv}CH + [Co(7,7'\text{-Me-salen})]^- \xrightarrow{THF/aq} CH_2{=}CHCo(7,7'\text{-Me-salen}) + OH^- \quad (30)^{16}$$

$$H_2C{=}C{=}CH_2 + [Co(dmgH)_2py]^- \xrightarrow{MeOH} CH_2{=}CMeCo(dmgH)_2py + MeO^- \quad (31)^{40}$$

(*c*) *Preparation via addition of hydridocobalt species to unsaturated organic compounds.* In less basic solution the cobalt(I) species tend to form covalent hydrides[41], which undergo distinct reactions with many of the unsaturated compounds described above. These reactions usually have a different stereochemistry from those with the nucleophilic cobalt(I) species. The hydriodopentacyanocobaltate(III) ion does not appear to dissociate even in strongly alkaline solution[42] and appears always to react as the covalent hydride, but the less basic cobalt(I) species, such as the bis(dimethylglyoximato)pyridinecobaltate(I) ion or vitamin B_{12s}, may require neutral or mildly acidic solution before the reaction of their hydrido species becomes dominant[41,43]. (Since many of the reactions described in Table 1 were carried out under ill-defined conditions it may be difficult to reproduce the yield and character of the product unless the pH is the same as that used previously.)

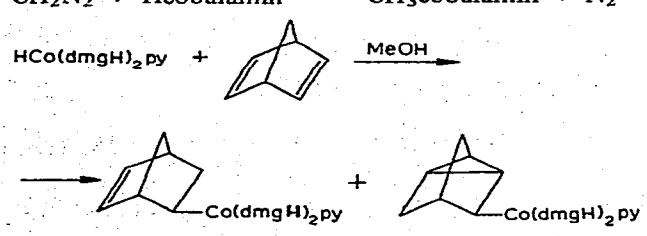
$$CH_2{=}CHCN + HCo(dmgH)_2PBu_3 \longrightarrow NCCHMeCo(dmgH)_2py \quad (32)^{44}$$

$$PhC{\equiv}CH + HCo(dmgH)_2py \longrightarrow H_2C{=}CHPhCo(dmgH)_2py \quad (33)^{37,38}$$

$$2\text{-}pyCH{=}CH_2 + HCo(CN)_5^{3-} \longrightarrow 2\text{-}pyCHMeCo(CN)_5^{3-} \quad (34)^{45,46}$$

Diazomethane and some strained olefins may also react with hydridocobalt species, *i.e.*:

$$CH_2N_2 + Hcobalamin \longrightarrow CH_3cobalamin + N_2 \quad (35)^{27,28}$$



(36)[47]

(IV) Preparation of cobalt(III), cobalt(II), and cobalt(I) reagents

The majority of the inorganic precursors of organocobalt(III) compounds are derived from simple cobalt(II) salts which, after complexing with appropriate ligands, are either oxidised to cobalt(III) species, reduced to cobalt(I) species, used directly, or allowed to disproportionate to a mixture containing both cobalt(I) and cobalt(III) species. The method used depends upon the influence of the chosen ligands on the redox potentials of

the complexes and upon the lability of the organic reagents and the organocobalt(III) products in the required media. The complex nature of the cobalamins, cobinamides, etc. and their hydrolysis products precludes their total synthesis except for the purposes of proving their structure[48,49]. They are usually prepared from the more readily isolated derivatives of naturally occurring cobalt(III) corrinoid compounds, such as vitamin B_{12}, B_{12a}, etc.

The following methods have been used for the preparation of the reactive cobalt(III), cobalt(II) and cobalt(I) species.

(a) Cobalt(III) reagents

Air stable cobalt(II) salts, such as cobalt acetate and cobalt chloride, complex readily with a variety of ligands, including those shown in Table 2, to give cobalt(II) complexes which are susceptible to oxidation and may be smoothly converted into the corresponding cobalt(III) complexes on exposure to oxygen. This method is used (i), for the preparation of those halogeno–cobalt(III) complexes[50] which react with Grignard reagents (method Ia; eq. 11–13) and (ii) for the *in situ* preparation of the solvated cobalt(III) cations which behave as electrophiles towards carbanions, enols etc. (method Ib; eq. 5 and 6).

(b) Cobalt(II) reagents

(i) *Direct preparation.* The pentacyanocobaltate(II) ion, formed by the reaction of cobalt(II) salts with a slight excess (*i.e.* 5+ fold) of cyanide ion under anaerobic conditions in aqueous solution, is suitable for direct reaction with organic compounds (method IIa, c, d). Dilute solutions of $Co(CN)_5^{3-}$ decompose slowly in water[51,52], but concentrated solutions decompose more rapidly and should be used when fresh. The bis(dimethylglyoximato)cobalt(II) complexes, which are also formed on mixing the cobalt(II) salt with the appropriate ligands in aqueous or alcoholic solution under anaerobic conditions, may be isolated or used directly (method IIa, b)[50], but are more commonly used for the preparation of the cobalt(I) species described below.

(ii) *Reduction of naturally occurring cobalt(III) species.* The reduction of naturally occurring cobalt(III) corrinoids, such as vitamin B_{12}, or cyanocobalamin, to the corresponding cobalt(II) species may be carried out by several methods. (i) Controlled[53,54], potentiometric reduction (see table 4). (ii) Reduction by metal ions at an appropriate pH that does not allow further reduction to cobalt(I) species. For example, by chromous acetate at pH 3[55]. (iii) Reduction by certain thiols at an appropriate pH; for example by cysteamine at pH > 8.9[56]. The latter reaction is believed to be catalysed by trace metals, because it is inhibited in the presence of EDTA. (iv) Reduction by carbon monoxide[57,58].

(c) Cobalt(I) reagents and hydridocobalt species

The cobalt(I) and hydridocobalt species are usually formed by reduction of cobalt(II) species. They are usually somewhat unstable in aqueous solution and tend to revert to cobalt(II) species and hydrogen. For example, B_{12s} reverts slowly to B_{12r}, particularly in mildly acidic solutions[59,60]. The following methods of reduction have been employed.

(i) *Reduction with borohydride ion.* More cobalt(II) and cobalt(III) complexes are readily

reduced by borohydride ion in aqueous or alcoholic solution[50,61–64]. The reduction may be carried out either in the presence of, or prior to the addition of, the organic substrate, depending upon the sensitivity of that substrate to sodium borohydride. In some cases the addition of a few drops of 10% palladium(II) solution has been found to catalyse the reaction. For example, though the bis(dimethylglyoximato)pyridinecobalt(II) ion is normally reduced by sodium borohydride, this reduction may be inhibited if traces of oxygen have been introduced. The addition of palladium(II) appears to remove this inhibition and the reduction to the dark blue cobalt(I) solution then proceeds smoothly. Cobalt(II), nickel(II) or, less satisfactory copper metal[64a], has also been found to catalyse the reduction[65]. However, in solutions of pH < 9.9, the decomposition of B_{12s} to B_{12r} and hydrogen is catalyed by Pt^{II} salts[66].

The tetradentate Schiff's base complexes, Co(salen), Co(acacen) and their derivatives, are only reduced by sodium borohydride in the presence of a palladium(II) salt and in alkaline solution[67], whereas cobalt(II) aetioporphyrin complexes are not reduced by borohydride ion[11]. The reduction of bis(dimethylglyoximato)chloropyridinecobalt(III) by sodium borodeuteride in methanol at pH 7 gives substantial quantities of $DCo(dmgH)_2py$[69].

(ii) *Disproportionation of cobalt(II) species.* The bis(dimethylglyoximato)cobalt(II) species disproportionate rapidly and completely in strongly alkaline solution to the corresponding cobalt(I) and cobalt(III) species[70–72], but do so more slowly in mildly alkaline and neutral solution. If the disproportionated alkaline solutions are wholly or partially neutralised, they form suitably mild reagents for reaction with organic substrates that are sensitive to strongly alkaline solutions or to borohydride[73,74]. Such disproportionation, which has unfortunately not been studied in much detail, is apparently less evident with those cobalt(II) complexes, like Co^{II}(acacen) and Co^{II}(salen), which have large negative reduction potentials (Table 4), but may also be substantial with the more readily reduced $Co^{II}(dotnH)B^+$ complexes[75] and the cobalt(II) corrinoids[71]. Pentacyanocobaltate(II) species[51] similarly 'age' in aqueous solution to give some $HCo(CN)_5^{3-}$.

(iii) *Hydrogenation.* Several cobalt(II) chelates may be reduced by treatment with hydrogen. In particular, the pentacyanocobaltate(II) ion may be reduced directly with molecular hydrogen to the hydridopentacyanocobaltate(III) ion[68,76]. Interesting variations include the formation of $DCo(CN)_5^{3-}$ by reduction of the pentacyanocobaltate(II) ion with deuterium in aqueous solution[46]. Bis(dimethylglyoximato)pyridinecobalt(II) is reduced

TABLE 4

Half-wave potentials for the reduction of some cobalt(III) and cobalt(II) reagents[16,95]

Solvent, pyridine; predominant species in solution $Co(chelate)py_2^+$ in the presence of $Et_4N^+ClO_4^-$ 0.2*M* at 0°?; units are volts *vs.* SCE.

Chelate		*acacen*	*7,7'-Me-salen*	*salen*	*salphen*	*(dmgH)₂*
$Co^{III} \rightarrow Co^{II}$	$E_{1/2}$(I)	−0.67	−0.52	−0.39	−0.35	−0.34
$Co^{II} \rightarrow Co^{I}$	$E_{1/2}$(II)	−1.83	−1.50	−1.38	−1.35	−1.24

by hydrogen in neutral or alkaline solution[66], but it is not known what part, if any, the disproportionation plays in this reduction. Reduction with deuterium in neutral solution gives the covalent $DCo(dmgH)_2py$, which only undergoes slow exchange with the solvent protons[69].

(iv) *Reduction by sulphur compounds.* Under appropriate conditions, thiols will reduce cobalt(III) compounds, especially the cobalamins, to the corresponding cobalt(I) species*. Reagents that have been shown to be effective are (a) NaSH[77–79], (b) Na_2S[77,78,80], (c) glutathione[77,78,81], (d) alkanethiols[65,79], (e) dithiols[82], such as dithiothreitol, (f) reduced ferredoxin (*i.e.*, reduced by hydrogen and hydrogenase[83]), and (g) hydroxyalkylthiols[83]. The mechanisms of these reductions have not been investigated in detail, and the role of metal catalysts is obscure. However, there is little doubt that thiols are important reagents in biological reduction of naturally occurring cobalamins. Sulphite ion is not an effective reducing agent[84].

(v) *Homogeneous reduction by metal ions.* Chromous salts are sufficiently effective reagents in EDTA to reduce cobalt(II)- to cobalt(I)-corrinoids[27,31], in contrast to their reaction at pH 3.

(vi) *Heterogeneous reduction by metals.* Sodium, potassium, and sodium amalgam are the commonest reagents for the reduction of the Schiff's base chelates such as Co^{II}(salen) and Co^{II}(acacen) and their derivatives[12,34,85–87]. Reductions are usually carried out in tetrahydrofuran, though acetonitrile has also been used[88,89]. Cobalt(II)aetioporphyrin, which has not been reduced successfully by borohydride ion[90], is best reduced by sodium amalgam in dimethoxyethane[11,91]. Zinc dust has been used for the cobalt(III) corrinoids in aqueous[27] acetic acid, in glacial[41] acetic acid, which gives hydridocobalamin, and in aqueous ammonium chloride[55,92–94], which gives B_{12s}.

(vii) *Electrolytic reduction.* Electrolytic reduction is not commonly used in preparative studies, but is valuable where pure materials are required. The cobalt(III) and cobalt(II) chelates are more readily reduced than the majority of the corresponding organocobalt(III) and organocobalt(II) products and hence, by accurate control of the potential, the cobalt(I) reagent may be formed under conditions where the organocobalt(III) product is not reduced[53,54]. Some half-wave potentials for the reduction of the cobalt(III) chelates[16,95] are shown in Table 4 and may be compared with those for the organocobalt(III) products shown in Table 24 (p. 94).

(viii) *Miscellaneous reduction methods.* Other reagents used for the reduction to cobalt(I) species include acyloins[64a], hydrazine[63,80], hypophosphorous acid[95a] and the dianion of cyclooctatetraene. The solid black hydridocobalt(III) species $HCo(dmgH)_2PPh_3$[44] has also been prepared by the pyrolysis of the β-cyanoethylbis(dimethylglyoximato)triphenylphosphinecobalt(III) complex in vacuo.

(ix) *Displacement reactions.* Cobalt(I) species have also been prepared by their nucleophilic displacement from acylcobalt(III) compounds[97] (see p. 63), and from main group metal cobaloximes such as $R_3SnCo(dmgH)_2py$[97a].

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* Reagents (a), (b), (c), (d) and (g) normally give only Co^{II}. In the presence of alkylating agents this behaves as if it were reduced further to Co^{I}. *Cf.* ref. 594.

MECHANISMS OF REACTIONS IN WHICH ORGANOCOBALT(III) COMPOUNDS ARE FORMED

Our discussion of the mechanisms of formation of the organocobalt(III) compounds is confined to the reactions of cobalt(II) and cobalt(I) species, as there have been no detailed mechanistic studies on the reactions of cobalt(III) species with organic compounds.

(I) Reactions involving cobalt(II) species

(a) Atom transfer reactions

Several atom transfer reactions have been studied in detail[98–100,100a]. As shown in eqs. 8 and 9, and in eqn. 10, the overall stoechiometry of the atom transfer reactions is:

$$2Co^{II} + RX \longrightarrow RCo^{III} + XCo^{III} \qquad (37)$$

though the rate is given by the expression:

$$-d[Co^{II}]/dt = 2k[RX][Co^{II}] \qquad (38)$$

The factor 2 is included in eqn. 38 for convenience to allow for the fact that two molecules of the cobalt(II) species are consumed for each rate determining reaction with the alkyl halide. Some of the rate coefficients that have been measured are shown in Table 5. They refer only to the reaction of five-coordinate cobalt(II) species after due allowance has been made for the proportions of the corresponding four- and six-coordinate species present in solution. It is probable that four-coordinate species are also effective atom transfer reagents, but it is unlikely that six-coordinate species, being coordinatively saturated, are capable of undergoing such reactions. The latter are, however, effective in some electron transfer reactions described below.

Unfortunately, the character and charge of the several cobalt(II) species studied so far preclude the use of the same solvent for all the kinetic studies. However, as virtually the same rate coefficients are obtained for the reaction of the uncharged bis(dimethylglyoximato)pyridinecobalt(II) radical with benzyl bromide in acetone and in benzene[99], it would appear that solvent effects are not dominant in these reactions. The reaction rate is largely determined by the following factors:

(i) *The character of the equatorial ligands.* The order of reactivity is $\cdot Co(CN)_5^{3-} \gg \cdot Co(dmgH)_2py >$ ·Co(salphen)py but variation of the nature of the bidentate oximato ligands (*e.g.*, dmgH to dpgH) has little effect.

(ii) *The character of the organic halide.* As the transition state involves marked radical character of the organic group, the rate of reaction is largely determined, for any particular cobalt(II) reagent, by the stability of the incipient organic radical. The reactivity orders to $Co(CN)_5^{3-}$, *i.e.*, $ClCCl_2CO_2^- > ClCHClCO_2^- > ClCH_2CO_2^-$ (overall rate difference $\times 10^3$) and $BrCH_2CO_2^- > BrCH_2CH_2CO_2^-$ ($\times$ 300) are due to the influence of the carboxylate ion group and the α-halogeno substituents on the stability of the forming radical in the transition state. The more reactive the cobalt(II) reagent, the less marked should be this influ-

TABLE 5

Rates of reaction[a] of alkyl halides with cobalt(II) species [CoL_nB] at 25°

Solvent	*RHal*	*Ln*	*B*	k_2	*Ref.*
H_2O	p-$^-O_2CC_6H_4CH_2Br$[b]	$(CN)_4$	CN^-	9.6×10^{-1}	98
H_2O	$^-O_2CCH_2I$[b]	$(CN)_4$	CN^-	8.9×10^{-2}	98
H_2O	$^-O_2CCH_2Br$[b]	$(CN)_4$	CN^-	2.8×10^{-1}	98
H_2O	$^-O_2CCH_2CH_2Br$[b]	$(CN)_4$	CN^-	8×10^{-4}	98
H_2O	$^-O_2CCH_2Cl$[b]	$(CN)_4$	CN^-	ca.2×10^{-4}	98
H_2O	$^-O_2CCHCl_2$[b]	$(CN)_4$	CN^-	1.9×10^{-2}	98
H_2O	$^-O_2CCCl_3$[b]	$(CN)_4$	CN^-	4.4×10^{-1}	98
H_2O	$^-O_2CCHBrCHBrCO_2^-$[b] (*meso*)	$(CN)_4$	CN^-	78	98
Benzene	$C_6H_5CH_2Br$[b]	$(dmgH)_2$	py	1.5×10^{-1}	99
Benzene	$C_6H_5CH_2Br$[b]	$(dmgH)_2$	$P(OMe)_3$	1.5×10^{-1}	99a
Benzene	$C_6H_5CH_2Br$[b]	$(dmgH)_2$	$P(p\text{-}ClC_6H_4)_3$	9.7×10^{-3}	99a
Benzene	$C_6H_5CH_2Br$[b]	$(dmgH)_2$	PPh_3	2.1×10^{-2}	99a
Benzene	$C_6H_5CH_2Br$[b]	$(dmgH)_2$	$P(p\text{-}MeC_6H_4)_3$	3.4×10^{-2}	99a
Benzene	$C_6H_5CH_2Br$[b]	$(dmgH)_2$	$P(p\text{-}MeOC_6H_4)_3$	4.8×10^{-2}	99a
Benzene	$C_6H_5CH_2Br$[b]	$(dmgH)_2$	PBu_3	1.6	99a
Benzene	$C_6H_5CH_2Br$[b]	$(dmgH)_2$	PMe_3	7.1	99a
Acetone	$C_6H_5CH_2Br$[b]	$(dmgH)_2$	py	1.7×10^{-1}	99
Acetone	$C_6H_5CH_2Br$[b]	$(dmgH)_2$	nicotinamide	9.5×10^{-2}	99
Acetone	$C_6H_5CH_2Br$[b]	$(dmgH)_2$	PPh_3	2.4×10^{-2}	99
Acetone	$C_6H_5CH_2Br$[b]	$(c\text{-}hgH)_2$	PPh_3	2.4×10^{-2}	99a
Acetone	$C_6H_5CH_2Br$[b]	$(dpgH)_2$	py	3.7×10^{-2}	99
Acetone	$C_6H_5CH_2Br$[b]	$(MeO\text{-}dpgH)_2$	py	2.7×10^{-1}	99
Acetone	$C_6H_5CH_2Br$[b]	$(O_2N\text{-}dpgH)_2$	py	5.5×10^{-2}	99
CH_2Cl_2	p-$NCC_6H_4CH_2Br$[b]	salphen	py	2.9×10^{-3}	100
CH_2Cl_2	p-$NCC_6H_4CH_2I$[b]	salphen	py	2.0×10^{-1}	100
CH_2Cl_2	p-$O_2NC_6H_4CH_2Br$[b]	salphen	py	5.5×10^{-2}	100
CH_2Cl_2	p-$NCC_6H_4CH_2Br$[b]	salphen	$PhCH_2NH_2$	8.0×10^{-3}	100
CH_2Cl_2	p-$NCC_6H_4CH_2Br$[b]	salphen	PPh_3	2.9×10^{-3}	100
CH_2Cl_2	p-$NCC_6H_4CH_2Br$[b]	salphen	PPh_2Me	3.7×10^{-2}	100
CH_2Cl_2	p-$NCC_6H_4CH_2Br$[b]	salphen	$PPhMe_2$	4.2×10^{-1}	100
CH_2Cl_2	p-$NCC_6H_4CH_2Br$[b]	salphen	PMe_3	9.0×10^{-1}	100
CH_2Cl_2	p-$O_2NC_6H_4CH_2Br$[c]	salphen	imidazole	4.3×10^{-1}	23
CH_2Cl_2	p-$O_2NC_6H_4CH_2Cl$[c]	salphen	imidazole	2.7×10^{-1}	23
CH_2Cl_2	p-$O_2NC_6H_4CH_2Cl$[c]	salen	Meimidazole	≥ 2.4	23

[a] Second order rate coefficients $M^{-1}\cdot s^{-1}$ for five coordinate species; additional examples are described in the references.

[b] Atom transfer reactions.

[c] Electron transfer reactions.

ence of substituents. The trend of reactivity with substituted benzyl bromides (Table 5) suggests that some degree of electron transfer may also be involved in transition state for these atom transfers, *i.e.*, $[B(dmgH)_2Co^{\delta+}\ldots X^{\delta-}\ldots R]^{\ddagger}$.

Only low yields are usually obtained from the reaction of secondary alkyl halides with the pentacyanocobaltate(II) ion[46]. This is in part due to alternative capability of the $Co(CN)_5^{3-}$ ion to act as hydrogen atom abstractor from organic radicals (eqn. 39) and in part to the ability of the $HCo(CN)_5^{3-}$ so formed to act as a hydrogen atom donor to organic radicals (eqn. 40). The latter process may be eliminated by addition of a suitable scavenger for the hydridocobalt species, in which case olefin is the major product.

$$R\dot{C}HMe + \cdot Co(CN)_5^{3-} \longrightarrow RCH{=}CH_2 + HCo(CN)_5^{3-} \quad (39)$$

$$R\dot{C}HMe + HCo(CN)_5^{3-} \longrightarrow RCH_2Me + \cdot Co(CN)_5^{3-} \quad (40)$$

In some cases, dimerisation of the intermediate organic radical may be the predominant process, *e.g.*:

$$PhCH{=}CHCH_2Cl + {}^{\cdot}Co(CN)_5^{3-} \longrightarrow ClCo(CN)_5^{3-} + PhCH{=}C\dot{H}CH_2 \quad (41)$$

$$2PhCH{=}C\dot{H}CH_2 \longrightarrow PhCH{=}CHCH_2CH_2CH{=}CHPh \quad (42)$$

(iii) *The nature of the abstracted halogen.* The reactivity order for the transferred atom is: RI > RBr > RCl in accord with the increasing carbon–halogen bond dissociation energy from RI to RCl. The importance of this change is evident in the fact that the reactivity difference on changing the halogen from iodine to chlorine in $HalCH_2CO_2^-$ is ca. 10^6 even with the highly reactive $Co(CN)_5^{3-}$ species.

The atom transfer reactions of the pentacyanocobaltate(II) and dioximatocobalt(II) species with the organic halides are all characterised by low activation energies (3–10 kcal/mol) and large entropies of activation (–20 to –36 e.u.). The latter have not been adequately explained.

(iv) *The nature of the axial ligand.* The influence of axial bases on the rate of atom transfer reactions can be quite marked, particularly with phosphine ligands[99a]. Separation of steric and electronic effects is not easy and the best indication of the influence of electronic factors comes from the effect of *para*-substitution of triarylphosphine ligands on the reaction rates. The Hammett ρ value for the reaction of cobalt(II) species containing triply *para*-substituted axial phosphines is –1.4, indicating that electron donation to the cobalt from the ligand assists the reaction, in accordance with the partial electron transfer described above.

The expected correlation between ligand basicity and reactivity of the cobalt species is, however, markedly distorted by steric effects, both with phosphorus and with nitrogen bases. In general, the more bulky the axial base, the less reactive the cobalt species.

The reactions of vicinal dihalides[98] follow the same mechanism except in so far as the intermediate β-haloethyl- or β-halovinyl-cobalt(III) intermediates are unstable. Thus,

meso-α,β-dibromosuccinate ion reacts with the pentacyanocobaltate(II) ion at a rate only slightly greater than that for the α-bromoacetate ion, but the first formed organometallic product, believed to be α-$[(NC)_5Co]^{3-}$-β-bromosuccinate (III), is unstable and decomposes by an independent first order process to $BrCo(CN)_5^{3-}$ and fumarate ion.

$$^{-}O_2CCHBrCHBrCO_2^{-} + 2Co(CN)_5^{3-} \longrightarrow BrCo(CN)_5^{3-} + {}^{-}O_2CCHBrCH(CO_2^{-})Co(CN)_5^{3-} \quad (43)$$
(III)

$$^{-}O_2CCHBrCH(CO_2^{-})Co(CN)_5^{3-} \longrightarrow BrCo(CN)_5^{3-} + {}^{-}O_2CCH{=}CHCO_2^{-} \quad (44)$$

If the reactions with $Co(CN)_5^{3-}$ are carried out in the presence of hydrogen, significant reduction of alkyl halides to the corresponding alkanes takes place, due largely to the hydrogen atom transfer to the organic radical, as shown in eqn. 40.

(b) Electron transfer reactions

The electron transfer mechanism, shown in eqns. 14–16, has only been observed in a few cases[23]. The prime requirements seem to be an appropriate organic electron acceptor, such as a nitrobenzyl halide which, after receiving the electron, will rapidly decompose to yield an organic radical, and a six-coordinate cobalt(II) species. As the rate determining step is the electron transfer process (eqn. 14), the rate of disappearance of the cobalt(II) species, which can be determined spectrophotometrically, is usually given by the equation:

$$-d[Co^{II}]/dt = 2k[Co^{II}][L][RX] \quad (45)$$

provided the unreactive five coordinate cobalt(II) species is present in large excess over the reactive six-coordinate species, as is usual with such cobalt(II) species. In eqn. 45, L is the ligand required to complete the sixth coordination site, and RX is the organic substrate. The factor 2 is to accommodate the fact that two molecules of cobalt(II) are consumed for each rate-determining reaction with RX. Though a six-coordinate complex is required to effect the electron transfer, the capture of the organic radical in eqn. 16 requires a five-coordinate cobalt(II) species. Since the latter is generally the predominant species in solution, no build up of the organic radical usually takes place. However, in those cases where the five-coordinate species is not in large excess, not only do the kinetics deviate from the rate law shown in eqn. 45, but the build up of organic radicals may be sufficient for significant dimerisation to take place.

An interesting feature of these reactions is that not all monodentate ligands are suitable for the formation of six-coordinate complexes which can undergo the electron transfer. So far, imidazole, 1-methylimidazole, and benzylamine have been found to be effective. In contrast to the results for atom transfer reactions, the rate coefficients for the electron transfer reactions, shown in Table 5, are insensitive to the nature of the departing halide ion.

(II) Reactions involving cobalt(I)

As expected from the redox potentials, the cobalt(I) species are generally more reactive than the cobalt(II) species. The most reactive cobalt(I) species studied so far is the pentacyanocobaltate(I) ion $[Co(CN)_5^{4-}]$ which is so reactive and basic that it has a half life of only ca. 10^{-5} sec in water [42], and reacts with quinone at about the encounter rate[68]. It forms the covalent hydride $HCo(CN)_5^{3-}$ the reactions of which are described above and discussed more fully below.

$$Co(CN)_5^{4-} + H_2O \longrightarrow HCo(CN)_5^{3-} + OH^- \qquad (46)$$

However, the majority of cobalt(I) species are markedly less reactive and less basic than the pentacyanocobaltate(I) ion. Little is known about the acid dissociation constants of many of the hydrido species (eqn. 47), but it is apparent[41,43,44] that several of the species with which we are concerned have p*K*a's in the region 7–12.

$$Co^{I}L_nB^{m-} + H_2O \rightleftharpoons HCo^{III}L_nB^{(m-1)-} + OH^- \qquad (47)$$

(a) Displacement reactions

The cobalt(I) species are more reactive towards alkyl halides than are the corresponding cobalt(II) species, as shown by a comparison of the rate coefficients in Tables 5 and 6. The reactions have the 1/1 stoechiometry shown in eqns. 21–26, and the rate law[101] is as shown in eqn. 48.

$$-d[Co^{I}]/dt = k_2[Co^{I}][RX] \qquad (48)$$

Selected values[101] of the second order rate coefficients k_2 are shown in Table 6. As both four and five coordinate cobalt(I) species are present in the reagent solutions and may have different reactivities, the observed value of k_2 depends upon (1) the rate of association of the fifth ligand, (2) the relative rate coefficients associated with the four* and five coordinate species, and (3) the concentration of added ligands in solution. Two examples[101] illustrate the effects that may be observed. First, in the reaction between ethyl bromide and the bis(dimethylglyoximato)pyridinecobaltate(I) ion in methanolic solution, the establishment of the four-five coordinate equilibrium is rapid and the observed rate coefficient is a linear combination of the rate coefficients of the four and five coordinate species. Secondly, in the reaction of ethyl bromide with the bis(dimethylglyoximato)aquocobaltate(I) ion in the presence of 0.5 mole Bu_3P, the rate plots shows two distinct but overlapping stages; an initial stage in which the solvated four coordinate cobalt(I) species is the

* The terms 'four coordinate complex' when used in connection with the cobalt(I) species, and 'five coordinate complex' when used in connection with the organocobalt(III) species, include true four and five coordinate complexes, respectively, and those in which a solvent molecule may occupy the fifth and sixth site, respectively.

TABLE 6

Second order rate coefficients[a] for the reaction of cobalt(I) species with organic halides in methanolic solution containing 0.1*M* NaOH

Substrate	*Temperature*	*Cobalt(I) species*	k_2	*Ref.*
MeCl	amb.[b]	$[Co(dmgH)_2PBu_3]^-$	8.5×10^{-1}	101
MeBr	25.0	$[Co(dmgH)_2PBu_3]^-$	2.2×10^{2}	101
MeI	25.0	$[Co(dmgH)_2PBu_3]^-$	2.5×10^{3}	101
EtBr	amb.	$[Co(dmgH)_2PBu_3]^-$	1.6	101
n-PrBr	amb.	$[Co(dmgH)_2PBu_3]^-$	1.5	101
i-PrBr	amb.	$[Co(dmgH)_2PBu_3]^-$	1.1×10^{-1}	101
i-BuBr	amb.	$[Co(dmgH)_2PBu_3]^-$	2.8×10^{-1}	101
$^-O_2CCH_2Br$	amb.	$[Co(dmgH)_2PBu_3]^-$	3.4	101
$PhCH_2Cl$	25.0	$[Co(dmgH)_2PBu_3]^-$	4.4×10^{2}	101
$PhCH_2Br$	25.0	$[Co(dmgH)_2PBu_3]^-$	1.9×10^{4}	101
Ph_2CHCl	amb.	$[Co(dmgH)_2PBu_3]^-$	1.0	101
EtBr	25.0	$[Co(dmgH)_2aq]^-$	10	101
n-PrCl	25.0	$[Co(dmgH)_2aq]^-$	7.4×10^{-2}	101
n-PrCl	25.0	$[Co(dpgH)_2aq]^-$	6.6×10^{-3}	101
n-PrCl	25.0	$[Co(c\text{-}hgH)_2aq]^-$	5.7×10^{-2}	101
n-PrCl	25.0	$[Co(c\text{-}pgH)_2aq]^-$	3.0×10^{-2}	101
n-PrCl	25.0	Co(dotnH)aq	4.4×10^{-3}	101
n-PrCl	25.0	Co(doenH)aq	1.2×10^{-2}	101
n-PrCl	25.0	Co(doenH)py	1.3×10^{-4}	101
n-PrCl	25.0	$Co(doenH)SMe_2$	5.5×10^{-5}	101
n-PrCl	25.0	$Co(doenH)PBu_3$	2.7×10^{-6}	101
n-PrCl	25.0	$Co(salen)^-$	1.2	101
n-PrCl	25.0	Cobinamide(I)	3.5×10^{-2}	101
MeCl	25.0	$[Co(dmgBF_2)_2aq]^-$	8.4×10^{-3}	101
MeCl	amb.	B_{12S}	5.0	66
MeBr	25.0	B_{12S}	1.6×10^{3}	66
MeI	25.0	B_{12S}	3.4×10^{4}	66
i-PrBr	25.0	B_{12S}	1.8	101

[a] Further examples are shown in refs. 66 and 101.
[b] 25 ± 2°.

more effective reagent ($k_2 = 10\,M^{-1}\cdot s^{-1}$) and a final stage in which the less reactive five coordinate phosphine complex is the effective reagent ($k_2 = 2M^{-1}\cdot s^{-1}$). The values of k_2 shown in the first part of Table 6 are therefore those for the five coordinate phosphine complexes, in order to limit any ambiguity.

Influence of axial bases. The influence of axial bases on the rate is dependent upon the nature of the equatorial ligand. In most cases the effect is small. For example, the reactivities of the various bis(dimethylglyoximato)cobalt(I) ions vary by a factor of less than

50; phosphines and isocyanides cause the largest rate reductions. However, of several equatorial ligands that have been studied[101], the results for the Co(doxnH) species (x=e or t) appear to be anomalous, because the influence of axial bases is very large indeed. For example, the change from the neutral solvated cobalt(I) species $Co(doenH)OH_2$ to the species Co(doenH)py, $Co(doenH)SMe_2$, and $Co(doenH)PBu_3$ is accompanied by a decrease in reactivity by factors of 10^2, 2×10^2, and 4×10^3 respectively. Such a dramatic change is surprising, even in view of the fact that these particular nucleophiles are neutral and may allow a greater interaction between the axial base and the metal orbitals. A more detailed examination of this question would be of interest.

Influence of equatorial ligands. The equatorial ligands have a large effect on reactivity. Of those studied so far, for any particular axial base, the most nucleophilic cobalt(I) species is the $Co(salen)^-$ ion and the least reactive is the $Co(dmgBF_2)_2^-$ ion; the reactivity difference being approximately four powers of ten. The lower reactivity of the Co(dotnH) species has also been noted[61] with respect to problems in the preparation of the alkyl derivatives other than methyl. The nucleophilic reactivities have been related to the logarithmic scale of nucleophilicities derived by Pearson[102], which is defined as follows:

$$n = \log[k/k_0] \tag{49}$$

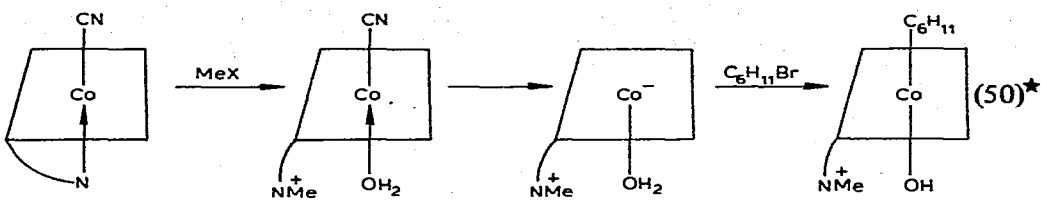
where n is the nucleophilicity factor, k is the second order rate coefficient for the reaction of that nucleophile with methyl iodide in methanol, and k_0 is the corresponding rate coefficient for the reaction of methanol with methyl iodide. The values of n for many other nucleophiles, *e.g.*, OMe^- (6.3), CN^- (6.7), I^- (7.4), PhS^-(9.9), etc., are much lower than those for the cobalt(I) complexes, *e.g.*, $Co(salen)aq^-$ (15.6)[103], (14.6)[104], $Co(dmgH)_2aq^-$ (14.3)[101], $Co(dmgBF_2)_2aq^-$ (12.2)[101], and vitamin B_{12s} (14.4)[66].

Influence of the organic substrate. The nucleophilic character of the reaction with alkyl halides is also apparent from the variation of the rates of reaction with different organic halides[101]. The order of reactivity: $PhCH_2 > CH_3 >$ Et > n-Bu ~ n-Pr > iso-Pr ≫ neopentyl is found with the bis(dimethylglyoximato)cobalt(I) ions, with vitamin B_{12s} and conventional nucleophiles such as methoxide ion. The order[101]: cyclopentyl ~ cyclobutyl > cyclohexyl > cyclopropyl is also found with the bis(dimethylglyoximato)cobalt(I) ions and with conventional nucleophiles. It would be surprising if other plausible mechanisms were to follow the above orders of reactivity so closely.

Some difficulties have been encountered in the preparative reactions of secondary halides, particularly with the cobalamins. Rate measurements indicate that the reactions with secondary halides take place less readily than with primary halides, and preparative reactions with the former fail in a number of cases. For example, much difficulty has been experienced in the preparation of cyclohexylcobalamin[65,105] and these have been overcome by some workers by a prior quaternisation of the axial benzimidazole ligand. It is suggested that the corrinoid ring is distorted upwards by the coordinated benzimidazole ligand, and that this causes steric hindrance both to reaction with the cyclohexyl halide[105] and in the final product[32,105,106]. Removal of the benzimidazole by quaternisation (eqn. 50) allows

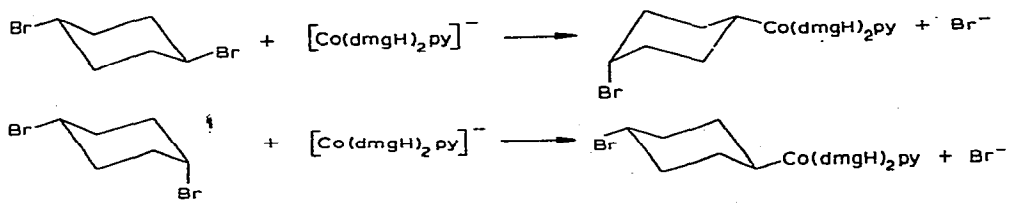
the corrinoid ring to attain planarity and thereby to reduce steric hindrance during and after reaction. Indeed, it has been observed that cyclohexylcobalamin does not complex significantly in solution with the benzimidazole ligand or with cyanide ion.

Though cobalt(I) species react with tertiary alkyl halides, no simple tertiary alkylcobalt(III) complexes have been isolated[41,101].



(50)*

Stereochemistry of the reaction at saturated carbon. The sterochemical studies have been restricted to consideration of reactions of the bis(dimethylglyoximato)cobalt(I) species. All the available evidence indicates that the displacement of halide ion from saturated carbon involves inversion of configuration at the α-carbon. Thus, the reaction of *cis*- and *trans*-1,4-dibromocyclohexanes with the bis(dimethylglyoximato)pyridinecobalt(I) ion gives *trans*- and *cis*-(4-bromocyclohexyl)bis(dimethylglyoximato)pyridinecobalt(III), respectively[107].



(51)

(52)

Similar inversion of configuration was demonstrated in the reactions of bis(dimethylglyoximato)pyridinecobalt(I) ion with cyclohexene oxide, *trans*-1-bromo-2-methoxycyclohexane, and the mono *p*-toluenesulphonates of *cis*- and *trans*-1,4-dihydroxycyclohexane. The postulate of inversion of configuration in the formation of (+)-sec-octylcobaloxime ($[\alpha]_D$ +50°) from (−)-sec-octylbromide ($[\alpha]_D$ −29°) was assumed[108] following the work on the cyclohexyl systems, and, as subsequent reactions of cyclohexyl- and sec-octylcobaloximes also parallel one another there seems no reason to doubt this assumption. Optically active sec-butylcobaloxime[109] has also been prepared from partially resolved sec-butyl alcohol via the tosylate, but optical activity could not be determined and was inferred from further reactions which produce optically active materials. Some loss of activity of the sec-butylcobaloxime is believed to occur in the presence of an excess of the bis(dimethylglyoximato)pyridinecobalt(I) ion[109] (*cf.*, p. 60–61).

In the reaction with allylic halides, both S_N2 and S_N2' mechanisms may occur[73]. However, unlike the reactions of the same halides with conventional nucleophiles, the prefer-

* The symbolism used in this equation represents the cobalamin and related ligands similar to those shown in Table 2 and in I.

ence of the cobalt(I) nucleophile for primary carbon seems sufficiently pronounced that only one of the two possible isomers is usually obtained from both γ- and β-substituted allyl halides, *e.g.*:

$$\begin{matrix}[Co(dmgH)_2py]^- + MeCH{=}CHCH_2Cl \\ \searrow \\ \nearrow \\ [Co(dmgH)_2py]^- + CH_2{=}CHCHClMe\end{matrix} \quad MeCH{=}CHCH_2Co(dmgH)_2py + Cl^- \qquad (53)$$

(b) Reactions with olefins

Certain substituted olefins react very rapidly with cobalt(I) species in methanol at pH ~ 10 [39,110]. The reaction is characterised by an immediate change in the ultraviolet spectrum, but no alkylcobalt(III) complex is apparently formed at this stage of the reaction[110]. In most cases the olefin may be slowly regenerated by the addition of electrophilic reagents that are more reactive towards the cobalt(I) than is the olefin. From the influence of olefin concentration on the rate of reaction between cobalt(I) species and alkyl halides, and from spectral changes in solution, it has been deduced that the olefin forms a π-complex directly with the cobalt(I) species. However, it is surprising that, whilst most olefins reduce the reactivity of the cobalt(I) species towards alkyl halides, the species $[Co(dmgBF_2)_2py]^-$ is apparently less reactive than its complex with acrylonitrile towards methyl iodide and towards benzyl chloride[110].

$$(Co^I) + CH_2{=}CHX \underset{RNC^-}{\overset{(pH\,10)}{\rightleftharpoons}} \underset{(Co^I)}{\overset{CH_2{=}CHX}{\downarrow}} \quad (IV) \qquad (54)$$

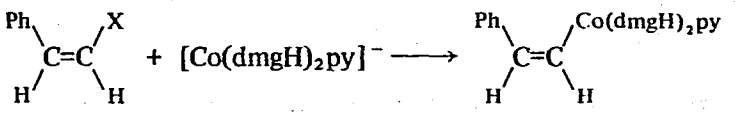
The olefin may also be displaced by the addition of a more strongly coordinating ligand, such as an isocyanide, but on standing the π-complex (IV) slowly rearranges to the β-substituted ethylcobalt(III) complex, with the uptake of a proton from the solvent.

$$\underset{\underset{(Co^I)}{\downarrow}}{CH_2{=}CHX} \quad \underset{pH>12}{\overset{slow}{\rightleftharpoons}} \quad XCH_2CH_2Co^{III} \qquad (X = CN, CO_2R, \text{etc.}) \qquad (55)$$

(IV)

The kinetics of the reaction of vinyl halides with cobalt(I) species have not been studied in detail, but it is apparent that the overall rate of displacement of halide ion is much slower than that from alkyl halides[111]. For example, the displacement of bromide ion from β-bromostyrenes by methoxide ion is very difficult to achieve[112]. It requires the presence of an activating group, such as a *p*-nitro group in the aromatic ring, and also the use of elevated temperatures, *e.g.* 100°. In contrast, bromide ion is displaced from β-bromostyrene by the bis(dimethylglyoximato)pyridinecobaltate(I) ion in a few hours at 40°[37,38]. Surprisingly even vinyl chloride undergoes fairly ready displacement of chloride ion by the bis(dimethylglyoximato)pyridinecobaltate(I) ion at 40°.

The role that π-complexes play in such reactions is not yet known, but the stereochemistry of several of the reactions has been investigated[37,38]. Thus, *cis*-iodostyrene reacts with the bis(dimethylglyoximato)pyridinecobalt(I) ion with complete retention of configuration[111]. *cis*- and *trans*-β-Bromostyrenes react similarly[37,38], but the low yield of organocobalt compound that can be obtained from the β-chlorostyrenes[111] shows some product isomerisation, but no isomerisation of the unreacted β-chlorostyrene. *cis*-β-Fluorostyrene does not appear to react with the cobaltate(I) ion over several hours at 50°, nor does it undergo isomerisation under these conditions[111].



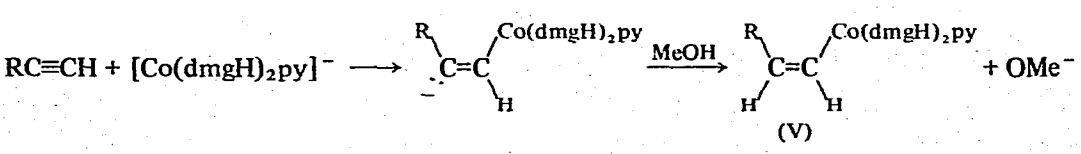
(56)

(X = I, Br)

The rate order suggests that the cleavage of the carbon–halogen bond is involved in the rate determining step, and the lack of isomerisation of the starting halide suggests that any intermediate carbanion that may be formed decomposes before rotation about the C_β–C_α bond can take place. It seems probable, from the results with other olefins, that the reaction involves a prior complexing with the cobalt(I) species, followed by attack of the coordinated cobalt(I) on the α-carbon with synchronous loss of halide ion. Further studies on this reaction would also be of interest. The slight isomerisation in the product from the β-chlorostyrene is probably a result of some radical reaction during the extended time required for reaction.

(c) Reactions with acetylenes

Similar π-complexes are not apparent in reactions with the acetylenes[110], but the corresponding slow addition to form a σ-complex does take place[38,69]. Thus, the addition of the bis(dimethylglyoximato)pyridinecobaltate(I) ion to phenyl acetylene under alkaline conditions (pH > 12) proceeds in reasonable yield, but with 100% *trans*-specificity, to give the same *cis*-styrylcobaloxime[37,38,69] (V) that is formed from the *cis*-β-iodo- and -bromo-styrenes[110]. This reaction also parallels that of phenylacetylene with the more conventional nucleophiles, such as methoxide ion in methanol[113], and is therefore believed to involve an initial nucleophilic attack of the cobalt(I) species on the β-carbon, perhaps via π-complex formation, with synchronous or subsequent rapid *trans*-addition of a proton from the solvent to the configurationally stable intermediate vinyl anion.



(V)

(R = Ph, ROCO, $HOCH_2$, CF_3, $MeCOOCH_2$) (57)

(d) Electron transfer reactions

No electron transfer reactions of cobalt(I) species with organic halides or olefins have yet been reported. However, in view of the ready electron transfer from cobalt(II) species, described above, it seems reasonable that cases will be reported in the future. Indeed, the first cases may involve the reaction of $Co(acacen)^-$ and $Co(salen)^-$ with the trimethylanilinium ion[529]. The latter, surprisingly, gives phenylCo(salen) rather than the expected methylCo(salen).

(III) Reactions of hydridocobalt species

(a) Addition to olefins

The main evidence for the intermediacy of covalent cobalt hydrides in these reactions comes from the marked changes in product character on changing from alkaline to neutral or acidic solution[38-41], and from a comparison with the reactions of a well defined hydridopentacyanocobaltate(III) ion[51]. Thus, only α-substituted ethylcobalt(III) compounds are formed[39,114] from the reaction of the covalent hydride with mono substituted olefins, whereas only β-substituted ethylcobalt(III) compounds are formed from the similar reaction of the cobalt(I) species in mildly alkaline solution.

$$HCo(dmgH)_2py + CH_2{=}CHX \longrightarrow MeCHXCo(dmgH)_2py \qquad (58)$$

Moreover, whereas B_{12S} does not react with simple olefins such as ethylene, hydridocobalamin reacts with ethylene to form ethylcobalamin[41].

The reactions of the hydridopentacyanocobaltate(III) ion have been studied in the most detail[115]. Thus, the reaction with olefins has the stoechiometry shown in eqn. 58, and obeys the rate law[115] shown in eqn. 59:

$$-d[CoH]dt = k_2[CoH][olefin] \qquad (59)$$

The second order rate coefficients, which are shown in Table 7, show rather perplexing trends, which are indicative of slight electrophilic rather than nucleophilic attack on the substrate. For example, the reaction is accelerated by the replacement of a carboxyl by either a cyano or a methyl group. The most likely mechanism[115] appears to involve the attack of the hydrogen atom on the terminal methylene group with the synchronous development of partial radical character on the cobalt atom and on the adjacent carbon atom, *i.e.*:

$$CH_2{=}CHX + HCo(CN)_5^{3-} \longrightarrow \left[\begin{array}{l} CH_2\cdots\overset{\delta-}{C}HX \\ \vdots \\ H\cdots\cdots\overset{\delta.}{C}o(CN)_5^{3-} \end{array}\right] \longrightarrow H_3CCHXCo(CN)_5^{3-} \qquad (60)$$

TABLE 7

Rates of reaction of hydridopentacyanocobaltate(III) ion with olefins in 50%aq methanol[115]

Olefin	k_2[a]
CH_2=$CHCO_2^-$	$1.5 \pm 0.5 \times 10^{-3}$[b]
CH_2=$CHCO_2H$	$2.0 \pm 0.5 \times 10^{-2}$
CH_2=CHCN	$1.8 \pm 0.2 \times 10^{-1}$
CH_2=CHpy	1.0 ± 0.1
CH_2=CH pyH^+	$4.7 \pm 0.5 \times 10^{2}$
CH_2=CHPh	1.1 ± 0.5
CH_2=CMeCN	4.0 ± 1.0
Butadiene	1.6 ± 0.2
	(7.4 ± 1.0)[c]
Isoprene	2.5 ± 0.6

[a] $M^{-1} \cdot s^{-1}$ at 25°.
[b] See also ref. 120.
[c] Ref 116.

The predominance of the direction of addition to vinyl pyridine[51,114] and to several other substituted olefins[51] has been demonstrated by examination of the deuterium content of the reduction product (*e.g.*, ethyl pyridine) formed during the decomposition of the adduct (*e.g.*, α-pyridylethylpentacyanocobaltate(III) ion) in D_2O.

$$pyCHMeCo(CN)_5^{3-} \overset{D_2O}{\rightleftharpoons} pyCH(CH_nD_{3-n})Co(CN)_5^{3-} \xrightarrow{DCo(CN)_5^{3-}} pyCHDCH_nD_{3-n} \quad (61)$$

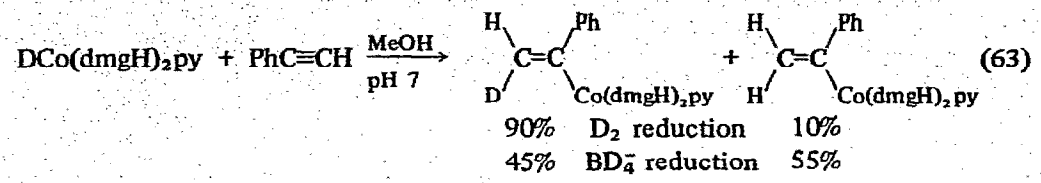
Such reductions of intermediate alkylcobalt(III) species are believed to be involved in the crucial stages of the extensively studied cobalt-catalysed hydrogenation of many mono- and poly-olefins, which has been well reviewed[51]. Among the intermediates that have been identified[116], the initially formed 1,2-adduct of butadiene with the hydridopentacyanocobaltate(III) ion, rearranges to the more stable 1,4-adduct ($k_1 = 4.0 \times 10^{-5} \cdot s^{-1}$ at 25°), probably via a π-allyl complex[117]. The 1,4-adduct has also been obtained from butadiene and from isoprene and hydridobis(dimethylglyoximato)pyridinecobalt(III)[118,119].

$$CH_2{=}CHCH{=}CH_2 + HCo(CN)_5^{3-} \rightarrow CH_2{=}CHCH(Me)Co(CN)_5^{3-} \rightarrow MeCH{=}CHCH_2Co(CN)_5^{3-} \quad (62)$$

(b) Addition to acetylenes

Only the α-styrylcobalt(III) complex is obtained from the reaction between phenylacetylene and hydridobis(dimethylglyoximato)pyridinecobalt(III)[38,69] or the hydridopentacyanocobaltate(III) ion[51] in neutral or acidic solution. The reaction of phenylacetylene with $DCo(dmgH)_2py$, prepared by reduction of cobalt(II) and cobalt(III) complexes with

deuterium and BD_4^-, respectively, shows that this is a stereospecific *cis*-addition of the metal hydride[69], in contrast to the *trans*-addition of the metal nucleophile and solvent proton.



The latter reaction also illustrates the relatively slow rate of proton exchange between the metal hydride and the protic solvent under approximately neutral conditions.

PHYSICAL PROPERTIES

(I) Character of the carbon–cobalt bond

The nature of the carbon–cobalt bond has been of interest since the discovery of the structure of the coenzyme. The discussion of carbon–metal bonds before that time was largely confined to reasons for their instability; since then to understanding their stability and the factors which control it. Unfortunately, some of the arguments about stability have been based on an inability to prepare certain compounds, which later prove to be stable when prepared by other methods.

Since there are few thermodynamic data available about the carbon–cobalt bond, arguments about the bond character have relied on X-ray crystallographic data, ultraviolet and infrared spectroscopic measurements, and upon the observations that homolysis of the alkylcobalt compounds usually requires relatively high temperatures (*e.g.* $\geqslant 200°$ for simple alkyl cobaloximes).

Approaches to the estimation of the bond character have largely relied on consideration of the changes in orbital energies on the formation of the bond between a d^7 cobalt(II) species and the organic radical. In a simplified version of this approach[121], the *d*-orbital arrangement of the d^7 cobalt system has been considered to be intermediate between that for the d^8 system, in which the d_{xy} orbital is believed to be appreciably higher in energy than the d_{z^2}, and the d^6 system in which the d_{z^2} orbital is of higher energy than the d_{xy} orbital. As the bond formation involves the pairing of the d_{z^2} orbital with the carbon orbital, the stability of that bond will depend upon the relative energies of these two orbitals and upon the relative energies of the d_{xy} and d_{z^2} orbitals; *i.e.*, if the d_{xy} orbital is the higher in energy, then the promotion of an electron to that orbital from the d_{z^2} orbital is necessary and the energy required for this must be more than offset by the pairing of the two bonding orbitals. As the relative energies of the d_{xy} and d_{z^2} orbitals are sensitive to the nature of the equatorial ligand in the d^7 configuration, so the character of the carbon–cobalt bond is dependent upon those ligands. The magnitude of these uncertainties therefore makes prediction about bond character extremely unreliable.

Busch has discussed the stability of organocobalt compounds in somewhat more practical terms[88], and has attempted to correlate the crystal field parameters of the dichlorocobalt cations $Cl_2Co(chelate)^+$ with the ability of the complexes to lead to stable cobalt alkyls. The suggestion that the relatively high parameters *Dq* and *Dt* for the complexes $Cl_2Co(tim)^+$ and $Cl_2Co(Cr)^+$, which are known to form stable alkyl derivatives, compared with those for other dichloro complexes, which have not so far led to the formation of stable alkyl derivatives, may well prove a useful guide for consideration of new cyclic ligand systems.

More complete molecular orbital descriptions have been attempted, based on HMO and modified Wolf–Helmholtz MO calculations of the cobalamin[65,122] and cobaloxime[65] series. These results indicate that the metal atom of the cobalamins has a slightly smaller partial positive charge than that of the cobaloximes; otherwise cobalamins and cobaloximes are strikingly similar. The relationship between these calculations and the observed electronic spectra has been discussed.

(II) Electronic spectra

The complex structure of the organocobalt(III) compounds usually results in complex electronic spectra, the main bands of which are difficult to resolve. The spectra of the cobalamins and cobinamides have been of interest since the early observations of the ready photolysis of the coenzyme and the characteristic shift from red to yellow on acidification. Consequently, these and the cobaloximes have been studied in the most detail.

The spectra of the cobalamins are dominated by transitions associated with the corrin ring[65]. Such π-transitions in the region 450–550nm have been designated α and, where vibrational fine structure is evident, this has been designated β. The intense transitions between 350 and 400nm are designated γ, and other bands have been designated D and E[122a]. The assignment of these transitions is not without ambiguity, but it is apparent that bands associated with the Co–C charge transfer are weak and largely obscured by the other bands.

In the electronic spectra of the alkylcobaloximes, the equatorial ligand transitions occur at much lower wavelengths, in a region where they may be indistinguishable from those of the axial base ligand. However, the intense bands in the region 400–500nm are probably due to *d–d* transitions[62] though they have also been ascribed to a charge transfer absorption involving promotion of an electron from the highest filled σ-bonding orbital to the corresponding σ-antibonding orbital[65].

This transition is shifted to higher energy when the α-carbon becomes more electronegative (*i.e.*, greater *s*-character) and with increasing σ-donor character of the axial base or of the equatorial ligands [65]. Some examples of the shifts observed are shown in Table 8.

Similar shifts to higher wavelengths are also observed with the several bands of the cobalamins and cobinamides, as the axial base is changed along the nephelauxetic series[124]. The circular dichroism of the cobalamins has also been investigated[122a,125].

TABLE 8

Characteristic transitions[a] for organocobalt(III) compounds

R	L_n	B	λ_{max}(nm)[b]	$10^{-3}\epsilon$[b]	Solvent	Ref.
Me	$(dmgH)_2$	aq	448	1.53	aq MeOH	65
Me	$(gH)_2$	py	405	1.27	aq MeOH	65
Me	$(dpgH)_2$	aq	475	2.1	aq MeOH	65
Me	doenH	aq	454	2.1	aq MeOH	65
Me	salen	aq	428	2.2	aq MeOH	65
Me	cr	aq	485	0.98	MeOH or aq	62
Et	dotnH	aq	463	0.56	aq MeOH	65
Me	$(dmgH)_2$	py	438	1.48	aq MeOH	65
			440	1.15	MeOH	62
Me	$(c\text{-}hgH)_2$	py	440	1.2	aq MeOH	65
Me	cr	py	502	1.12	MeOH or aq	62
Me	salen	py	490[c]	2.34	EtOH/py	183
Ph	salen	py	483[c]	2.04	EtOH/py	183
Ph	acacen	py	490	0.52	EtOH/py	183
Ph	$(dmgH)_2$	py	419	1.3	aq MeOH	65
Et	$(dmgH)_2$	py	452	1.35	MeOH	62
Et	acacen	py	497	0.56	EtOH/py	183
Pr	acacen	py	505	0.58	EtOH/py	34
Vinyl	acacen	py	485	0.58	EtOH/py	34
Me	cr	Br^-	490	1.05	MeOH	62
Me	$(dmgH)_2$	2-picoline	450	2.07	aq MeOH	65
Me	$(dmgH)_2$	benzimidazole	425	1.2	aq MeOH	65
Me	$(dmgH)_2$	imidazole	410	1.95	aq MeOH	65
Me	$(dmgH)_2$	CNC_6H_{11}	425	0.32	aq MeOH	65
Me	$(dmgH)_2$	Ph_3P	446	1.37	aq MeOH	65
Me	$(dmgH)_2$	Ph_3As	446	0.82	aq MeOH	65
Me	$(dmgH)_2$	Ph_3Sb	447	2.48	aq MeOH	65
Me	$(dmgH)_2$	NH_3	412	1.08	aq MeOH	65
Me	$(dmgH)_2$	N_3^-	435	1.3	aq	123
Me	$(dmgH)_2$	CN^-	420[c]	0.24	aq	123
CF_3	$(dmgH)_2$	py	335	2.3	aq MeOH	65
PhC≡C	$(dmgH)_2$	py	370	0.95	aq MeOH	65
4-MeC_6H_4	$(dmgH)_2$	py	424	1.3	aq MeOH	65

[a] Other values in references. Only the lowest energy band is quoted.
[b] May be influenced by dissociation in solution.
[c] Shoulder.

The spectra of some alkylpentacyanocobaltate(III) species show strong charge transfer bands, particular with the 2-, 3-, and 4-pyridiniomethylpentacyanocobaltates and with the α-(2-pyridinio)ethylpentacyanocobaltate ion, which have intense maxima at 326.5nm (log ε 4.3), 292.5 (4.2), 326 (4.3), and 340nm (4.3), respectively[45,114].

(III) Infrared spectra

Infrared spectra have provided further insight into the *cis*- and *trans*-influences of equatorial and axial ligands on one another. The most detailed studies have been carried out on the axial cyanide stretching frequencies of derivatives of the alkylcobalamins[126], alkylcobaloximes[123], and the alkylpentacyanocobaltates[19,98]. Unfortunately, not all the measurements have been carried out in solution, because of problems of stability. Nevertheless, the correlations between the different sets of results are reasonable.

A selection of the measured frequencies, shown in Table 9, shows the decrease in frequency of the terminal axial cyanide as the α-carbon of the organic group becomes more electronegative, *i.e.* CN > RC≡C > RCH=CH > 5′-deoxyadenosyl > methyl > n-alkyl and, for equatorial ligand variation; $(dmgH)_2$ > $(CN)_4$ > cobalamin. A similar variation with the change of alkyl group, though in the same direction, is evident in the stretching frequencies of the bridged cyanide ligand in compounds of the type $[RCo(dmgH)_2CNCo(dmgH)_2Me]^-$ [123]. A selection of these values are included in Table 9.

Attempts have been made to correlate these cyanide stretching frequencies with other physical parameters, such as the ultraviolet spectra, dissociation constants[126], and NMR chemical shifts. These have been summarised[127].

(*continued on p. 36*)

TABLE 9

Bridged and terminal axial cyanide stretching frequencies[a] of organocobalt(III) complexes

R	*RcobalaminCN*[b]	$RCo(CN)_5^{3-}$[c]	$RCo(dmgH)_2CN$[d]	$[RCo(dmgH)_2CNCo(dmgH)_2Me]^-$[e]
CN	2119	2134	2130	2170(2134)[f]
PhC≡C			2130	2167
HC≡C	2110			
H_2C=CH	2093		2118	2153
5′-Deoxyadenosyl	2091			
$PhCH_2$		2093	2112	2148
Me	2088	2094	2112	2145
Et	2082	2094		
n-Octyl			2109	2145

[a] In cm^{-1}.
[b] KCl discs.
[c] Nujol mull.
[d] In $CHCl_3$, ± 1 cm^{-1}.
[e] In $CHCl_3$, ± 2 cm^{-1}.
[f] Terminal cyanide.

TABLE 10

^{1}H NMR spectra of some methylcobalt(III) compounds[a]

L_n	B	Solvent	Temperature	τ(CoMe)	τ(other)		Ref.
$(dmgH)_2$	py	CH_2Cl_2	−30	9.35	7.91(dmgH)[b]	−8.75(O–H O)[c]	136
$(dmgH)_2$	NMe_3	CH_2Cl_2	5	9.43	7.81(dmgH)	−8.40(O–H O)	136
$(dmgH)_2$	NCMe	CH_2Cl_2	−52	9.53	7.80(dmgH)	−8.59(O–H O)	136
$(dmgH)_2$	PPh_3	CH_2Cl_2	−44	8.97	8.18(dmgH)	−8.57(O–H O)	136
$(dmgH)_2$	$P(OEt)_3$	CH_2Cl_2	−40	9.18	7.97(dmgH)	−8.40(O–H O)	136
$(dmgH)_2$	$P(OMe)_3$	CH_2Cl_2	−40	9.08	7.81 (dmgH)	−8.53(O–H O)	136
$(dmgH)_2$	$AsPh_3$	$CDCl_3$[d]	33	8.70	8.10(dmgH)		152
$(dmgH)_2$	SMe_2	$CDCl_3$	33	9.24	7.78(dmgH)		152
$(dmgH)_2$	SMe_2	CH_2Cl_2	−30	9.09	7.79(dmgH)	−8.39(O–H O)	136
$(dmgH)_2$	Me_2SO[e]	CH_2Cl_2	−44	9.59	7.78(dmgH)	−8.68(O–H O)	136
$(dmgH)_2$	Me_2SO[f]	CH_2Cl_2	−44	8.84		−8.35(O–H O)	136
$(dmgH)_2$	CN^-	$CDCl_3$	33	9.47	7.98(dmgH)		123
$(dmgH)_2$	CN^-[g,h]	$CDCl_3$	33	9.56	7.90(dmgH)		123
$(dmgH)_2$	CN^-[g,i]	$CDCl_3$	33	9.48	7.92(dmgH)		123
$(dmgH)_2$	N_3^-	$CDCl_3$	33	9.48	7.88(dmgH)		123
$(dmgH)_2$	NCS^-[h]	$CDCl_3$	33	9.53	7.98(dmgH		123
$(dmgH)_2$	SCN^-[e]	$CDCl_3$	33	9.19	7.87(dmgH)		123
$(dmgH)_2$	aq	$CDCl_3/CD_3OD$[j]	33	9.27	7.78(dmgH)		123
$(dmgH)_2$	aq	H_2O	33	9.24	7.75(dmgH)		132
$(dmgH)(dmgH_2)$	H_2O	H_2SO_4[k]	33	8.80	7.65($dmgH_n$)[l]		132
$(dmgH_2)_2$	H_2O	H_2SO_4[m]	33	7.79	7.55($dmgH_2$)		132
$(CN)_4$	CN^-	D_2O	33	9.41			45
acacen	–	$CDCl_3$		7.75	7.91(OCMe)	6.60(CH_2)[n] 7.97(NCMe) 4.88(HC=)	139
acacen	py	$CDCl_3$		7.43	8.07(OCMe)	7.06(CH_2)[n] 8.10(NCMe) 5.16(HC=)	139
acacen	piperidine	$CDCl_3$		7.66	8.10(OCMe)	6.87(CH_2) 8.12(NCMe) 5.26(HC=)	139
acacen	4-Mepy	$CDCl_3$		7.46	8.08(OCMe)	7.07(CH_2)[n] 8.11 (NCMe) 5.18(HC=)	139

acacen	4-NCpy,	$CDCl_3$		7.41	8.07(OCMe) 7.01$(CH_2)^n$ 8.09(NCMe) 5.12(HC=)	139
acacen	Ph_3P	$CDCl_3$		7.64	7.97(OCMe) 6.80(CH_2) 8.10(NCMe) 4.99(HC=)	139
salen	aq	Me_2SO-d_6	33	7.87	2.75–3.73(aryl) 6.42$(CH_2)^y$ 2.05[139], 1.98[148](N=CH)	139,148,152
salen	py	Me_2SO-d_6		7.78	6.48(CH_2)	148
cobalamin		D_2O 0.1*M*	30	10.14		153
cobinamide	aq	D_2O 0.1*M*	30	10.24		153
aetpor	aq	$CDCl_3$		15.15		11
tspc	aq	H_2O		16.1		63
tim	I^-			8.85		88
tim	Me^-			9.64		88
cr	Br^-			9.47		88
cr	Me^-			9.82		88

a Many other examples in these and other refs.
b Methyl of dmgH.
c Hydrogen bonded bridge.
d τ(Me) is ca. 0.15 ppm higher in $CDCl_3$ than in CH_2Cl_2.
e Bonding via S.
f Bonding via O.
g $[MeCo(dmgH)_2CNCo(dmgH)_2Me]^-$.
h Bonding via N.
i Bonding via C.
j 5%.
k $H_0 = -1.5$.
l $n = 1.5$ av.
m $H_0 = -6$.
n Multiplet.

Other bands which have been studied in some detail, include ν(C–Co'), ν(C=N'), ν(Co–N'), ν(N–O')[74,118,128,129]. Some of the problems of correlation of such data are evident on a comparison of the various sets of data from different workers, using different media. The frequencies $\nu(Co-CH_3)$ and $\nu(Co-CD_3)$ have been compared[129] and the changes in axial ν(C=O) and ν(N=CR) from those of the free ligands has been ascribed to the presence of some π-bonding with the metal[130].

(IV) Nuclear magnetic resonance spectra

The organocobalt(III) compounds are diamagnetic and hence much information about their structure, intramolecular interactions, and reactions, has come from studies of their NMR spectra. In view of the many results that have been reported, this section merely outlines some of the main features of interest.

(a) Proton magnetic resonance spectra

(i) *The organic groups.* The chemical shifts of the organic group are dependent upon a number of factors, including the electronic effects of the equatorial and axial ligands. For example, small variations in the methyl resonance of the methyl cobaloximes[118,123,130] (up to 1ppm; Table 10) are brought about by changes in the axial base component. However, much larger changes in the chemical shift may be brought about by changing the equatorial ligand, particularly where that ligand has an induced ring current. This is apparent on comparison of the chemical shifts of the methyl group in the methylbis(dimethylglyoximato)cobalt(III) complexes (ca. τ 9), in which there is no equatorial ring current, with those of the methyl group in the corresponding methylcobalt(aetioporphyrin) complex (τ15.15 in $CDCl_3$)[91] and the methylcobalt(tetrasulphonatophthalocyanine) complex (τ16.1 in D_2O)[63]. The very much larger chemical shifts in the latter complexes are due almost entirely to diamagnetic shielding caused by the equatorial ring currents. Such ring currents also have a marked effect on the chemical shifts of protons more remote than the α-carbon; for example, the α-, β-, γ-, and δ-protons of the n-butyl group of the nBuCo(aetpor) complex[91] have chemical shifts τ14.3, 15.3, 11.61 and 11.0, respectively, which are far higher than would normally be expected for the n-butyl group attached to the metal. A similar, but less marked effect is apparent in the alkylcobalamins and cobinamides[131].

Electronic effects of the equatorial and axial ligands also influence the chemical shift of the organic group. Thus, when the effective charge on methylbis(dimethylglyoximato)-aquocobalt(III) is progressively increased by mono- and di-protonation in aqueous sulphuric acid, the chemical shifts of the methyl protons of both the organic goup and the equatorial ligands are moved successively downfield (eqn. 64)[132]. The very large shifts of the axial methyl group resonance indicates that the protonation probably does have a sizeable effect on the charge on the central metal atom. Though there is no direct correlation between the chemical shift of the Co-methyl with the pK of the axial base, the difference between $\tau(CH_2)$ and $\tau(CH_3)$ ($\Delta(CH_2CH_3)$) for ethylcobaloximes does decrease

with increasing basicity of the axial base[132a].

$$\underset{9.24}{\uparrow}\ \underset{7.76}{\uparrow}\qquad \underset{8.71}{\uparrow}\qquad \underset{7.65}{\underline{\quad}}\qquad \underset{7.79}{\uparrow}\ \underset{7.55}{\uparrow}$$

$$\mathrm{MeCo(dmgH)_2aq} \overset{\mathrm{H^+}}{\rightleftharpoons} \mathrm{[MeCo(dmgH)(dmgH_2)aq]^+} \overset{\mathrm{H^+}}{\rightleftharpoons} \mathrm{[MeCo(dmgH_2)_2aq]^{2+}} \qquad (64)$$

Where other magnetic nuclei are present in the alkylcobalt(III) complexes, structural information may also be obtained from the heteronuclear coupling constants. Thus, long range P–H coupling constants have been observed between axial phosphine ligands and protons of both the organic group and the equatorial ligands[133–135]. Studies of such coupling have been of value in the determination of the stereochemistry of substituted vinylcobaloximes[69].

Information about dynamic processes has also been obtained from the variations in proton NMR spectra with temperature and with added ligand concentration[136,137]. The observation of a single proton resonance for the organic group of α,β-dicyanoethylcobaloxime at room temperature and of a multiple resonance at low temperatures has been ascribed to changes in the rate of the equilibration[110,138]:

$$\mathrm{NC\overset{\beta}{C}H_2\overset{\alpha}{C}H(CN)Co(dmgH)_2py} \rightleftharpoons \mathrm{py(dmgH)_2Co\overset{\beta}{C}H(CN)\overset{\alpha}{C}H_2CN} \qquad (65)$$

(ii) *The equatorial ligand.* Similar effects are evident in the proton resonances of equatorial ligands. The chemical shifts of the methyl resonances of the dimethylglyoximato ligands in alkylcobaloximes are susceptible to the nature of the two axial ligands[135]. For a series of axial triphenylphosphine complexes, the variation of the ligand methyl resonances is an approximately linear function of the σ_p value of the other axial ligands which includes some alkyl ligands. Similarly, the very small changes in the methine proton resonances of the equatorial ligand in *p*-substituted arylCo(acacen) complexes have been ascribed[139] to the electronic effect of the *p*-substituent.

Where either of the axial ligands is asymmetric, otherwise symmetrical ligand resonances may be split. For example in complexes of the type $\mathrm{MeCH(CN)Co(dmgH)_2py}$ and $\mathrm{MeCo(dmgH)_2NHMeCH_2Ph}$, two sets of equatorial ligand methyl resonances are observed[140,140a]. Two equal methyl equatorial resonances are also observed for 2-propynylcobaloxime ($\mathrm{CH{\equiv}CCH_2Co(dmgH)_2py}$) at room temperature [73], possibly due to restricted rotation about the Co–C_α bond. The formation of dimeric complexes of the otherwise five-coordinate methylcobaloxime complexes also gives rise to splitting of the equatorial methyl resonance[137,141]. Observations of changes in the latter have been used to determine the rates of cleavage of the dimeric species by added ligands[136] (p. 49). The temperature variation in the spectra of the alkylcobaloximes shows that the hydrogen bonded bridge O–H···O exchanges at a rate of 50 s^{-1} at 25° and 10 s^{-1} at 5°.

The proton NMR of the alkylcobalamins is complicated[131,142,143] but the resonance due to the C_{10} proton stands out and has proved to be very useful. Not only does its chemical shift change with the character of the axial ligands[144], but its exchange with

deuterium[145] may be followed kinetically and has been shown to be acid-catalysed[144] (p. 65). Moreover, the fact that this resonance disappears on halogenation of the alkylcobalamins has been used as evidence that such substitution takes place at C_{10}[84,144].

(b) Other nuclei

Carbon-13, fluorine-19, and cobalt-59 NMR have all been studied briefly. The proton decoupled carbon-13 spectrum of the coenzyme[146,147] demonstrates dramatically the power of this method because of the almost complete resolution of all of the individual carbon resonances, and because of the information that can be obtained about their environment by relaxation techniques. It is interesting that the α-carbon resonance of the organic group has not been observed by this method, either in the cobalamins[147] or the simple cobaloximes[47], presumably because of its more rapid relaxation and consequent wide line width.

Cobalt-59 NMR studies[148] of Co(salen) complexes show that both alkyl and acyl groups cause a large downfield shift (ca. 7000 ppm) compared with the standard $Co(CN)_6^{3-}$.

Fluorine-19 NMR studies on 3- and 4-fluorobenzylcobalt(III) complexes have provided information about the electronic effects of substituents of the type $-CH_2CoL_nB$ on the benzene ring in the ground state[47]. They demonstrate more clearly than many other studies the very marked effects that both axial and equatorial ligands have on the organic groups. The order of the upfield shift of the fluorine resonance, which is also an indication of the extent of electron donation by the substituent, is $CH_2Co(dmgH)_2CN^- > CH_2Fe(CO)_2cp > CH_2Co(dmgH)_2aq > CH_3 > CH_2Co(dotnH)aq^+$. It is interesting that the group $CH_2Co(dmgH)_2CN^-$ has a larger effect than the group $CH_2Fe(CO)_2cp$, which is known to be extremely strongly electron donating from its effect on a number of chemical reactions and equilibria[150,151].

Similarly, the chemical shift of the fluorine resonances of 3- and 4-fluorophenylcobalt(III) compounds $ArCo(dotnH)^+$ show that the metal with its appendant ligands is both a π- and a σ-electron-donating group[149]. The extent of this electron donation is strongly dependent upon the nature of the axial base, in the order: $Me > 3\text{-}FC_6H_4 > NCO > SCN$ for σ-donation, and $I > Br > SCN > OCN > Me$ for π-donation.

(V) X-ray crystallography

Since X-ray analysis[154] of the coenzyme revealed for the first time the presence of a stable carbon–cobalt bond in a naturally occurring material, some ten other much less complex organocobalt(III) compounds (Table 11) have been examined. It is convenient to consider the crystal structures in terms of the steric and electronic effects and their variation with (i) the coordination number, (ii) the equatorial ligands, and (iii) the axial organic groups and base ligands.

(i) *Coordination number.* The only compound examined that is truly five-coordinate with respect to cobalt is MeCo(acacen) in which the equatorial ligand donor atoms form the base of a square pyramid, the apex of which is occupied by the methyl group[155]. The

TABLE 11

Bond lengths (Å) in organocobalt(III) compounds

Compound	*R–Co*	*Co–L*	*Co–B*	*Ref.*
$3K^+ CHF_2CF_2Co(CN)_5^{3-}$	1.99	1.89	1.93	162
$MeOCOCH_2Co(dmgH)_2py$	2.04	1.88	2.04	164
MeCo(acacen)	1.95	1.87(N) 1.87(O)		155
CH_2=CHCo(acacen)OH_2	1.93	1.89(N) 1.92(O)	2.22	173
PhCo(acacen)OH_2	1.93	1.89(N) 1.91(O)	2.33	174
EtCo(salen)	1.99	1.88(N) 1.89(N) 1.90(coord. O) 1.94(O)	2.34(O)	156
$MeCOCH_2Co(salen)OHMe$	2.02	1.89(N) 1.90(O)	2.20	161
$NCCH_2Co(salen)$, MeOH	1.99	1.89(N) 1.90(O)	2.09(N)	161
$(NC)_2CHCo(salpn)py$	2.02	1.87(N) 1.90(N) 1.89(O) 1.88(O)	2.07	14
$MeCo(dotnH)OH_2^+ ClO_4^-$	1.99	1.93(bridge N) 1.87(oxime N)	2.14	178
5′-Deoxyadenosylcobalamin	2.05	1.92(N of ring A) 1.91(N of ring B) 1.97(N of ring C) 1.98(N of ring D)	2.23	154,106
MeCo(acacen)py	1.99	1.92(N and O)	2.16	179a
CH_2=CHCo(salen)py	1.98	1.86(N) 1.88(O)	2.12	176a

cobalt atom is raised 0.12 Å above the basal plane supposedly to strengthen the C–Co α-bond without losing much of the π-bonding potential from the chelate.

All the other compounds studied are six-coordinate and, whilst some distortion from octahedral symmetry is always apparent, it is not usually very large. The cobalt-four-donor-atom group is always planar or very nearly so. Although two of the compounds contain no added axial base component, the sixth site is nonetheless occupied by a donor atom from within an adjacent molecule of complex. EtCo(Salen) forms dimeric species in which one of the chelating oxygens of the Schiff's base of each molecule becomes an axial base to the neighbouring cobalt of the other molecule[156]. This behaviour has been found for

(salen) in inorganic cobalt(III)[157] and cobalt(II)[158,159] complexes where added axial bases are absent, the only exception being the oxygen-active crystals Co^{II}(salen)$CHCl_3$[160]. It results in a rather long Co–B (*i.e.* Co–O) bond, and the equatorial bond from the other cobalt to the same donor atom is somewhat weakened. X-ray data and calculations[156] of π-overlap populations indicate a lesser availability of the $1p_z$ orbital on the equivalent acacen oxygen and this may account for the absence of such bonding in the Co(acacen) complexes studied so far. Dimer formation of $MeCo(dmgH)_2$ in solution and in the solid state[141a] is believed to be due to an interaction of this type also[141].

In contrast, in the compound $NCCH_2Co$(salen), the cyanide nitrogen is a much better donor to a neighbouring cobalt atom than is an oxygen of the already complexed salen ligand, and consequently the crystal is built up of polymeric chains[161].

(ii) *Equatorial ligands.* In the complexes studied so far, the bond lengths from cobalt to the four equatorial donor atoms (see Table 11) are very similar to those of the closely related inorganic cobalt(III) complexes. Thus the Co–L distance of 1.89 Å for $CHF_2CF_2Co(CN)_5^{3-}$[162] compares with that of 1.89 Å for $Co(CN)_6^{3-}$[163] and the Co–L distance of 1.88 Å for $MeOCOCH_2Co(dmgH)_2py$[164] compares with that of 1.89 Å for $ClCo(C_{12}[mgH]_2)py$[165] (where $C_{12}[mgH]_2$ *is cis*-1,12-*bis*(methylglyoximinato)dodecane). Values for dmfCo(salen)O_2Co(salen)dmf [1.88 Å (N) 1.90 Å (O)][166], MeOCo(salen)py [1.89 Å (N) 1.90 Å (O)][161] and for cyanocobalamin ['wet' 1.80 (A), 1.92 (B), 1.86 (C), 1.87 (D); 'dry', 1.86 (A), 1.90 (B), 1.91 (C), 1.95 (D) Å[167,168] and cyanocobalamin-5′-phosphate [1.87 (A), 1.99 (B), 2.10 (C), 1.94 (D) Å][169] are comparable with those for the organic derivatives listed in Table 11. Thus, there is no significant effect of the organic group on the equatorial bond lengths.

While the four donor atom group remains nearly planar in all the compounds, the remaining parts of the chelate are often subject to considerable conformational changes brought about by steric interaction with the axial groups. In the cobalamins interaction of C-5 and C-6 of the corrin ring with H-4 of the coordinated benziminazole causes a pronounced upward bowing of the 'top' half of the corrin containing rings A and B. This bowing, with the axis approximately along Co–C (10), amounts to 15° in the coenzyme[106], 11° in vitamin B_{12}-5′-phosphate[169] and 19° in B_{12} itself[167]. It is not surprising that a bulky group *trans* to the benziminazole, as in sec-alkylcobalamins, will tend to reverse this interaction with consequent loss, in solution at least, of the coordinated base. Corrinoids such as the hexacarboxylic acid[170] and cobyric acid[171], that have small axial ligands, do not suffer this distortion. All the natural corrins, however, exhibit alternate puckering of the β-carbons in the pyrroline rings owing to the substituents carried in these positions. The orientations of these side chains are subject to considerable variation between different compounds, often moving to give more favourable hydrogen bonding. The latter is rampant in these molecules and involves axial groups as well as water of crystallisation. Such bonding may sometimes be significant in chemical transformations.

In MeCo(acacen)[155], as in Co(acacen) PhH[172], where there is little or no steric interaction from axial groups, the chelate is very nearly planar with an eclipsed ethylene bridge.

However, in CH_2=CHCo(acacen) · OH_2 [173] the vinyl group sits over one half of the chelate and pushes it down some 11° causing a gauche ethylene bridge. The phenyl group in PhCo(acacen) · OH_2 [174] sits across the halves of the chelate and bends both down, but considerably less than 11°. In the EtCo(salen) dimer[156] the half of the chelate containing doubly coordinated oxygen is bent upwards towards the alkyl group due to interaction with the other molecule. In $NCCH_2$Co(salen)[161], where the methanol of crystallisation is hydrogen-bonded to one of the salen oxygen atoms, steric interaction in the polymeric chains again causes bending of the chelate. The organic group in $MeCOCH_2$ Co(salen) · MeOH[161] overhangs half of the chelate which is consequently bent down. All these Co-(salen) examples, and $(NC)_2$CHCo(salpn)py[14] have puckered gauche ethylene bridges.

Several inorganic Co(salen) complexes have been examined as a result of the property of some of them to absorb oxygen reversibly. The ability of salen to function in non-planar fashion with one oxygen dropped to the axial position[175,176], has been demonstrated and salen has also been found bridging two cobalt atoms[176]. The crystal structure of a peroxo-bridged Co^{III}(salpr)[177] complex shows a chelate oxygen rather than the expected NH as the axial base with the other four donor atoms, including NH, wrapped around the plane. Such bonding might also be the norm for salpr in its organocobalt compounds.

In the cobaloxime[164] and in MeCo(dotnH) · OH_2^+ [178] the two halves of the ligand system lie approximately in a plane. The short hydrogen-bond lengths (2.50 and 2.39 Å, respectively) are indicative of the strength of the hydrogen bonds. The hydrogen atoms were not located and the hydrogen bonds are probably bent as in other metaloximes[179]. In both cases, within experimental error, the N–O bond lengths on either side of the hydrogen bond are the same and thus the O · · · · H · · · · O linkage is probably symmetrical, or nearly so.

Several of the ligands contain a two carbon bridge between donor nitrogen atoms and this always imposes some constraint by influencing the ideal 90° angle at cobalt. Typical values obtained for cobalt(III) complexes are: dmgH (78–80°), acacen (87°), salen (85°), corrin (81–86°).

(iii) *Axial organic group and base ligands.* The *trans*-effect of the organic group R is evident when one compares the Co–B bond lengths of the organocobalt(III) complexes (Table 11) with those for related inorganic complexes where R is replaced by Cl or CN. Thus the Co–B bond length in $CHF_2CF_2Co(CN)_5^{3-}$ (1.93 Å) is larger than that in $Co(CN)_6^{3-}$ (1.89) and that in $MeOCOCH_2Co(dmgH)_2py$ (2.04 Å) is larger than that in $ClCo(C_{12}[mgH]_2)$-py (1.97 Å). Similarly, the Co–B bond in vitamin B_{12}('wet' 1.97 Å, 'dry' 2.07 Å) and vitamin B_{12}-5′-phosphate (1.97 Å) is markedly shorter than that in the coenzyme (2.23 Å) which is in accord with the greater ease of base protonation ('pK_a') of the latter. Other comparisons are provided by the dimeric species $ClCo^{III}$(salen) (Co–O = 1.99 Å) and $EtCo^{III}$(salen) (2.34 Å), with Co^{II}(salen) (2.25 Å) intermediate between these. Bulky axial base ligands may suffer distortion from octahedral symmetry owing to steric interactions. In all the cobalamins, the benzimidazole is thus affected due to its interaction between its coordinating nitrogen and the bridge-head methyl group of C-1 of the corrin ring. In some

of the compounds there may be steric effects on axial bond length in cases where the chelate is forced downwards by the bulky organic group. This will tend to weaken the bond as will any intermolecular hydrogen bonding in which the base is involved. Such effects may be important in CH_2=CHCo(acacen). It is of interest that the crystal structure of a peroxo-bridged Co^{III}(salen) complex shows axial dimethylformamide coordinating through oxygen rather than nitrogen.

The R–Co bond lengths (Table 11), and their changes with different hybridisation of the bonded α-carbon, are consistent with covalent σ-bond character. In the examples studied, there appears to be no marked effect of the charge on the complex on the bond length. As the axial group affects the chelate conformation so does the chelate produce a distortion in the Co–C–C angles at the α-carbon. Typical values are $CHF_2CF_2Co(CN)_5^{3-}$ (120°), $MeOCOCH_2Co(dmgH)_2py$ (115°), EtCo(salen) (120°), 5′-deoxyadenosylcobalamin (125°), and CH_2=CHCo(acacen)OH_2 (127°). The α-carbon is itself distorted from the octahedral symmetry to varying degrees, and one can envisage that, for t-alkylcobalt(III) compounds where such distortion would be greatly limited, the resulting strain in the angles at the α-carbon might give these as yet unprepared compounds a very low stability.

REACTIONS OF ORGANOCOBALT(III) COMPOUNDS

The reactions of organocobalt(III) compounds are complicated by the several reactive sites that are present in most molecules. Thus reactions commonly occur at the metal, at the organic ligand with and without cleavage of the carbon–metal bond, at the equatorial ligands, and at the axial base ligand. The following discussion of the reactions is therefore arranged in terms of the type of reagent, the way in which it may function, and the various sites at which it may react.

(I) Reactions with nucleophilic reagents

The reactions of nucleophiles with organocobalt(III) compounds are dependent upon three main properties of the nucleophile: (i) its affinity for cobalt(III); (ii) its nucleophilicity at carbon and at cobalt; and (iii) its proton basicity.

(a) Nucleophiles as axial ligands

The commonest reaction, and one which is fundamental to consideration of nearly all others, is that in which one axial base is replaced by another. Since such reactions are reversible, both thermodynamics and the kinetics of the replacement reaction are of interest. Much of our knowledge of cobalt(III) compounds comes from detailed studies of the inorganic complexes[180]. For example, there is much evidence that most inorganic cobalt(III) complexes are relatively inert to substitution, particularly towards associative substitution, and that this inertness is kinetic rather than thermodynamic. However, the presence of an organic group, or of certain other groups, such as sulphite[181], on the cobalt makes the five coordinate intermediate relatively more stable, and allows a much faster dissociation

of the axial ligand in the position *trans* to the organic group. Consequently equilibria between axial ligands of organocobalt(III) compounds are established relatively rapidly and a solution of such a compound may contain significant proportions of more than one six-coordinate species as well as some of the five coordinate species.

$$RCoL_nB + B' \rightleftharpoons RCoL_nB' + B \qquad (66)$$

In a few cases stable five coordinate complexes have been prepared by removal of a ligand from the corresponding six coordinate complex. For example, by azeotropic dehydration of several aquo-complexes in boiling benzene solution, or by standing the solid over a suitable desiccant[182,183,148,34,118]. Five coordinate complexes are also believed to be formed on irradiation of alkylcobaloximes (see p. 95).

$$RCo(acacen)\cdot OH_2 \longrightarrow RCo(acacen) \qquad (67)$$

$$RCo(salen)\cdot OH_2 \longrightarrow RCo(salen) \qquad (68)$$

$$RCo(dmgH)_2B \longrightarrow RCo(dmgH)_2 \qquad (69)$$

$$(B = H_2O, Me_2S; R = Me, Et)$$

The complex MeCo(salen) is green, soluble in most organic solvents, but turns red on treatment with ethers, and is readily reconverted to the orange six coordinate complexes[148]. The complex $RCo(dmgH)_2$ is associated in solution; at low temperatures (*e.g.* $-50°$) in methylene chloride, two molecules are bound together by coordination of an oxygen of an equatorial ligand of one molecule to the cobalt atom of the other molecule[141]. Consequently two distinct equatorial methyl resonances are observed in the ^1H NMR spectrum at this temperature. At higher temperatures (*e.g.* 40°) where the complex undergoes rapid dissociation and reassociation, only a singlet resonance is observed for these protons. Such dimeric species are also partially broken by the addition of even weakly coordinating ligands to the solution, including MeNC and CO[130,136].

$$[MeCo(dmgH)_2]_2 + 2B \rightleftharpoons 2MeCo(dmgH)_2B \qquad (70)$$

(i) *Thermodynamic measurements of axial ligand exchange.* The association constants of a range of alkyl- and aryl-cobalt(III) compounds are shown in Table 12. The relevance of these figures to other reactions of organocobalt compounds is evident from the fact that, in an 0.1*M* aqueous solution of methylbis(dimethylglyoximato)pyridinecobalt(III) (log K = ca. 3)[184,185], some 5% is present as methylaquobis(dimethylglyoximato)cobalt(III).

Though the media used for the determinations were not all the same, several features are evident. First the more electron withdrawing the organic group, the higher the association constant. It is interesting to note that, as the *p*-methoxy group in *p*-$MeOC_6H_4Co$-(acacen) apparently[186] behaves as an electron-withdrawing substituent, there can be little

TABLE 12

Some formation constants for organocobalt(III) compounds

R	B_1[a]	B_2[b]	*Temperature*	*log K*	*Ref.*
(a) Cobinamides in water					
Me	aq	NH_3	amb	−1	191
Me	aq	py[c]	amb	0.8	191
Me	aq	imidazole	amb	1.04	191
Me	aq	CN^-	amb	2.1	126
Me	aq	CN^-	amb	2.36	191
Me	aq	1-Me-imidazole	amb	0.7	191
Me	aq	ethanolamine	amb	−1.5	191
Me	aq	piperidine	amb	<−2	191
Me	benzimidazole[d]	CN^-	amb	0.1	193
Et	aq	CN^-	amb	0.6	126
Pr	aq	imidazole	amb	−1.0	191
vinyl	aq	CN^-	amb	2.7	126
vinyl	aq	MeNC	amb	0.6	190a
vinyl	aq	N_3^-	amb	0.6	190a
vinyl	aq	I^-	amb	0	190a
vinyl	benzimidazole[d]	CN^-	amb	0.7	193
HC≡C	benzimidazole[d]	CN^-	amb	2.7	193
CN	aq	MeNC	amb	2.8	190a
CN	aq	N_3^-	amb	2.7	190a
CN	aq	OH^-	amb	3.0	193
(b) Cobaloximes in water					
Me	aq	CN^-	10	6	184
Me	aq	NH_3	10	3.6	184
Me	aq	N_3^-	10	2.3	184
Me	aq	SCN^-	10	2.0	184
Me	aq	OH^-	10	1.4(1.3)	184(205a)
Me	aq	py	10	3.68[f]	184
Me	aq	py	20	3.3[e]	185
Me	aq	py	45	3.0[e]	185
Me	aq	HSR[h]	25	−0.13	205a
Me	aq	$^-$SR[h]	25	5.30	205a
Me	aq	RSR[i]	25	1.95	205a
Me	aq	$^-$SR[j]	25	5.43	205a
Me	RSH	RS^-[h]	25	4	205a
(c) Cobaloximes in $CDCl_3$					
Me	4-CNpy	Benzylamine	39	0.57	132a
Me	4-MeO_2Cpy	Benzylamine	39	0.15	132a
Me	4-Brpy	Benzylamine	39	−0.20	132a
Me	py	Benzylamine	39	−0.62	132a
Me	4-Mepy	Benzylamine	39	−0.85	132a
Me	imidazole	Benzylamine	39	−1.82	132a
(d) Co(acacen) compounds in $CDCl_3$					
Me	none[g]	aniline	30	0.7	289
Me	none	*p*-Cl-aniline	30	0.58	289
Me	none	*p*-Me-aniline	30	0.85	289
Me	none	py	30	1.7	289

TABLE 12 (continued)

R	B_1 [a]	B_2 [b]	Temperature	log K	Ref.
Me	none	4-Me-py	30	0.92	289
Et	none	aniline	30	0.06	289
Ph	none	aniline	30	0.92	289
vinyl	none	aniline	30	0.74	289
p-$O_2NC_6H_4$	none	piperidine	30	1.9	186
p-NCC_6H_4	none	piperidine	30	1.7	186
p-BrC_6H_4	none	piperidine	30	1.3	186
p-IC_6H_4	none	piperidine	30	1.25	186
Ph	none	piperidine	30	0.7	186
p-$O_2NC_6H_4$	none	$^2H_5$-py	30	1.9	186
p-NCC_6H_4	none	$^2H_5$-py	30	1.7	186
p-BrC_6H_4	none	$^2H_5$-py	30	1.3	186
p-IC_6H_4	none	$^2H_5$-py	30	1.3	186
p-$MeOC_6H_4$	none	$^2H_5$-py	30	0.8	186
p-MeC_6H_4	none	$^2H_5$-py	30	0.7	186
Ph	none	$^2H_5$-py	30	0.7	186

[a] Outgoing axial ligand.
[b] Incoming axial ligand.
[c] Pyridine.
[d] Cobalamin side chain.
[e] $\Delta H^{\neq} = -5.1 \pm 0.4$ kcal/mol, $\Delta S^{\neq} = -2 \pm 1.5$ e.u.
[f] $\mu = 1.0$.
[g] Possibly dimeric RCo(acacen)?
[h] 2-Mercaptoethanol.
[i] *S*-Methyl-2-mercaptoethanol.
[j] Mercaptoacetate.

conjugative interaction between that substituent and the metal, *i.e.* little π-electron donation from the aromatic ring to the metal. Similarly, the greater the electronegativity of the α-carbon, the higher the association constant, *i.e.*, $HC{\equiv}C > H_2C{=}CH > MeCH_2$. There is no direct correlation between the proton basicity of the axial base and its affinity for cobalt, but, within a series of bases of similar structure, such as pyridine and its derivatives, the affinity of the axial base for the metal increases with the basicity of the former (Table 12). For a series of similar bases with different donor atoms, the affinity for the metal increases in the order: O < S < N < P which is characteristic of the behaviour of a relatively soft or class B metal acid. Ambident ligands, such as thiocyanate and cyanate, bond predominantly through nitrogen, but appreciable proportions of the other isomers may be present in solution[123]. Cyanide ion bonds predominantly through carbon, but bridged complexes of the type (VI) are readily formed in aqueous solution and in chloroform, in the presence of the corresponding aquo compound (eqn. 71; R = R'). Such bridged complexes have also been isolated in the solid state[123].

$$[RCo(dmgH)_2CN]^- + R'Co(dmgH)_2aq \underset{}{\overset{CHCl_3}{\rightleftharpoons}} \underset{(VI)}{[RCo(dmgH)_2CNCo(dmgH)_2R']^-} + H_2O \qquad (71)$$

Where the organocobalt components of the bridged cyanide complex are not the same (eqn. 71; R ≠ R'), the initially formed cyanide bridge may slowly rearrange to a mixture of bridged isomers which can be detected by proton NMR and infrared spectroscopy.

The benzimidazole group of the cobalamin side chain is particularly firmly held. However, as coordination of this group does require distortion of the corrin ring from the equatorial plane[106], the formation constants are greatly reduced where the organic ligand has an appreciable steric requirement[41,65,187]. The planar asymmetry of the corrin ring allows two isomers of alkylcobalt(III) corrinoids with the alkyl group 'above' or 'below' the plane of the corrin ring. These have been detected by ultraviolet spectroscopy and thin layer chromatography, and the equilibria between the respective pairs have been studied. Examples are known for methylcobyric acid, methylcobinamide monocarboxylic acid, methylcobalamin and methylcobinamide phosphoribose[188,189].

(ii) *Kinetics of axial ligand exchange.* The considerable amount of detailed work on the kinetics and mechanism of substitution reactions of inorganic cobalt(III) complexes has established (*i*) that such reactions are exclusively dissociative and (*ii*) that small amounts of cobalt(II) impurities may have a profound influence on the reaction rate because of redox processes coupled with the large difference in rate of substitution of cobalt(III) and cobalt(II) complexes[195]. With the organocobalt(III) complexes, the latter effect may probably be ignored, because of the much higher rates of substitution at the position *trans* to the organic group, which may be sufficiently fast as to require the use of stopped-flow methods for their study. However, the dissociative mechanism involves a rather complicated kinetic form, which has been derived by use of the steady state approximation based on the mechanism shown in eqns. 72 and 73, where R(Co) is the five coordinate intermediate.

$$R(Co)solv. \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R(Co) + solv. \tag{72}$$

$$R(Co) + B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R(Co)B \tag{73}$$

$$k_{obs} = (k_1[B] + k_{-1}k_{-2}/k_2)/(k_{-1}/k_2 + [B]) \tag{74}$$

The form of k_{obs}f(B) depends upon the magnitudes of the various rate coefficients; several different types of behaviour may be observed:

(a) k_{obs} may be a linear function of [B] and effectively zero when [B] = zero; *i.e.* k_{-2} must be small; and k_{-1}/k_2 is large compared with [B];

(b) k_{obs} may be a linear function of [B] and have a finite value (k_{-2}) with [B] = zero; *i.e.* k_{-2} is significantly large; and k_{-1}/k_2 is large compared with [B];

(c) $1/k_{obs}$ may be a linear function of 1/[B], particularly when the reaction is studied at relatively high concentrations of B;

(d) k_{obs} may be independent of B; *i.e.* k_2/k_{-1} is large.

Kinetics of type (a), (b), and type (c) have been observed so far with organocobalt(III)

compounds. The rate coefficients obtained in several studies are shown in Table 13, together with their relationship to the rate eqn. 74. The second order term k_1k_2/k_{-1} is the most significant, because this usually determines the overall rate of the forward reaction.

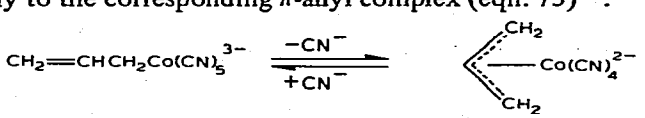
These results indicate that the incoming ligand has little influence on the reaction rate, except in so far as it may compete with the solvent or with other ligands for the five-coordinate intermediate (R(Co)) and be involved in the solvation of, or ion-pairing with, the complexes concerned. The higher rates of these reactions compared with those for the inorganic cobalt(III) complexes are due to the higher positive entropy and energy of activation of the latter[185]. For example, for $MeCo(dmgH)_2aq$ with SCN^-, $\Delta H^{\neq} = 17.5 \pm 0.4$ kcal/mole and $\Delta S^{\neq} = +10 \pm 1.5$ e.u., and, for a typical inorganic complex[196] $O_2NCo(dmgH)_2aq + SCN^-$, $\Delta H^{\neq} = 19.4$ kcal/mole and $\Delta S^{\neq} = -9 \pm 4$ e.u. This difference has been ascribed in part to the need for greater flexibility of the partially five-coordinate transition state for the alkylcobalt(III) compounds[185], resulting in greater reactivity.

The kinetics and thermodynamics of exchange of several sulphur ligands have been studied[205a] in considerable detail (Tables 12–13). As expected, the rates of substitution of thiols, thioethers, and thiolate ions are not dissimilar, but the thiolate ions are the much more firmly attached (Table 12).

The rates of axial base exchange are lower with aryl- than with alkylcobalt(III) compounds and the very high rate of exchange with isopropyl compounds is probably a result of a relief of steric strain present in the six coordinate complex, aided by the inductive effect of that group[197].

The rates of axial base exchanges in methylcobaloximes have been shown by semiquantitative ^1H NMR methods to lie in the order[137,136]: $MeCN \sim Ph_2SO \sim Me_2SO > Me_2S >$ thioxane (via S), $Me_3N > PPh_3 > P(OMe)_3$ *i.e.*, in the order expected for the cobalt acting as a class B acid. Dimethyl sulphoxide exhibits coordination isomerism with the equilibrium between S and O bonded species observable by ^1H NMR at low temperatures. The ratio O-bonding/S-bonding decreases from 4.6 at $-72°$ to 3.1 at $-25°$ [136]. The rates of phosphine ligand exchange are conveniently measured by observation of the collapse of intramolecular P–H coupling as the temperature is raised, and the fact that this process involves a dissociative rate determining step is apparent from the NMR line shapes.

No quantitative data are available for the exchange of axial ligands in alkylpentacyanocobaltates, but it is apparent from a number of kinetic studies[198] of their reactions that one of the five cyanide ligands, presumably the *trans*-ligand, is readily lost. This may have important consequences. For example, the reversible loss of cyanide ion from allylpentacyanocobaltate(III) ions gives a five coordinate σ-allyl complex which rearranges reversibly to the corresponding π-allyl complex (eqn. 75)[20].



(75)

syn-π-(1-Methylallyl) complexes have been observed, together with *cis*- and *trans*-σ-but-2-enyl complexes, in the products of hydrogenation of butadiene in the presence of the pentacyanocobaltate(II) ion[117].

(*continued on p. 50*)

TABLE 13

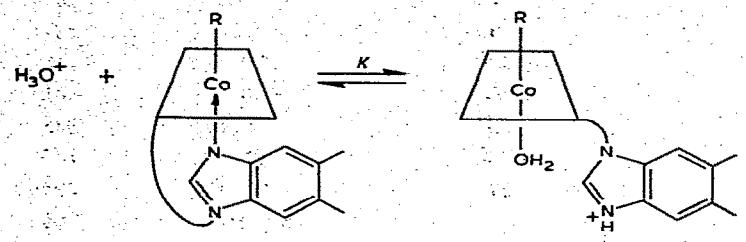
Kinetics of axial base exchange in organocobalt(III) compounds

R	L_n	B_1	B_2	*Solvent*
Me	$(dmgH)_2$	aq	NH_3	H_2O
Me	$(dmgH)_2$	aq	CN^-	H_2O
Me	$(dmgH)_2$	aq	py	H_2O
Me	$(dmgH)_2$	aq	N_3^-	H_2O
Me	$(dmgH)_2$	aq	SCN^-	H_2O
Me	$(dmgH)_2$	aq	SCN^-	H_2O
Me	$(dmgH)_2$	aq	SCN^-	H_2O
Me	$(dmgH)_2$	aq	py	H_2O
Me	$(dmgH)_2$	aq	py	H_2O
Me	$(dmgH)_2$	aq	SR^{-i}	H_2O
Me	$(dmgH)_2$	aq	SR'^{-j}	H_2O
Me	$(dmgH)_2$	aq	HSR'^{j}	H_2O
Me	$(dmgH)_2$	aq	HSR^{i}	H_2O
NO_2	$(dmgH)_2$	aq	SCN^-	H_2O
Me	(dotnH)	aq	iminazole	acetone + 1% H_2O
Me	(dotnH)	aq	benzylamine	acetone + 1% H_2O
Et	(dotnH)	aq	iminazole	acetone + 1% H_2O
i-Pr	(dotnH)	aq	iminazole	acetone + 1% H_2O
$PhCH_2$	(dotnH)	aq	iminazole	acetone + 1% H_2O
Ph	(dotnH)	aq	iminazole	acetone + 1% H_2O
Ph	(dotnH)	aq	benzylamine	acetone + 1% H_2O
Ph	(dotnH)	aq	Ph_3P	acetone + 1% H_2O
5'-Deoxyadenosyl	cobinamide	benziminazole	CN^-	H_2O
Me	$(dmgH)(dmgH_2)$	SCN^-	aq	$HClO_4$(4*M*)
Me	$(dmgH)_2$	SCN^-	aq	$LiClO_4$(4*M*)

[a] s^{-1}.
[b] *M*.
[c] $M^{-1} \cdot s^{-1}$.
[d] s^{-1}; calc. from the intercept k_{obs} *vs.* $[B_2]$, or from the product $k_1k_2/k_{-1}K_f$.
[e] $\mu = 1.0$.
[f] $\Delta H^{\neq} = 20.5 \pm 0.4$ kcal/mole; $\Delta S^{\neq} = 19 \pm 1.5$ e.u.
[g] $\Delta H^{\neq} = 17.5 \pm 0.4$ kcal/mole; $\Delta S^{\neq} = 10 \pm 1.5$ e.u.
[h] Relative rates only.
[i] Mercaptoethanol = RSH.
[j] Mercaptoacetate = R'SH.
[k] Product of formation constant and forward rate coefficient.

$T°$	k_1[a]	k_{-1}/k_2[b]	k_1k_2/k_{-1}[c]	10^2k_2[d]	Ref.
10			3.1[e]		184
10			14.0[e]		184
10			29.9[e]		184
10			34.7[e]		184
10			49.6[e]		184
15			52[f]	70	185
40			630[f]	1400	185
15			20[g]	0.88	185
47			880[g]	98	185
25			27	1.4×10^{-2}	205a
25			13	5×10^{-3}	205a
25			50	–	205a
25			50	6.7×10^{3}[k]	205a
25			5.8×10^{-3}		196
25	24.8 ± 5.6	0.18	138		197
25	40.9	0.18	227		197
25	251 ± 23	0.13	1930		197
25	602 ± 139	0.35	1720		197
25	226 ± 28	0.15	1500		197
25	3.6 ± 0.3	0.1	36 ± 3		197
25	6.9	0.15	46		197
25	4.9	0.013	377		197
25			2.9×10^{-2}		199
25			x[h]		200
25			4.7x[h]		200

The loss of basic axial ligands may be markedly affected by mineral acid. With monodentate ligands, the equilibrium position is influenced by competition between the mineral acid and the metal for the base. With ambident ligands, the acid may also increase the rate of loss of the ligand from the metal by attack at the uncoordinate basic site. The equilibria studied in the most detail involve the loss of the fifth (benzimidazole) ligand from the alkylcobalamins (eqn. 76). The equilibrium constants decrease in the order[193,192,201] (Table 14) ethyl(3.87) > 5′-deoxyadenosyl(3.35) > methyl(2.5) > vinyl(2.4) > alkynyl (0.7).



(76)

Other Lewis acids are also effective in removing the benzimidazole[202,203] ligand and in accelerating the removal of other ambident ligands, such as thiocyanate and cyanide, from other cobalt(III) complexes, *i.e.*:

$$RCo(dmgH)_2NCS^- + Ag^+ \xrightarrow{aq} RCo(dmgH)_2aq + AgSCN \quad (77)^{184}$$

$$RCo(CN)_5^{3-} + Hg^{2+} \xrightarrow{aq} RCo(CN)_4aq^{2-} + HgCN^+ \quad (78)^{198}$$

TABLE 14

Protonation of axial bases on organocobalamins

R	$^tpK_a^a$	*Ref.*
HC≡C	0.7	193, 201
$HOCOCH_2$	1.50, 2.20	204, 192
$MeOCOCH_2$	2.25, 2.5	192, 193, 201
H_2C=CH	2.4	193, 201
Me	2.72	192
2′,3′-Isopropylidene-5′-deoxyadenoxyl	2.94	192, 204
$NCCH_2CH_2$	2.95	192
$MeOCH_2CH_2$	3.10	192
$HOCH_2CH_2$	3.15	192
$HOCOCH_2CH_2$	3.25	192
$MeOCOCH_2CH_2$	3.27	192
5′-Deoxyadenosyl	3.55, 3.52	193, 204
n-Pr	3.84	204
Et	3.87	192
n-Bu	3.93	204
n-Heptyl	4.01	204

[a] Eqn. 76.

The reversible change in the spectrum of alkylpentacyanocobaltates in aqueous acidic solution has been ascribed to the protonation of one of the cyanide ligands, *i.e.*

$$RCo(CN)_5^{3-} + H_3O^+ \rightleftharpoons RCo(CN)_4CNH^{2-} + H_2O \qquad (79)^{45}$$

(b) Nucleophiles as proton bases

Some nucleophiles, such as hydroxide ion are relatively inert towards cobalt(III), but are strong bases. The majority of molecules concerned in this review have acidic sites at which such bases may react, as follows.

(i) *Acidity of axial ligands.* One of the simplest examples, but which is indistinguishable from a simple ligand exchange, involves the removal of a proton from a coordinated water molecule, *i.e.*

$$OH^- + RCoL_n \cdot OH_2 \rightleftharpoons RCoL_n \cdot OH^- + H_2O \qquad (80)$$

The p*K*a of the coordinated water parallels the stability of the aquo complexes. Thus the alkylaquocobalt(III) complexes are much less acidic (*e.g.* MeCo(dmgH)$_2$aq p*K*a 12.3[184]; 12.7[205a]) than the corresponding less labile inorganic aquocobalt(III) complexes[184], though there is some doubt as to which proton is removed from the dimethylglyoxime complexes[205a]. Though the effect of equatorial ligands on the pK_a of the aquo ligand has not been investigated in detail, the results from inorganic complexes suggest that the acidity decreases in the order[72]: 7,7′-Me-salen > salen > salphen > dmgH > dotnH.

The effect of acidity of thiolate ions on the degree of complex formation has been studied in some detail[205a]. For example, the pK_a of the complex of methylcobaloxime with 2-mercaptoethanol (*i.e.* for losses of thiol-H from the complexed thiol) is 4, whereas the free thiol has pK_a 9.51[205a].

(ii) *Acidity of equatorial ligands.* Many equatorial ligands, such as glyoximato ligands, also have acidic sites. Few direct measurements of the pK_a of these sites have been made, although nuclear magnetic resonance measurements, particularly of the O· · · · H —— O bridges between glyoximato ligands of inorganic complexes, indicate that the chemical shift is an approximately linear function of the pK_a[205,206,207]. Some examples of the very low chemical shifts of these protons are shown in Table 10.

The loss of these protons, which undoubtedly occurs in strongly alkaline solution, has a profound effect of the reactivity of the carbon–cobalt bond. For example, in the reactions of styrylcobaloximes with methyllithium in ethereal solution, cleavage of the carbon–cobalt bond is hindered by the formation of the less reactive and less soluble anion (VII; eqn. 81)[208]. Such disadvantages may perhaps be overcome by prior selective methylation of the hydroxyl groups.

$$RCo(dmgH)_2B + MeLi \longrightarrow \underset{(VII)}{RCo(dmgH)(dmg)B^-\,Li^+} + CH_4 \qquad (81)$$

(iii) *Acidity of the organic ligand.* In alkaline solution acidic functional groups on the organic ligand may be converted into their conjugate bases. The influence of the metal and its appendant ligands on the acidity of these functional groups therefore provides a useful measure of the electronic effect of the metal. For example, the β-carboxyethylcobaloxime (pK_a 5.7) is slightly less acidic than propionic acid (pK_a 4.87), but carboxymethylcobaloxime (pK_a 7.14) and α-carboxyethylcobaloxime (pK_a 7.14) are both significantly less acidic than acetic acid (pK_a 4.76) and propionic acid[39]. These are indications that the group $-CH_2Co(dmgH)_2py$ is more electron donating than is the methyl group, under such circumstances.

The group $-CH_2Co(CN)_5^{3-}$ is even more effective in its electron donating capacity than are the groups described above. Thus, the 2-, 3-, and 4-pyridiniomethylpentacyanocobaltate(III) ions (VIII, IX and X; pK_a 10.5, 8.1, and 9.2, respectively)[209,45] are very much less acidic than the unsubstituted pyridinium ion (pK_a 5.2). Since the inductive effect of a substituent in the 3-position of the pyridinium ion influences the acidity of that ion more than does the inductive effect of the same substituent in the 4-position of the pyridinium ion[150] (unlike the corresponding effects in benzoic acid), the much greater effect of the substituent $-CH_2Co(CN)_5^{3-}$ in the 4- than in the 3-position, indicates that this electron donation is largely conjugative in origin. It seems probable that the effect of the other methylene–cobalt substituents *i.e.* CH_2cobalamin and $CH_2Co(dmgH)_2B$, is also partly conjugative though less pronounced. Such effects have been termed $\sigma-\pi$-conjugation or vertical stabilisation, and are apparent in a number of other methylene–metal substituents, both of the transition metals[151] and of main group metals[210].

(82)

2– VIII
3– IX
4– X

(iv) *Base-catalysed fission of the carbon–cobalt bond.* A number of organocobalt(III) compounds undergo reductive elimination reactions promoted by attack of basic nucleophiles at a β-proton of the organic group. For example, several β-substituted ethylcobalamins and cobaloximes that may be prepared by the addition of the cobalt(I) species to an olefin under mildly alkaline conditions (p. 14 and p. 26–27), are also reconverted into that olefin by the action of base, *i.e.*

$$XCH_2CH_2CoL_nB + OH^- \rightleftharpoons XCH{=}CH_2 + [CoL_nB]^- + H_2O \qquad (83)$$

The earliest studies of this reaction involved the reaction of β-cyanoethylcobalamin with base[211]. In solutions of pH greater than 9, the rate of reaction was first order in the substrate concentration and first order in alkali concentration (eqn. 84), but at higher acidities, the kinetics were more complicated.

$$-d[\text{organocobalt}]/dt = k_2\,[\text{organocobalt}]\,[OH^-] \qquad (84)$$

The formation of the cobalt(I) species during the forward reaction was confirmed by the isolation of methylcobalamin from the products of reaction of β-cyanoethylcobalamin with base in the presence of methyl iodide under anaerobic conditions. The fate of the organic ligand (eqn. 83, X = CN) was determined using α-^{14}C-β-cyanoethylcobalamin and the method of isotopic dilution[211].

The complicated kinetics in the less basic solutions is almost certainly a result of the incursion of the reverse reaction, described more fully on p. 26–27, but as there have been no detailed rate studies of this reverse reaction, the kinetic form is uncertain. However, the related studies on the β-substituted ethylcobaloximes are of interest, because of the observation that π-complexes are formed between the product olefin and the product cobalt(I) species[110,138]. It has been assumed that such complexes are the immediate reaction products of the forward reaction and that, in the reverse reaction, the π-complex is the immediate precursor of the σ-complex[138].

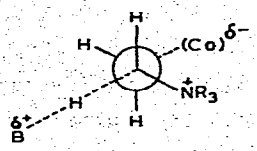
However, whilst this seems to be the most reasonable mechanism, it is not yet completely proven. An alternative mechanism might involve π-complex formation after formation of the free olefin and cobalt(I) species in the forward reaction. Indeed, the formation of the σ-complex from the olefin and the cobalt(I) species (discussed earlier, p. 26–27) might actually be retarded by π-complex formation, if it involves reaction between free olefin and free cobalt(I) species. It may even be possible for the π-complex to react with a further molecule of olefin to form the σ-complex. A detailed analysis must await kinetic studies involving the reverse reaction.

Two pieces of evidence quoted in favour of the formation of the π-complex in the forward reaction may also be questioned. First, it has been suggested that the increase in rate coefficient for the forward reaction with the increasing nucleophilicity of the displaced cobalt(I) species is due to *d*-orbital participation in the formation of the olefin π-complex[138,110]. However, there is no reason to suppose that this is not the order to be expected for the leaving group tendencies of the several cobalt(I) species in a normal bimolecular elimination (*E* 2) reaction[212]. Certainly, the nucleofugal character of the halide ions decreases from iodide to chloride as does their nucleophilicity[213] (see however, the leaving group order on p. 57).

Secondly, the observed primary isotope effect (k_D/k_H = 1.60) has been considered to be too low for a simple bimolecular elimination reaction[110,138]. This is not necessarily so because the isotope effect for such a reaction rises to a maximum of ca. 6 and then falls again as the transition state for bimolecular elimination involves progressively more carbon–hydrogen bond breaking[214]. The observed isotope effect is therefore consistent with either (a) a small amount, or (b) a large amount, of C–H bond breaking in the *E* 2 transition state, more probably the former.

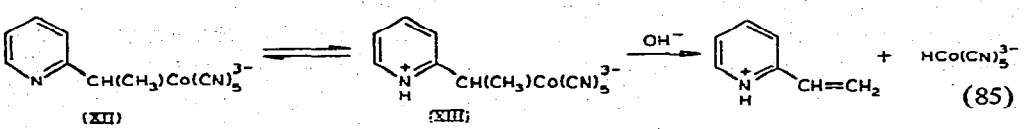
The observation that the β-trimethylaminoethylcobalamin does not give the vinyltrimethylammonium ion has been interpreted in terms of steric hindrance to the formation

of the required *trans*-antiperiplanar transition state (XI) because of interaction between the bulky NMe_3^+ group and the corrin ring[219].



(XI)

α-Substitued ethylpentacyanocobaltates do decompose under alkaline conditions in aqueous solution[114]. Under anaerobic conditions there is a slow decomposition to the olefin and the corresponding alkyl derivative, whereas under aerobic conditions the olefin is the main product. For example, the α-2-pyridinioethylpentacyanocobaltate(III) ion decomposes in alkaline solution in the presence of air to 2-vinylpyridine. The rate of this reaction increases linearly with the alkali concentration in the region pH 6 to pH 9, but reaches an upper limit at ca. pH 12. This levelling off in the rate is consistent with either a unimolecular loss of the hydridopentacyanocobaltate(III) ion from the pyridylpentacyanocobaltate (XII) or a base catalysed elimination of the same hydride from the pyridinomethylpentacyanocobaltate(III) ion (XIII; pK_a ca. 10.5), probably the latter, eqn. 85.



(XII) (XIII) (85)

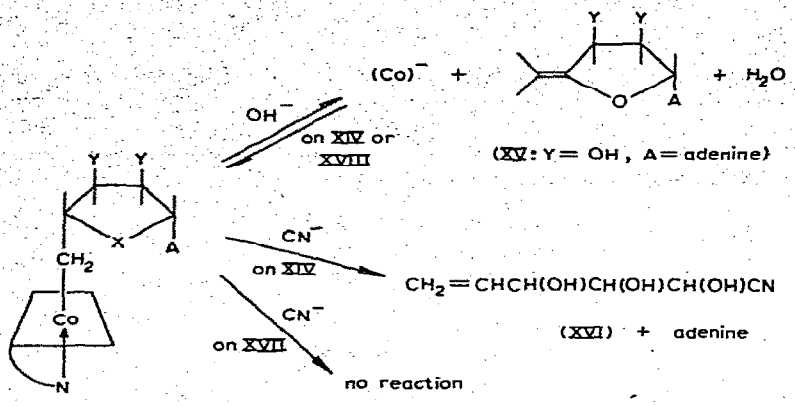
In some of those reactions where cyanide ion apparently promotes the decomposition of organocobalt(III) compounds, this has been shown to be a result of the reaction of hydroxide ion present in aqueous cyanide ion solutions. One example of this is the cyanide ion promoted decomposition of β-cyanoethylcobalamin[211]. The observed rate coefficient (k_1 = 1.15 × 10^{-3} s^{-1}; in 35 m*M* KCN) is the same as that observed at the same pH (10.5) in the absence of cyanide ion. Some, but not all, of the reactions of cyanide ion may be explained in this way. For example, the decomposition of 5′-deoxyadenosylcobalamin (XIV) in 1*M* sodium hydroxide to give 4′, 5′-dehydro-5′-deoxyadenosine (XV) (eqn. 86)[104] is several powers of ten slower than the corresponding reaction with 0.01*M* cyanide ion[104], which gives the cyanhydrin (XVI) of the open chain 2,3-dihydroxypent-4-en-1-al[199,216,217]. Rate coefficients for several of these reactions are shown in Table 15. Interpretation of these values is complicated by the fact that the extent of cyanide coordination as the axial base is not known. In 0.1*M* KCN in bicarbonate buffers at 25°, the coordination of cyanide ion has been shown to take place in a rapid first stage of the overall reaction[199].

TABLE 15

Kinetics of reaction of β-substituted ethylcobalt(III) compounds with alkali and with cyanide ion

L	*B*	*Reagent*	k_1 (s^{-1})	k_2	*T*°	*Ref.*
(a) 5'-Deoxyadenosylcobalt(III) compounds (eqns. 86, 87)						
Cobalamin		1*M* NaOH	5.0×10^{-6}	5.0×10^{-6}	27	104
Cobalamin		0.01*M* NaCN	8.3×10^{-3}	8.3×10^{-1} [a]	27	104
Cobalamin		0.1*M* KCN[c]	8.4×10^{-4}	8.4×10^{-3} [a]	25	199
$(dmgH)_2$ [b]	py	1*M* NaOH	1.6×10^{-3}	1.6×10^{-3}	27	104
$(dmgH)_2$	py	0.01*M* NaCN	2.3×10^{-4}	2.3×10^{-2} [a]	27	104
(b) β-Hydroxyethylcobalt(III) compounds (in aqueous solution[d]?, eqn. 88–90)						
$(dmgH)_2$	H_2O/OH^-			9.6×10^{-3}		104
$(dmgH)_2$	benzimidazole			1.6×10^{-3}		104
$(dmgH)_2$	py			4.3×10^{-2}		104
$(dmgBF_2)_2$	py			2.9×10^{-1}		104
(dotnH)	H_2O/OH^-			1.2×10^{-1}		104
salen	H_2O/OH^-			5.2×10^{-4}		104
Cobinamide	H_2O/OH^-			9.9×10^{-4}		104
Cobalamin				1.5×10^{-4}		104
Cobinamide[e]	py			1.4×10^{-4}		104
Cobinamide[f]	py			8.8×10^{-3}		104
(c) β-Cyanoethylcobalt(III) compounds (in aqueous solution, eqn. 83)						
Cobalamin		pH 10.5	1.4×10^{-3}	3.8		110
Cobalamin		33m*M* KCN	1.15×10^{-3}	3.5[g]		110
Cobalamin		pH 9.89	1.48×10^{-3}	18		192
Cobalamin[h]		pH 9.89	4.0×10^{-4}	5.2		192
(d) α-(2-Pyridyl)ethylcobalt(III) compounds (eqn. 85)						
$(CN)_4$	CN^-	pH 8.7	4.71×10^{-4}	9.4×10^{1}	25	215
$(CN)_4$	CN^-	pH 9.4	1.17×10^{-3}	4.6×10^{1}	25	215
$(CN)_4$	CN^-	pH 10.1	4.8×10^{-3}	4.0×10^{1}	25	215
$(CN)_4$	CN^-	pH 10.7	1.13×10^{-2}	2.3×10^{1}	25	215

[a] Assuming reagent is CN^-.
[b] Probably as conjugate base form, *e.g.* (dmg)(dmgH).
[c] Buffered at pH 10, first stage is rapid coordination of cyanide ion to cobalt.
[d] Not stated; aerobic conditions.
[e] β-Methyl derivative.
[f] β-Hydroxymethyl derivative.
[g] Assuming reagent is OH^-.
[h] β-Methoxycarbonylethylcobalamin.



(86)

(87)

(XIV: X = O, Y = OH, A = adenine)
(XVII: X = CH_2, Y = OH, A = adenine)
(XVIII: X = O, Y = H, A = H)

The reaction of the coenzyme with alkali is probably reversible under anaerobic conditions, because the very similar reaction with the corresponding tetrahydrofurfurylcobalamin (XVIII) has been shown to be so[104]. It is possible therefore that the overall rate of reaction with alkali depends upon the rate at which either the organic product or the cobalt(I) species may be removed from the system, and upon the rate of the reverse reaction as is the case with the elimination from the β-cyanoethylcobalt(III) compounds. For example, this reversal should be prevented under aerobic conditions, owing to the removal of the cobalt(I) species.

The presence of cyanide ion might influence the reaction in a number of ways. First, it might effectively remove the initial organic product of a base-catalysed reaction by formation of the cyanhydrin. Secondly it might react directly with the nucleoside group, thereby assisting in a base-catalysed cleavage. Thirdly, and most likely, it might attack the metal from either above or below the plane of the corrin ring; attack from below is known to occur and results in the formation of the relatively stable species with cyanide ion as the axial base. Attack from above might distort the stabilising ligands and cause cleavage of the carbon–cobalt bond irreversibly, provided this could be assisted by synchronous cleavage of the C(5)–O bond[217,221]. In the latter case, the cyanhydrin formation would be a subsequent reaction which should have no effect on the cleavage rate. Similarly, there is no reason why oxygen should interfere with this reaction as the oxidation state of the cobalt remains high. No effect of oxygen is apparent[87].

The corresponding carbocyclic derivative[218] (XVII), which cannot undergo the corresponding cyanhydrin formation or give the same synchronous C(5′)–O bond cleavage with formation of the anion, is practically inert to cyanide ion and also to borohydride ion[218]. However, a β-oxygen is not the only requirement, for β-alkoxyethyl-cobalamins and -cobaloximes are stable to cyanide ion, as is 6-deoxyglucosylcobalamin[199], except in so far as axial base exchange takes place. Clearly, the aza-acetal or a similar glycosidic arrangement is important. The rate of cyanide cleavage of cobalamins has been studied as a func-

tion of the nucleoside base; the more electron attracting is the base, the slower the decomposition, but the differences in rate are small[199]. The rate is also affected by the axial base; for example, 5′-deoxyadenosylcobinamide is more reactive than 5′-deoxyadenosylcobalamin, which is more reactive than 2′,3′-isopropylidene-5′-deoxyadenosylcobalamin[222].

The β-carboxyethylcobalt(III) compounds are relatively stable to base because ionisation of the carboxyl group reduces the tendency to olefin formation[50]. Similarly, β-methoxyethylcobalt(III) compounds are also stable[33], but the β-hydroxyethylcobalt(III) compounds decompose[33] in alkaline solution by a different mechanism to the corresponding carbonyl compound and cobalt(I) *i.e.*

$$HOCH_2CH_2\text{cobalamin} + OH^- \longrightarrow MeCHO + B_{12S} + H_2O \quad (88)$$

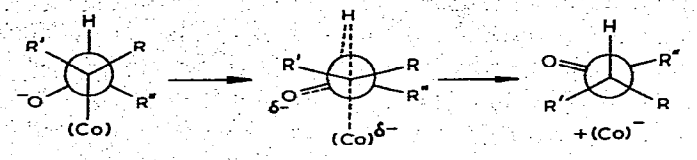
$$MeCH(OH)CH_2Co(dmgH)_2py + OH^- \longrightarrow MeCOMe + [Co(dmgH)_2py]^- + H_2O \quad (89)$$

$$HOCH_2CH(OH)CH_2Co(dmgH)_2py + OH^- \longrightarrow HOCH_2COMe + [Co(dmgH)_2py]^- + H_2O \quad (90)$$

The hydride shift involved in this reaction has been the subject of much interest because of its apparent relation to the diol dehydrase reaction[33,220] described more fully in the final section. That the base-catalysed decomposition of the hydroxyethylcobalt(III) complexes requires the conjugate base of the hydroxyethyl group is apparent because the corresponding alkyl ethers are inert even to 50% NaOH[46]. When there is no β-hydrogen capable of undergoing the shift, as in 2-hydroxy-2-methylpropylcobalt(III) compounds, the reaction with hydroxide ion does not appear to take place.

The kinetics of this reaction, which follow the rate law of eqn. 84, have been studied as a function of the nature of the equatorial ligand, the axial base, and the β-hydroxyethyl substituent. The rate coefficients shown in Table 15 clearly decrease as the nucleophilicity of the displaced cobalt(I) species increases. In accord with this, the displacement of the very reactive Co^{I}(aetpor) species (which cannot be made by borohydride reduction of the Co^{II}(aetpor) species) from β-hydroxyethylCo(aetpor) is very slow in alkaline solution.

The isotope effect ($k_H/k_D = 5.5$; observed with 2-hydroxypropylcobaloxime[2-$^2H_1$] in 2*M* NaOH) is consistent with a concerted mechanism in which a *trans*-β-hydrogen migrates to the α-carbon as the cobalt(I) species departs (eqn. 91). The conformational requirements of this mechanism also support the low rate of reaction of the 2-hydroxycyclohexylcobaloxime. However, the analogy between this mechanism and that of the diol dehydrase reaction has been challenged[11,46,220]. In fact, the surprising thing about this reaction is that apparently no epoxide is formed, whereas the corresponding β-hydroxyethyl halides readily form the epoxide by an intramolecular displacement of the halide ion via attack of the β-oxygen on the α-carbon. These reactions of organocobalt compounds appear to involve attack of the β-hydrogen on the α-carbon, as follows:



(91)

(c) Nucleophilic attack on the organocobalt(III) compound

(i) *Nucleophilic attack at the α-carbon.* In principle, nucleophilic attack at the α-carbon of an organocobalt(III) complex may involve the displacement of cobalt, with its appendant ligands, in the +1 oxidation state (eqn. 92). The conditions for such a reaction are as follows: (*i*) Only a strong nucleophile towards saturated carbon will be effective. (*ii*) The reaction may be reversible, because the displaced cobalt(I) species is known to be an excellent nucleophile.

The reversibility will therefore depend upon the leaving group ability (nucleofugal character)[223] of the cobalt(I) species and the incoming nucleophile, and upon their carbon basicities[224]. It will also depend upon the presence of materials which remove the displaced cobalt(I) species from solution. For example, reactions carried out under aerobic conditions may proceed smoothly, whereas the same reaction carried out under anaerobic conditions may not be apparent.

$$RCH_2CoL_nB + N^- \rightleftharpoons RCH_2N + CoL_nB^- \qquad (92)$$

Though there are a number of reagents of sufficiently great nucleophilicity and carbon basicity to be potentially effective in such a displacement, few have been tried and the results are largely shrouded in ambiguity. One of the reasons for this ambiguity is that some workers have used aerobic conditions for their studies, others have used anaerobic conditions, and sometimes the conditions are not specified. Another reason is that it is not always clear whether the nucleophilic attack occurs at the α-carbon or elsewhere in the molecule. As much of this ambiguity involves the reactions of cyanide (see also previous section) and thiolate ions, these are discussed first.

It has been reported that cyanide does[118] and does not[184] react with methylcobaloxime. For example, no reaction has been observed between methyl cobaloxime (10^{-4} *M*) and sodium cyanide (1*M*), presumably other than coordination of cyanide as the axial base, over 1 hour at 65°. AlkylCo(aetpor) complexes are also reported to be stable to cyanide ion in the absence of oxygen[11]. However, it is well established that cyanide ion causes the decomposition of the coenzyme[217,199], probably via attack at centres other than the α-carbon. Such reactions are also photocatalysed. The existence of the coenzyme was at first concealed by the fact that, *inter alia*, the stable cyanocobalamin (vitamin B_{12}) was readily isolated from the reaction of the coenzyme-containing materials with cyanide ion, and was therefore the first cobalamin to be studied in detail[225].

In contrast to cyanide ion, which is a good nucleophile and a moderately strong proton

base, as well as having a strong affinity for cobalt(III), thiolate ions are better nucleophiles towards saturated carbon, but much poorer bases[102]. The role of thiolate ions in the promotion of base-catalysed reactions is therefore negligible, but their reactions have the additional complication of the possible role of the readily formed thiyl radicals.

It has been reported[82] that several thiolate ions displace cobalt(I) species from methylcobalt(III) compounds, (eqn. 93), but unfortunately no indication has yet been given as to the conditions, including the important question of the presence or absence of oxygen. Some approximate relative rate coefficients have been measured and are shown in Table 16. The order of reaction is not stated, but the rate coefficients presumably refer to second order reactions. More detailed studies of the reaction of methylcobaloxime with thiolate ions under anaerobic conditions[205a] suggest that no carbon–cobalt cleavage occurs.

TABLE 16

Relative rates of reaction of thiolate ions with alkylcobalt(III) complexes

Substrate	*K*(relative)[a]
Mecobalamin	1.0
$MeCo(dmgH)_2py$	4.0×10^{-4}
$MeCo(dmgH)_2PPh_3$	9.1×10^{-3}
$MeCo(dmgBF_2)_2py$	4.0×10^{-1}
$MeCo(salen)\cdot OH_2$	4.5×10^{-2}

[a] Reaction order not specified.

$$RS^- + MeCoL_nB \rightleftharpoons RSMe + [CoL_nB]^- \quad (93)$$

However, other studies on the reaction of thiols with methylcobalamin suggest a more complex behaviour[226]. It has been shown that this reaction is dependent upon the pH, and the concentration of added B_{12r}, but appears to be independent of the thiol concentration. In some cases an induction period is observed and it is confirmed that oxygen is required for reaction to take place, but its role is ascribed to the cobalt catalysed oxidation of thiolate ions to thiyl radicals. The following mechanism has been proposed:

$$RS^{\cdot} + \text{Mecobalamin} \longrightarrow B_{12a} + Me^{\cdot} + RS^- \quad (94)$$

$$RS^- + B_{12a} \longrightarrow B_{12r} + RS^{\cdot} \quad (95)$$

$$RS^{\cdot} + Me^{\cdot} \longrightarrow RSMe \quad (96)$$

However, it is surprising that the methyl radicals generated in such a reaction should react with the thiyl radicals present in low concentration and not with the thiol present in higher concentration, because thiols are known to be excellent radical traps, even in the presence of other radical traps such as chromous ion[227]. If methyl radicals are formed in the

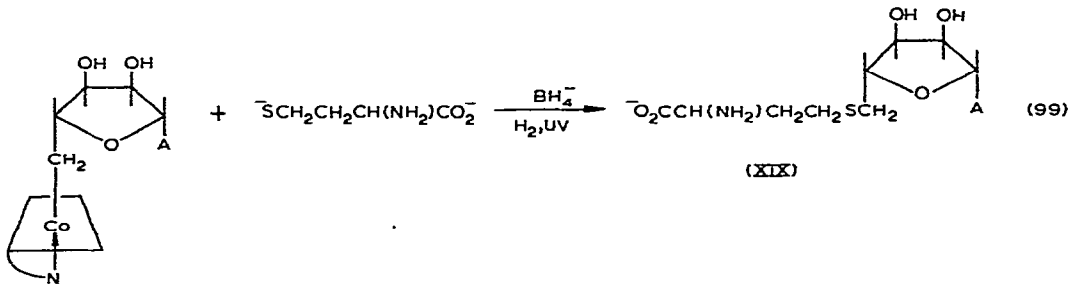
presence of thiols, one would expect to find appreciable quantities of methane and of the dialkyldisulphide, *i.e.*:

$$RSH + Me^{\bullet} \longrightarrow RS^{\bullet} + CH_4 \quad (97)$$

$$2RS^{\bullet} \longrightarrow RSSR \quad (98)$$

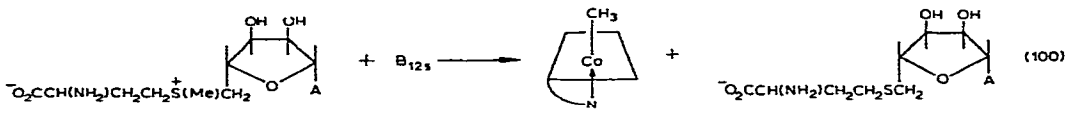
A number of reactions between sulphur amino acids and organo-cobalamins and -cobaloximes are also of interest, because of the role played by methylcobalamin in the biological formation of methionine from homocysteine[228]. Homocysteine itself reacts only very slowly and not very cleanly with methylcobaloxime in the dark[79], but this may in part be because the intramolecular condensation of homocysteine to the thiolactone in neutral and acidic solution reduces the concentration of active reagent. However, in solutions of pH ca. 10, where homocysteine exists largely in the thiolate form, the reaction is much cleaner and methionine can be isolated (~ 8% yield), together with unreacted material[79]. Similarly, methylcobalamin reacts smoothly with homocysteine, but not apparently with cysteine, and the reaction of ethylcobalamin with homocysteine is slow[229]. The transfer of $^{14}CH_3$ to homocysteine from $^{14}CH_3$cobalamin has also been demonstrated[229].

Several of the studies are difficult to interpret because of the conditions used; for example, that between sodium homocysteinate and 5′-deoxyadenosylcobalamin XIV in the presence of sodium borohydride under hydrogen and with ultraviolet irradiation, which is reported[230] to give some *S*-adenosylhomocysteine XIX (eqn. 99).



(XIV: A = adenosine)

The reversibility of such a nucleophilic reaction has not been demonstrated, but the corresponding reaction of the cationic *S*-adenosylmethionine does take place[93] *i.e.*:



A = adenine

The role of the thiolate ion coordinated to the cobalt in these reactions has not been elucidated, but anionic alkylcobalt(III) complexes have been isolated[123] and it would be

expected that these would reduce the nucleofugal character of the cobalt(I) species in a reaction of the type:

$$RS^{-\cdot} + [MeCoL_nSR]^- \longrightarrow RSMe + CoL_nSR^{2-\cdot} \qquad (101)$$

The role of thiolate ions as reducing agents is discussed below.

(ii) *Nucleophilic metal–metal exchanges.* If the nucleophilic displacement of cobalt(I) species by attack of a nucleophile is possible, then it should certainly be observed when the attacking reagent is as nucleophilic and carbon basic as the outgoing cobalt(I) nucleophile. Such a reagent would be a similar cobalt(I) nucleophile or another metallic nucleophile of similar power. It is not surprising therefore to find that the exchange of methyl groups between two similar cobalt(I) species is rapid[223]. For example, the equilibrium involving methylbis(dimethylglyoximato)pyridinecobalt(III) ($RCoL_nB$ in eqn. 102) and the bis(cyclohexanedione dioximato)pyridinecobalt(I) ion ($[CoL'_nB]^-$ in eqn. 102) is effectively complete within five minutes in methanol at 0°, using $10^{-3}M$ reagents.

$$[CoL'_nB]^- + RCoL_nB \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} RCoL'_nB + [CoL_nB]^- \qquad (102)$$

The approximate half-lives for this reaction and for reactions of other alkylcobaloximes (ca. $10^{-3}M$) are shown in Table 17. Since most of these reactions are expected to proceed to an equilibrium mixture containing ca. 50% of each alkylcobaloxime, the use of half-lives is justified, despite the fact that the forward and back reactions are bimolecular.

TABLE 17

Half lives[223] for the exchange of alkyl groups between alkylcobaloximes ($10^{-3}M$) in methanol at 0°

R	$t_{1/2}$
Me	≪5 min
Et	≪5 min
Pr	1h
n-octyl	1h
s-octyl	>10h
s-butyl	>10h
isobutyl	>10h

It is interesting to note that, had the exchange of secondary alkyl groups been rapid, the optically active secondary octylcobaloxime would probably not have been obtained[108], because for each exchange with inversion of configuration at the α-carbon, there is effective racemisation of two molecules of optically active halide[231]. Some decrease in the optical activity of the secondary butylcobaloxime, described earlier (p. 25), has been ascribed to such exchange[109].

These exchange reactions seem to be subject to a very large steric effect, because any exchange of the primary isobutylcobaloxime must be at least 100 times slower than that of the ethylcobaloxime, as is the exchange of the secondary alkylcobaloximes. Such steric hindrance would be expected when both incoming and outgoing nucleophiles are very large in a transition state that requires the alkyl group to be sandwiched between them, (*i.e.* XX). Branching at either the α- or the β-carbon appears to be sufficient to prevent the ready attainment of this configuration.

The rapid exchange of methyl groups between two cobalt(I) species is of considerable interest in consideration of the role of biological methylation[232,233] for it implies, contrary to previous belief[82], that a methyl group might be readily transferred from methylcobalamin to a cobalt(I)-enzyme system without the need for intermediate transferring agents such as thiols.

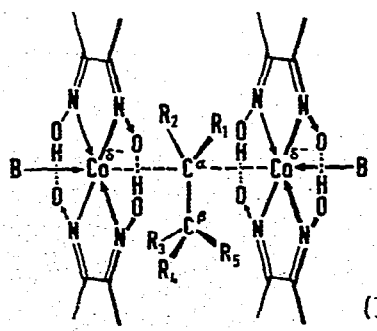
Other nucleophilic reactions of metal ions at the α-carbon include the displacement of cobalt(I) by rhodium(I) (eqn. 103), which tends to produce mainly the alkylrhodium(III) species, and the S_N2 displacement of cobalt(I) from the α-carbon of allylic systems (eqn. 104)[73]. In contrast, S_N2' displacement of cobalt(I) by cobalt(I) has been observed for the related propynyl cobaloxime (eqn. 105)[40,73].

$$[Rh(c\text{-}hgH)_2py]^- + MeCo(dmgH)_2py \rightleftharpoons MeRh(c\text{-}hgH)_2py + [Co(dmgH)_2py] \quad (103)$$

$$MeCH{=}CHCH_2Co(dmgH)_2py + [Co(c\text{-}hgH)_2py]^- \rightleftharpoons MeCH{=}CHCH_2Co(c\text{-}hgH)_2py + [Co(dmgH)_2py]^- \quad (104)$$

$$HC{\equiv}CCH_2Co(dmgH)_2py + [Co(c\text{-}hgH)_2py]^- \rightleftharpoons H_2C{=}C{=}CHCo(c\text{-}hgH)_2py + [Co(dmgH)_2py]^- \quad (105)$$

Both alkoxide and hydroxide ion might be expected to displace halide ion from α-haloalkylcobaloximes. However, though halide ion is displaced when the mono-chloro-, -bromo-, or -iodo-methylcobaloxime reacts with methoxide ion under anaerobic conditions, this is not a direct displacement by the methoxide ion[21]. Instead, it is believed that the methoxide ion first displaces the cobalt(I) species with the formation of the α-halomethylether which is itself very susceptible to nucleophilic attack. Consequently, the cobalt(I) species



(XX)

then displaces the halide ion from the halomethyl ether with the formation of the α-methoxymethylcobaloxime. Some acetal $(MeO)_2CH_2$ might also be expected in the presence of an excess of methoxide ion.

$$MeO^- + XCH_2Co(dmgH)_2py \longrightarrow MeOCH_2X + Co(dmgH)_2py^- \quad (106)$$

$$Co(dmgH)_2py^- + MeOCH_2X \longrightarrow MeOCH_2Co(dmgH)_2py + X^- \quad (107)$$

A similar initial reaction is believed to take place with hydroxide ion, but the subsequent reactions are more complicated and the final products include methanol, methane, and formaldehyde[21]. Dihalomethylcobaloximes[21] do not give isolable organometallic products with hydroxide ion, and generally lead to the carbonyl complex of the cobalt(I) species, under anaerobic conditions. The trihalomethylcobaloximes (halogen = Cl,Br,I) are very reactive in alkali, but trifluoromethylcobaloxime[21] is less reactive. For example, trichloromethylcobaloxime with methoxide ion gives methoxycarbonylcobaloxime in 25% yield.

(iii) *Displacement of cobalt(I) from acyl carbon.* Cobalt(I) species are themselves largely inert as nucleophiles towards carbonyl carbon and are consequently very readily displaced from acylcobalt(III) compounds by attack of other nucleophiles on the carbonyl-carbon[97]. Ammonia and hydroxylamine are sufficiently nucleophilic to displace B_{12s} from acylcobalamins to give the corresponding amide and hydroxamic acid, respectively.

$$YCH_2CO\,\text{cobalamin} + H_2NX \longrightarrow YCH_2CONHX + B_{12s} \quad (108)$$

(Y = H, NH_2, $NHCOCH_3$; X = H, OH)

(iv) *Displacement of cobalt(I) from unsaturated carbon.* Nucleophilic displacements at vinylic carbon are not common, but there is some evidence that methyllithium may attack both the α-carbon and the metal of styrylcobaloximes. Whereas methyllithium is reported to be inert towards alkylcobaloximes, *cis*-β-styrylcobaloxime reacts with methyllithium in ethereal solution to give, after further treatment with water, a mixture of *cis*-phenylpropene, styrene, unreacted styrylcobaloxime, and methylcobaloxime[208]. The stereospecificity of the phenylpropene formation suggests a nucleophilic attack of the methyllithium at the α-carbon with retention of configuration (see p. 27), and the methylcobaloxime formation suggests an attack of the methyllithium at the metal with formation of the styryl anion which, on treatment with water, gives the observed styrene.

$$cis\text{-}PhCH{=}CHCo(dmgH)_2py + MeLi \longrightarrow cis\text{-}PhCH{=}CHMe + Li^+Co(dmgH)_2py^- \quad (109)$$

$$cis\text{-}PhCH{=}CHCo(dmgH)_2py + MeLi \longrightarrow MeCo(dmgH)_2py + cis\text{-}PhCH{=}CH^-Li^+ \quad (110)$$

(v) *Reaction of nucleophiles on organic groups without carbon–cobalt bond cleavage.* Few hydrolyses of functional groups on the organic ligand have been carried out under basic conditions, because of the alternative base-catalysed reactions that may occur. Ex-

ceptions include the alkaline hydrolyses of the acetyl groups of for example 2′, 3′-di-*O*-acetyl-5′-deoxyadenosylcobalamin in a synthesis of the coenzyme[27].

(d) Nucleophiles as reducing agents

Several potentially nucleophilic species are also capable of behaving as reducing agents. The most common such reagent is borohydride ion, less common are thiols and dithiols. However, the mechanism of these reactions have not been ascertained except in a few cases, and may involve attack on either the metal or the organic group, but it is not known in all cases whether the cobalt(I) species observed in the products are formed by direct displacement or by subsequent reduction of other inorganic cobalt species.

Allenylcobaloximes are reduced by borohydride ion to allene and cobalt(I) species[234] and the latter will react with added organic halide to regenerate more allenylcobaloxime (eqn. 111). In contrast, when the reduction of haloalkylcobaloximes is carried out in the presence of benzyl chloride, no benzyl cobaloxime is formed[32]. The transient green colour apparent during this reaction is therefore ascribed to the presence of the reduced substrate in which the carbon–cobalt bond remains intact, rather than to displaced cobalt(I) species (eqn. 112). The loss of halide ion from such reduced haloalkylcobaloximes would then give novel nucleophilic carbene complexes that would be readily protonated by the protic solvent to give the observed product, the corresponding alkylcobaloxime (eqn. 113 and 114). Similarly, the reduction of $Cl_2CDCo(dmgH)_2py$ with borohydride ion in the presence of methyl iodide gives only $CDH_2Co(dmgH)_2py$.

$$R_2C{=}C{=}CHCo(dmgH)_2py + BH_4^- \longrightarrow R_2C{=}C{=}CH_2 + [Co(dmgH)_2py]^- \quad (111)$$

$(R_2 = H_2 \text{ or } (CH_2)_5)$

$$RCHXCo(dmgH)_2py + BH_4^- \longrightarrow [RCHXCo(dmgH)_2py]^{2-} \quad (112)$$

$(X = Cl, Br)$

$$RCHXCo(dmgH)_2py^{2-} \longrightarrow X^- + [RCHCo(dmgH)_2py]^- \quad (113)$$

$$RCHCo(dmgH)_2py^- + R'OH \longrightarrow RCH_2Co(dmgH)_2py + R'O^- \quad (114)$$

The absence of direct attack on the α-carbon is apparent from the reactions of α-halocobaloximes with sodium borodeuteride and sodium borohydride in methanol and *O*-^{2}H-methanol respectively, *i.e.*:

$$RCHXCo(dmgH)_2py \xrightarrow[MeOH]{BD_4^-} RCH_2Co(dmgH)_2py \quad (115)$$

$$RCHXCo(dmgH)_2py \xrightarrow[MeOD]{BH_4^-} RCHDCo(dmgH)_2py \quad (116)$$

The stepwise reduction of dihaloalkylcobaloximes has also been demonstrated (eqn. 117).

$$X_2CHCo(dmgH)_2py \xrightarrow{BH_4^-} XCH_2Co(dmgH)_2py \xrightarrow{BH_4^-} CH_3Co(dmgH)_2py \qquad (117)$$

Some organocobalt(III) compounds are also rapidly and quantitatively reduced by thiols to the corresponding hydrocarbon[79]. It has been suggested that the reaction involves carbanion formation following nucleophilic attack of thiolate ion on the metal, but the reactivity order: $ROCOCHMe(Co) > ROCOCH_2CH_2(Co) > NCCHMe(Co) > NCCH_2CH_2(Co)$ suggests that free carbanions are not formed. It seems more likely that the reduction of the alkylcobalt(III) compound greatly increases the tendency for electrophilic attack by the protic solvent on the α-carbon. Evidence in support of this mechanism comes from the reaction of methylcobalt(III) compounds with dithioerythritol[82], which yields the intramolecular disulphide and the alkane, *i.e.*:

$$Me(Co)B + {}^{-}S\ SH \rightleftharpoons Me(Co)\text{–}S^{-}\ SH + B \qquad (118)$$

$$Me(Co)\text{–}S^{-}\ SH \rightleftharpoons Me(Co)S^{-}\ S^{-} + H^{+} \qquad (119)$$

$$Me(Co)\text{–}S^{-}\ S^{-} + ROH \longrightarrow CH_4 + (Co)^{-} + S\text{—}S + OR^{-} \qquad (120)$$

alternatively,

$$Me(Co)\text{–}S^{-}\ S^{-} \longrightarrow Me(Co)^{2-} + S\text{—}S \qquad (121)$$

$$Me(Co)^{2-} + HOR \longrightarrow CH_4 + (Co)^{-} + OR^{-} \qquad (122)$$

(II) Reaction with acids and other electrophilic reagents

(a) Protonation of axial and equatorial ligands

The protonation of axial ligands, either after their dissociation from the cobalt, or whilst still attached to cobalt, has been discussed above (p. 50). Protonation of equatorial ligands has also been observed and, in some cases, this may have an even greater influence on the reactions than the removal of the axial ligand. The various types of equatorial ligand protonation are discussed below.

(i) *Protonation of the corrin ring of alkylcobalamins.* The methine bridge proton on C(10) of the corrin ring is readily identifiable from the ^1H NMR spectrum. Acid-catalysed exchange of this proton for deuterium has been measured[144] in several cases; the rate in-

creases in the order: Methylcobalamin ($t_{1/2}$ 5 min in solutions of pD 1.5) < methylcobinamide ($t_{1/2}$ 10 min at pD 1.66) ~ ethylcobalamin ($t_{1/2}$ large at pD 6.0, small at pD 1.5) < ethylcobinamide ($t_{1/2}$ 30 min at pD 5.7).

(ii) *Protonation of dioximato ligands.* The protonation of dimethylglyoximato ligands of the alkylcobaloximes has a marked influence on the reactivity at the carbon—cobalt bond. Spectroscopic studies on the equilibria in perchloric acid at 21° (μ = 1.0 and μ = 0.5) show that the pK_a for the monoconjugate acid (eqn. 123) is only slightly sensitive to the character of the organic group[200] (Table 18). The addition of the second proton takes place at a much higher acidity, *e.g.* in solutions of ca. 30% sulphuric acid for benzylcobaloxime[235].

$$RCo(dmgH)_2aq + H_3O^+ \overset{K_{a(1)}}{\rightleftharpoons} \underset{(XXI)}{RCo(dmgH)(dmgH_2)aq^+} + H_2O \quad (123)$$

$$RCo(dmgH)(dmgH_2)aq^+ + H_3O^+ \overset{K_{a(2)}}{\rightleftharpoons} \underset{(XXII)}{RCo(dmgH_2)_2aq^{2+}} + H_2O \quad (124)$$

As mentioned earlier (p. 36) the protonation has a marked effect on the ^1H NMR spectrum and also on the rates of reaction at the α-carbon described below and on p. 82. It also has an appreciable effect on the stability of various alkylcobaloximes. For example, methylcobaloxime is stable for many months in concentrated sulphuric acid, secondary alkylcobaloximes show signs of decomposition after several days and decomposition of benzylcobaloxime is evident almost immediately.

The kinetics of the aerobic decomposition of benzylcobaloxime have been studied as a function of the sulphuric acid concentration[235]. The rate of decomposition increases linearly with acid concentration in solutions of up to ca. 15% sulphuric acid, thereafter, the increase tails off and there is no significant increase in rate between 40 and 80% sulphuric acid. The decomposition products change gradually over the same range, being mainly the *O*-benzylether of dimethylglyoxime and its acid hydrolysis product the *O*-benzylether of diacetylmonoxime, together with benzyl alcohol in the lower acid range, and changing to dibenzyl as the acid concentration increases.

This has been ascribed to the change from the decomposition of the monoprotonated species (XXI) to that of the diprotonated species (XXII) as the acidity increases. The latter certainly decomposes predominantly by a homolytic process, and this gives mostly dibenzyl. Little benzaldehyde is formed, even in dilute solutions of the complex from which the air has not been excluded.

The monoprotonated complex (XXIII) may also partly decompose homolytically, but the main mode of reaction would appear to involve a nucleophilic attack of solvent water (eqn. 125), of other anions present in solution (eqn. 126), or of the remaining glyoximinato ligand (eqn. 127), to give benzyl alcohol, a benzyl derivative, or the benzyl ether (XXIV), respectively.

TABLE 18

Formation constants[a] for protonation of some alkyl- and aryl-aquobis(dimethylglyoximato)cobalt(III) compounds

R	*Me*	*Et*	*n-Pr*	*i-Pr*	$ClCH_2$	$PhCH_2$	$4\text{-}O_2NC_6H_4CH_2$	$4\text{-}MeOC_6H_4CH_2$	*Ph*	$4\text{-}MeOC_6H_4$	$4\text{-}MeC_6H_4$
K_1	3.5[c]	3.9[b]	4.7[b]	4.0[c]	1.0[c]	2.4[b] (3.5[c])[d]	1.1[b]	2.6[b]	1.0[b]	2.4[b]	0.8[b]
Ref.	200 235a	235a	235a	200	200	235a 235	235a	235a	235a	235a	235a

[a] Eqn. 123; other examples in references.
[b] $\mu = 1.0$.
[c] $\mu = 0.5$.
[d] K_2 (eqn. 124)[c] $= 1.4 \times 10^{-3}$ (ref. 235).

$$PhCH_2Co(dmgH)(dmgH_2)aq^+ + H_2O \longrightarrow PhCH_2OH + Co(dmgH)(dmgH_2)aq + H^+ \quad (125)$$
(XXIII)

$$PhCH_2Co(dmgH)(dmgH_2)aq^+ + X^- \longrightarrow PhCH_2X + Co(dmgH)(dmgH_2) \quad (126)$$

$$PhCH_2.Co(dmgH)(dmgH_2)aq^+ \xrightarrow{H^+} PhCH_2ON{=}CMeCMe{=}NOH + Co^{2+} + dmgH_2 \quad (127)$$
(XXIV)

(ii) *Protonation of cyanide ligands; cyanide insertion reactions.* The majority of alkyl-, aryl-, benzyl-, and vinyl-pentacyanocobaltate(III) ions undergo reversible protonation of one or more of the cyanide ligands in concentrated mineral acid. For example, the pK_a's of the conjugate acids, 2-,3-, and 4-$HpyCH_2Co(CN)_4(CNH)^{2-}$ are −1.2, −1.1, and −1.6, respectively[45]. Such protonation may merely assist in the removal of a cyanide ligand to give the tetracyano species, or it may promote a more interesting and complex intramolecular migration.

Thus the protonation of one of the cyanide ligands (presumably but not necessarily one of the equatorial cyanide ligands) also promotes a migration of the organic group from the cobalt to the carbon on one of the cyanide ligands with the formation of the green 'insertion' product XXV (eqn. 128)[45,114,238].

$$RCH_2Co(CN)_4CNH^{2-} \longrightarrow RCH_2C(=NH)Co(CN)_4^{2-}aq \quad (128)$$
(XXV)

At low acidities in which the pentacyano species predominates, the rate of this reaction increases linearly with the acidity[45], but reaches an upper limit at high acidity (ca. $H_0 = -8$), corresponding to an acid-catalysed rearrangement of the pentacyano complex or a unimolecular rearrangement of the protonated complex. It is not known whether it is the protonated cyanide which is involved or whether an unprotonated cyanide is involved, which is later protonated; probably the former. Such a migration is analogous to the more familiar carbonyl-insertion reaction of organometal carbonyl compounds, in which the organic group migrates to the carbon of one of the carbonyl ligands. Indeed, the similarity of mechanism is to be expected as CNH is isoelectronic with C=O[239].

If the green cyanide insertion product XXV is kept in acidic solution, then hydrolysis to the corresponding substituted acetic acid takes place (eqn. 129), but if the fresh solution of the insertion product is basified, a reductive elimination reaction (eqn. 130) takes place to give the corresponding substituted acetonitrile; the fate of the displaced cobalt(I) species has not been investigated.

$$RCH_2C(=NH)Co(CN)_4^{2-} \xrightarrow{H_2O} RCH_2CO_2H + Co(CN)_4^{3-} + NH_4^+ \quad (129)$$

$$RCH_2C(=NH)Co(CN)_4^{2-} \xrightarrow{OH^-} RCH_2CN + Co(CN)_4^{3-} \quad (130)$$

In solutions of low acidity, where the cyanide insertion reaction is slow, an alternative decomposition may intrude, in which loss of a cyanide ligand gives the tetracyano-aquo complex XXVI which undergoes further decomposition, probably via homolysis of the carbon–cobalt bond. This reaction may be suppressed by the addition of an excess of HCN[209].

$$\underset{\text{(XXVI)}}{RCH_2Co(CN)_4aq} \longrightarrow RCH_2^{\cdot} + {}^{\cdot}Co(CN)_4^{2-} \qquad (131)$$

These reactions are not apparent with the allylcobalt complexes, because of the alternative π-allyltetracyanocobaltate(III) ion formation (p. 47) and/or decomposition according to eqn. 136.

(b) Protonation of the organic group

Protonation of the organic group may lead to a number of interesting reactions in which the carbon–cobalt bond is broken.

In common with a great many σ-bonded organotransition metal compounds, there is little evidence of direct attack of the proton on the α-carbon of the organic ligand in mineral acid solution[236]. An exception might be the formation of methane from the reaction of $Me_2Co(dotnH)$ in aqueous acid[237].

(i) *Acid-catalysed cleavage and solvolysis of β-hydroxy-, β-alkoxy-, and β-acetoxy-ethylcobalt(III) complexes.* Reaction of β-hydroxy-, β-acetoxy-, or β-alkoxy-ethylcobalt(III) complexes with mineral acid leads to the formation of ethylene, or a substituted ethylene and an inorganic cobalt(III) complex. Two distinct mechanisms have been postulated for this reaction: (a) protonation of the β-oxygen followed by a one step reaction[33] in which there is synchronous cleavage of the carbon–oxygen and carbon–cobalt bonds (eqn. 132); and (b) protonation of the β-oxygen followed by a two step reaction[240] in which the carbon–oxygen bond cleavage precedes the carbon–cobalt bond cleavage (eqn. 133). Both mechanisms may well occur, for there are few kinetic studies on the reaction, which has been observed with β-substituted ethyl-cobaloximes[33,240], -cobalamins[33,192] and -pentacyanocobaltates[114,51]. However, there seems little doubt that the second (two step) mechanism operates with the cobaloximes[240].

$$\overset{+}{R}O(H)CH_2CH_2(Co) \longrightarrow ROH + CH_2{=}CH_2 + (Co)^+ \qquad (132)$$

$$\overset{+}{R}O(H)CH_2CH_2(Co) \rightleftharpoons ROH + \underset{\text{(XXVII)}}{{}^+CH_2CH_2(Co)} \longrightarrow CH_2{=}CH_2 + (Co)^+ \qquad (133)$$

For example, the methanolysis, ethanolysis, and hydrolysis of β-acetoxyethylpyridinecobaloximes give good yields of the corresponding β-methoxy-, β-ethoxy-, and β-hydroxycobaloximes. The kinetics of these reactions (Table 19) are comparable with those of other

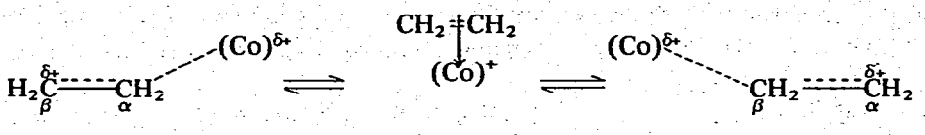
TABLE 19

Kinetics[a] of reaction of organocobalt(III) compounds in neutral and acidic solution

R	*B*	*pH*	*solvent*	10^5k^a	*Temperature*	*Ref.*
(a) Cobaloximes						
$PhCH_2$	aq	−0.9[b]	H_2O	0.6	25	235
$PhCH_2$	aq	−1.95[b]	H_2O	1.8	25	235
$PhCH_2$	aq	−2.9[b]	H_2O	3.0	25	235
$PhCH_2$	aq	−3.9[b]	H_2O	5.5	25	235
$PhCH_2$	aq	−5.1[b]	H_2O	6.8	25	235
$PhCH_2$	aq	−7.6[b]	H_2O	7.1	25	235
$PhCH_2$	aq	−8.8[b]	H_2O	7.5	25	235
$AcO.CH_2CH_2$	py	*c,e*	EtOH	0.44	25	240
5′-Deoxyadenosyl	py	O[d]	H_2O	220	27	104
(b) Cobamides						
5′-Deoxyadenosyl-cobalamin		O[d]	H_2O	7.4	27	104
(c) Pentacyanocobaltates						
$3H\overset{+}{p}yCH_2$		−3.1[f,g]	H_2O	550	40	45
$3H\overset{+}{p}yCH_2$		−2.5[f]	H_2O	520	40	45
$3H\overset{+}{p}yCH_2$		−2.0[f]	H_2O	500	40	45
$3H\overset{+}{p}yCH_2$		−1.5[f]	H_2O	330	40	45
$3H\overset{+}{p}yCH_2$		−1.0[f]	H_2O	270	40	45
$3H\overset{+}{p}yCH_2$		−0.71[f]	H_2O	190	40	45
$3H\overset{+}{p}yCH_2$		−0.14[f]	H_2O	89	40	45
$4H\overset{+}{p}yCH_2$		−3.1[f]	H_2O	140	40	209
$2H\overset{+}{p}yCH_2$		−3.1[f]	H_2O	15	40	45
$2H\overset{+}{p}yCHMe$		−3.1[f]	H_2O	42	25	114

[a] First order rate coefficients (s^{-1}), further examples in references.
[b] $-H_0$, H_2SO_4.
[c] In neutral ethanol.
[d] 1*M* H^+.
[e] $\Delta H^\ddagger = 19.9 \pm$ kcal/mol, $\Delta S^\ddagger = -18.2 \pm 4$ e.u.
[f] $-H_-$, $HClO_4$.
[g] $\Delta H^\ddagger = 20.6 \pm 1.2$ kcal/mol, $\Delta S^\ddagger = -3 \pm 4$ e.u.

solvolytically active acetates. The exact nature of the intermediates is uncertain, and the reaction may involve the formation of a transient π-complex XXVIIa and/or a cation stabilised through σ–π-conjugation or vertical stabilisation[210] (see p. 52) as in XXVIIb and XXVIIc.



(XXVIIb) (XXVIIa) (XXVIIc)

That free olefin and inorganic cobalt(III) species are not intermediates is apparent from the ethanolysis of β-acetoxyethyl(pyridine)cobaloxime in the presence of propylene and the ethanolysis of β-acetoxypropyl(pyridine)cobaloxime in the presence of ethylene, which give no crossed products. Nor does α- or β-proton exchange take place with the solvent when β-acetoxyethyl(pyridine)cobaloxime is solvolysed in $^2H_4$-methanol[240]. The formation of equal amounts of $pyCo(dmgH)_2CH_2CD_2OMe$ and $pyCo(dmgH)_2CD_2CH_2OMe$ in the methanolysis of $pyCo(dmgH)_2CH_2CD_2OAc$ does suggest that a symmetrical intermediate is formed at some stage of the reaction (*e.g.*, XXVIIa), and the retention of configuration observed in the benzylolysis of chiral [(+)-(*S*)]-β-methyl-β-acetoxy-ethyl(pyridine)-cobaloxime shows that the configuration of the β-carbon is held in the cationic intermediate[240a].

The nature of the axial base can have a profound effect on the solvolysis products. For example, the ethanolysis of β-acetoxyethyl(triphenylphosphine)cobaloxime gives a high yield of ethylene. Few kinetic studies have been carried out, but the formation of ethylene is reported to be faster in HCN than in $HClO_4$ and H_2SO_4[33]. The presence of a strongly coordinating ligand like cyanide ion would be expected to increase the electron donating character of the group $-CH_2Co(dmgH)_2B$ thereby stabilising the cationic intermediate XXVII, and it may also increase the electrofugal character of the group $-Co(dmgH)_2B$ thereby aiding the formation of ethylene.

In an interesting variation of these solvolyses, the acid-catalysed decomposition of 4-hydroxy-2-butenylpentacyanocobaltate gives butadiene[51], *i.e.*,

$$HOCH_2CH{=}CHCH_2Co(CN)_5^{3-} \xrightarrow{H^+} H_2O + CH_2{=}CHCH{=}CH_2 + Co(CN)_5^{2-} \qquad (134)$$

(ii) *Acid-catalysed cleavage of unsaturated ligands.* Similar cleavage of the carbon–cobalt bond also occurs on protonation of unsaturated organic ligands, *i.e.*,

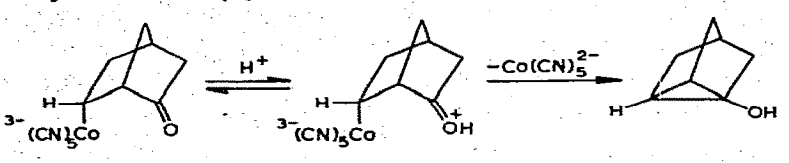
$$RCOCH_2Co(CN)_5^{3-} \overset{H^+}{\rightleftharpoons} R\overset{+}{C}(OH)CH_2Co(CN)_5^{3-} \longrightarrow RC(OH){=}CH_2 + Co(CN)_5^{2-} \quad (135)^{20}$$

$$MeCH{=}CHCH_2(Co) \overset{H^+}{\rightleftharpoons} MeCH_2\overset{+}{C}HCH_2(Co) \longrightarrow MeCH_2CH{=}CH_2 + (Co)^+ \qquad (136)$$

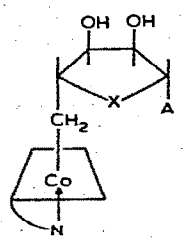
$(Co) = Co(dmgH)_2py$[33] or $Co(CN)_5^{3-}$ [20]

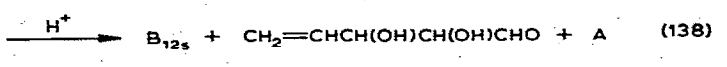
In the reaction shown in eqn. 135, the first formed enol rearranges to the corresponding ketone. In the reaction shown in eqn. 136, only 1-butene is formed in each case. It is possible that this is also a result of the preferential $\sigma-\pi$-conjugation of the β-carbon by the group $-CH_2(Co)$. An interesting variation of these reactions occurs with the *endo*-pentacyanocobaltate(III) ion XXVIII, which undergoes an intramolecular cyclisation reaction (eqn. 137). In contrast, the *exo*-isomer undergoes the normal cyanide 'insertion' reaction[51].

(iii) *Acid-catalysed cleavage of the coenzyme and its analogues.* As the coenzyme (XIV) also contains an oxygen on the β-carbon, it is not surprising that an acid-catalysed elimination reaction takes place[192,217,241]. The products of this reaction are B_{12s}, adenine, and *erythro*-2,3-dihydroxy-4-pentenal XXIX (eq. 138). The rate of this reaction (k_1 = 7.4×10^{-5} s^{-1} at 27° in 1*M* HCl) is less than that for the corresponding 5′-deoxyadenosylcobaloxime ($k_1 = 2.2 \times 10^{-3}$ s^{-1})[104].



(XXVIII)





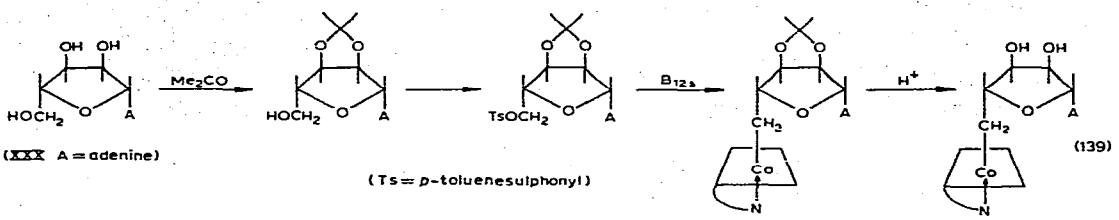
(XXIX)

XIV: X = O, A = Adenine
XVII: X = CH_2, A = Adenine

It is not surprising that this reaction also involves loss of activity as a cofactor, but it is interesting that the corresponding carbocyclic derivative (XVII; X = CH_2) also loses its activity as a cofactor in the dioldehydrase reaction (see pp. 98–103) at about the same rate as the coenzyme in acidic solution[218]. It is possible that one or both of these reactions involve attack of acid on the adenine residue.

(iv) *Hydrolysis of organic functional groups.* In view of the ready loss of the olefin from β-alkoxycarbonylethylcobalt(III) complexes in basic solution, it is more usual to carry out the hydrolysis of such esters in acidic solution. For example, both α- and β-carboxyethylcobalt(III) complexes are best prepared via their esters[39], because of difficulties encountered in their direct formation from cobalt species and organic compounds. One of the successful methods used in the synthesis of the coenzyme from

cobalt corrinoids and the nucleoside XXX has involved (i) protection of the 2′- and 3′-hydroxy groups by formation of the 2′,3′-isopropylidene derivative of the nucleoside (eq. 139); (ii) formation of the 5′-*O*-*p*-toluenesulphonyl derivative; (iii) displacement of the tosylate group by B_{12s}; and (iv) acid hydrolysis of the isopropylidene group[27,28,31,64,124]. One disadvantage of this method is that some cleavage of cobalamin amide groups may also occur. Alternatively, the 2′- and 3′-hydroxy groups have been protected by phenylboronic acid[242,243]. The formylmethylcobaloxime may also be prepared by acid hydrolysis of the dimethyl acetal[39].



(139)

The hydrolysis of the α-methoxycarbonylalkylcobaloximes is of interest not only because it is reported that the alkaline hydrolysis does not take place[39], but also because hydrolysis can be achieved by dissolving the ester in sulphuric acid and pouring the solution into water. This method of hydrolysis is reminiscent of the hydrolysis of highly hindered esters of mesitoic acid[244], and may therefore involve the corresponding acyl cation (eq. 140) which may also be stabilised through σ—π-conjugation with the group $-CH_2\,Co(dmgH)_2\,B$.

(140)

$$EtOCOCH_2\,Co(dmgH)_2\,B \underset{OEt^-}{\overset{H^+}{\rightleftharpoons}} O{=}C^+CH_2\,Co(dmgH)_2\,B \xrightarrow[-H^+]{H_2O} HOCOCH_2{\cdot}Co(dmgH)_2B$$

$$O{=}C^+CH_2Co(dmgH)_2B \xrightarrow{H_2O} HOCOCH_2Co(dmgH)_2B + H^+ \qquad (141)$$

(c) Reaction with metallic electrophiles

In contrast to the reactions of the mineral acids, metallic electrophiles are much more prone to attack the α-carbon. In many cases this results in a clean displacement of the cobalt in the (+3) oxidation state, but in a few cases there are complications due to the attack of the electrophile at other sites in the molecule.

(i) *Mercury (II) reagents.* Mercury(II) species are particularly effective reagents for the displacement of cobalt by attack at the α-carbon. The first demonstration[19] of this reaction involved the formation of methylchloromercury(II) from the reaction of mercury (II) chloride with the methylpentacyanocobaltate(III) ion (eq. 142; R = Me). Subsequently it was shown that, though mercury(II) chloride and the trichloromercurate(II) ion preferred to attack the α-carbon of the pyridiniomethylpentacyanocobaltate(III) ion (eq. 142; $R = H\overset{+}{p}yCH_2$), the attack of the chloromercury(II) cation, $HgCl^+$, took place main-

ly at a coordinated cyanide[198] with the formation of the relatively unreactive pyridinio-methyltetracyanoaquocobaltate(III) ion (eq. 143).

$$RCo(CN)_5^{3-} + HgCl_2 \longrightarrow RHgCl + Cl^- + Co(CN)_5^{2-} \quad (142)$$

$$\overset{+}{H}pyCH_2Co(CN)_5^{3-} + HgCl^+ \xrightarrow{aq} \overset{+}{H}pyCH_2Co(CN)_4\,aq^{2-} + HgClCN \quad (143)$$

Similar displacements by the more reactive mercury(II) species such as Hg^{2+} take place at the α-carbon of the alkyl- and aryl-cobaloximes in aqueous solution[200,203,235,235a]. These reactions are sensitive to the concentration of acid present because the conjugate acid of the cobaloxime, in which one of the dimethylglyoximinato ligands is protonated, is appreciably less reactive than the cobaloxime itself[200]. In that region of acidity where the unprotonated cobaloxime is the reactive species, the following rate law is obeyed:

$$d[RHg^+]/dt = k[RCo(dmgH)_2aq]\,[Hg^{2+}]/(1 + [H^+]/K) \quad (144)$$

where K is the dissociation constant of the conjugate acid of the cobaloxime and k is the second order rate coefficient for the reaction of the organocobaloxime with Hg^{2+}.

Some values of the rate coefficients are shown in Table 20. These results show that the displacement is generally slower with the aquo complexes than with those having more basic axial bases. For example, methylcobalamin is more reactive than methylcobinamide [202,203] towards mercury(II) acetate, and methylbis(dimethylglyoximinato)imidazole-cobalt(III) is more reactive than methylaquobis(dimethylglyoximinato)cobalt(III)[245] towards Hg^{2+}. With the higher alkylcobalamins, the mercury(II) species may remove the axial base at a rate comparable with the carbon–cobalt bond cleavage[203].

The very moderate accelerating effect of electron-donating substituents on the organic ligand on the bimolecular displacement is apparent from the rates of reaction of 4-substituted benzyl- and phenyl-cobaloximes with Hg^{2+}. The rate of displacement at the aryl carbon is not only faster than at benzylic carbon, but is also more sensitive to the character of the 4-substituent[235a].

Though mercury(I) ions also appear to react with alkylcobaloximes, comparison of the rate coefficients for this reaction with those for the mercury(II) reactions show that it is probably the small proportion of mercury(II), in equilibrium with the mercury(I), which is the reactive species[246].

$$Hg_2^{2+} \rightleftharpoons Hg^{2+} + Hg^0 \quad (145)$$

The reactions with mercury species have assumed much importance in recent years because of the potential role of methylcobalamin in the formation of methylmercury(II) compounds which have been found in high concentrations in certain fish. These fish have been found in particular bays off the coasts of Japan and Scandinavia, and in the Great

TABLE 20

Kinetics of reaction of metallic electrophiles with organocobalt(III) compounds

R	L_n	*B*	*Reagent*	k_2^a	*T*	*Solvent*	*Ref.*
Me	$(dmgH)_2$	aq	Hg^{2+}	65	25	water [b]	200
Me	$(dmgH)_2$	aq	Hg^{2+}	54	25	water [b]	235a
Et	$(dmgH)_2$	aq	Hg^{2+}	0.12	25	water [b]	200, 235a
n-Pr	$(dmgH)_2$	aq	Hg^{2+}	0.09	25	water	200, 235a
i-Pr	$(dmgH)_2$	aq	Hg^{2+}	$\leqslant 7 \times 10^{-6}$	25	water	200
i-Bu	$(dmgH)_2$	aq	Hg^{2+}	0.36	25	water	200
$PhCH_2$	$(dmgH)_2$	aq	Hg^{2+}	7.5×10^{-2}	25	water [b,c]	235a, 235
$4\text{-}O_2NC_6H_4CH_2$	$(dmgH)_2$	aq	Hg^{2+}	6.5×10^{-3}	25	water [b]	235a
$4\text{-}FC_6H_4CH_2$	$(dmgH)_2$	aq	Hg^{2+}	2.8×10^{-2}	25	water [c,b]	235a, 235
$4\text{-}MeOC_6H_4CH_2$	$(dmgH)_2$	aq	Hg^{2+}	11.3×10^{-2}	25	water [b]	235a
$4\text{-}FC_6H_4$	$(dmgH)_2$	aq	Hg^{2+}	2.5×10^{2}	25	water [b]	235a
$4\text{-}MeC_6H_4$	$(dmgH)_2$	aq	Hg^{2+}	4.5×10^{3}	25	water [b]	235a
$4\text{-}MeOC_6H_4$	$(dmgH)_2$	aq	Hg^{2+}	3.0×10^{4}	25	water [b]	235a
C_6H_5	$(dmgH)_2$	aq	Hg^{2+}	4.0×10^{2}	25	water [b]	235a
Me	(dmgH) $(dmgH_2)$	aq	Hg^{2+}	$\leqslant 0.6$	25	water [b]	200
Me	$(dmgBF_2)_2$	aq	Hg^{2+}	$\leqslant 3.5 \times 10^{-4}$	25	water [b]	200
Me	$(dmgH)_2$	aq	Hg_2^{2+} [d]	8×10^{-2}	25	water [c]	246
Me	$(dmgH)_2$	py	$Hg(OAc)_2$	6.6×10^{-2}	26	HOAc/aq [e]	203
Et	$(dmgH)_2$	py	$Hg(OAc)_2$	7.7×10^{-4}	26	HOAc/aq [e]	203
n-Pr	$(dmgH)_2$	py	$Hg(OAc)_2$	7.0×10^{-4}	26	HOAc/aq [e]	203
sec-alkyl	$(dmgH)_2$	py	$Hg(OAc)_2$	$\leqslant 10^{-6}$	26	HOAc/aq [e]	203
Me	cobalamin		$Hg(OAc)_2$	300	26	HOAc/aq [e]	203
Et	cobalamin		$Hg(OAc)_2$	1.3×10^{-4}	26	HOAc/aq [e]	203
i-Pr	cobalamin		$Hg(OAc)_2$	3.5×10^{-5}	26	HOAc/aq [e]	203
Me	cobinamide	aq	$Hg(OAc)_2$	6.4×10^{-2}	26	HOAc/aq [e]	203
Et	cobinamide	aq	$Hg(OAc)_2$	5.7×10^{-5}	26	HOAc/aq [e]	203
Me	cobalamin		$Hg(OAc)_2$	370	30	aq?	202
Et	cobalamin		$Hg(OAc)_2$	2×10^{-1}	30	aq?	202
Me	cobinamide	aq	$Hg(OAc)_2$	1.2×10^{-1}	30	aq?	202
$CH_2{=}CH$	cobalamin		$Hg(OAc)_2$	7×10^{-1}	30	aq?	202
$CH_2{=}CH$	cobinamide	aq	$Hg(OAc)_2$	1.75×10^{-1}	30	aq?	202
5'-Deoxyadenosyl	cobalamin		$Hg(OAc)_2$	$\leqslant 10^{-5}$	30	aq?	202
5'-Deoxyadenosyl	cobinamide	aq	$Hg(OAc)_2$	$\leqslant 10^{-5}$	30	aq?	202
$2H\overset{+}{p}yCH_2$	$(CN)_4$	CN^-	$HgCl_2$ [f]	0.57	25	water [c]	198
$3H\overset{+}{p}yCH_2$	$(CN)_4$	CN^-	$HgCl_2$ [f]	ca. 5	25	water [c]	198
$4H\overset{+}{p}yCH_2$	$(CN)_4$	CN^-	$HgCl_2$ [f]	8.5	25	water [c]	198
$2H\overset{+}{p}yCH_2$	$(CN)_4$	CN^-	$HgCl_3^-$ [f]	0.17	25	water [c]	198
$3H\overset{+}{p}yCH_2$	$(CN)_4$	CN^-	$HgCl_3^-$ [f]	$\leqslant 1$	25	water [c]	198

(Table continued)

TABLE 20 (continued)

R	L_n	B	Reagent	k_2^a	T	Solvent	Ref.
$4\overset{+}{H}pyCH_2$	$(CN)_4$	CN^-	$HgCl_3^-$ [f]	2.4	25	water [c]	198
$2\overset{+}{H}pyCH_2$	$(CN)_4$	CN^-	$TlCl_2^+$ [f]	5.7	25	water [c]	198
$4\overset{+}{H}pyCH_2$	$(CN)_4$	CN^-	$TlCl_2^+$ [f]	157	25	water [c]	198
$2\overset{+}{H}pyCH_2$	$(CN)_4$	CN^-	$TlCl_3$ [f]	3.3	25	water [c]	198
$3\overset{+}{H}pyCH_2$	$(CN)_4$	CN^-	$TlCl_3$ [f]	ca. 150	25	water [c]	198
$4\overset{+}{H}pyCH_2$	$(CN)_4$	CN^-	$TlCl_3$ [f]	58.2	25	water [c]	198
$2\overset{+}{H}pyCH_2$	$(CN)_4$	CN^-	$TlCl_4^-$ [f]	0.31	25	water [c]	198
$4\overset{+}{H}pyCH_2$	$(CN)_4$	CN^-	$TlCl_4^-$ [f]	2.8	25	water [c]	198
CH_3	$(dmgH)_2$	aq	Tl^{3+}	1.2	25	water [b]	235a
C_6H_5	$(dmgH)_2$	aq	Tl^{3+}	1.4	25	water [b]	235a
$C_6H_5CH_2$	$(dmgH)_2$	aq	Tl^{3+}	0.7	25	water [b]	235a

[a] $M^{-1}\text{-}s^{-1}$. [b] $\mu = 1.0$. [c] $\mu = 0.5$. [d] Reaction through Hg^{2+}. [e] 0.1M NaOAc buffer. [f] Calculated from overall rate of reaction of thallium(III) or mercury(II) species.

Lakes of North America into which flow effluents containing high concentrations of inorganic mercury waste[247]. There seems little doubt that methylcobalamin does play a part in these reactions, because a number of workers have demonstrated both enzymic and non-enzymic formation of methylmercury(II) compounds from methylcobalt(III) species and mercury(II) halides[248,249]. The most interesting difference between the enzymic and most non-enzymic processes seems to be the formation of methylmercury(II) salts in the latter and of dimethylmercury in the former.

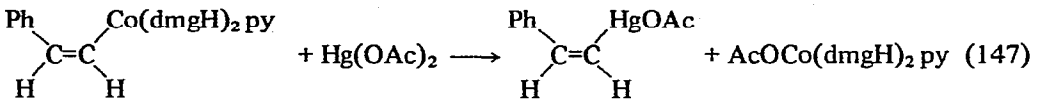
The non-enzymic reaction of methylcobalamin with mercuric chloride in aqueous solution, which gives methylmercury(II) chloride, has been studied in some detail[250]. The reaction is apparently faster in unbuffered solutions and in aqueous sodium chloride, which suggests that $HgCl_3^-$ may well be more reactive than $HgCl_2$, as is also found with some other σ-bonded organotransition metal compounds[251]. As is usual with such electrophilic displacements[252], the monoalkylmercury(II) species MeHgCl, PhHgCl, $MeOCH_2CH_2HgBr$, PhHgOH, and MeHg-dicyandiamide are less reactive than $HgCl_2$. The rate is also reduced in the presence of thiols, presumably because of the lower reactivity of mercury(II) sulphide complexes[253].

However, it is reported that in phosphate buffers[250,253] under reducing conditions[254], dimethylmercury is formed prior to the monomethylmercury(II) salt. Similarly, the enzyme reaction is also believed to give dimethyl- rather than monomethyl-mercury as the main product[248,254]. A direct formation of dimethylmercury from methylcobalamin [254–255] seems improbable and more work is required to elucidate the mechanism of this process. One factor that may be of particular importance in this reaction is the observation that, under some conditions, monoalkylmercury(II) species, undergo ready symmetriza-

tion[256] to give dialkylmercury(II) and inorganic mercury(II) species (eq. 146). This symmetrization is particularly dependent upon the character of the other ligands on the metal and upon the rate of removal of one or both of the symmetrised products. In the case of the enzyme systems *in vivo*, the preferential absorption of dimethylmercury by the lipid material, and the sulphur ligands available to complex with the metal, may well be the deciding factors in shifting the equilibrium of eq. 146 to the right, such that monomethylmercury(II) species are not observed.

$$2RHgX \rightleftharpoons R_2Hg + HgX_2 \qquad (146)$$

Electrophilic attack of mercury(II) reagents at unsaturated carbon. Electrophilic displacement of cobalt from vinylcobalt(III) compounds is faster than from alkylcobalt(III) compounds. The reaction of pure *cis*- and *trans*-β-styrylcobaloxime with mercury(II) acetate in acetic acid gives stereospecific formation of the corresponding *cis*- and *trans*-β-styrylmercury(II) acetate, respectively[257]. However, in impure solvents the *cis*-β-styrylcobaloxime gives appreciable quantities of the *trans*-β-styrylmercury(II) acetate. The reasons for this change are not known, but the incursion of a free radical process cannot be ruled out.



(147)

(ii) *Thallium(III) reagents.* Thallium(III) species, such as Tl^{3+}, $TlCl_2^+$, $TlCl_3$, and $TlCl_4^-$ may also attack the α-carbon of organocobalt(III) compounds by the bimolecular mechanism[198]. The initial product from this reaction is generally unstable and decomposes in many cases as fast as it is formed, to the alkyl halide and/or the corresponding alcohol. For example, the 4-pyridiniomethylpentacyanocobaltate(III) ion[198] and methylcobalamin[258] react with $TlCl_3$ to give mainly the chloromethylpyridinium ion and methyl chloride, respectively. Selected rate coefficients for some of these reactions are included in Table 20.

$$H\overset{+}{p}yCH_2Co(CN)_5^{3-} + TlCl_3 \longrightarrow Co(CN)_5^{2-} + Cl^- + H\overset{+}{p}yCH_2TlCl_2 \longrightarrow$$
$$\longrightarrow H\overset{+}{p}yCH_2Cl + TlCl \qquad (148)$$

$$\text{Mecobalamin} + TlCl_3 \longrightarrow Cl^- + B_{12a} + MeTlCl_2 \longrightarrow MeCl + TlCl \qquad (149)$$

(iii) *Platinum, palladium, gold and cobalt reagents.* Pure platinum(IV) chlorides are apparently inert towards alkylcobalt(III) compounds, as are pure platinum(II) halides[258]. However, platinum(IV) halides become reactive in the presence of platinum(II) halides

and displace the cobalt from methylcobalt(III) complexes by a process which obeys the rate law of eq. 150 and with the stoechiometry of eqn. 151.

$$-\mathrm{d}[\text{Mecobalamin}]/\mathrm{d}t = k_3\,[\text{Mecobalamin}]\,[Pt^{IV}]\,[Pt^{II}] \quad (150)$$

$$\text{Methylcobalamin} + Pt^{IV} \xrightarrow{Pt^{II}} MePt^{IV} + B_{12a} \quad (151)$$

A similar reaction, stoechiometric in gold(III) and methylcobalamin, is observed in the presence of gold(I)[258]. As with the thallium(III) reactions, the observed organic product is the alkyl halide when gold and platinum halides are the reagents. The exact role of the platinum and gold species is not known, but it seems likely that coordination of platinum(II) or gold(I) as the axial base, or some other interaction of these species with the cobalt(III) species, would greatly facilitate the susceptibility of the methylcobalamin to electrophilic attack at the α-carbon (eqn. 152). Such a reaction would be comparable with the activation of electrophilic attack by reduction with dithiols (p. 65). It is also interesting to compare this reaction with the activation of nucleophilic attack by oxidation described on p. 81.

$$Me(Co)PtX_2 + PtX_3^+ \longrightarrow \overset{\displaystyle X_3Pt^{\delta+}\cdots Me}{\overset{\displaystyle \vdots}{(Co)^{\delta+}}\overset{\displaystyle \vdots}{}_{PtX_2}} \longrightarrow (Co)PtX_2^+ + MePtX_3 \longrightarrow PtX_2 + MeX \quad (152)$$

Organopalladium compounds are believed to be intermediates in the alkylation of olefins by organocobaloximes in methanol catalysed by palladium(II) salts[259]. Some examples of this reaction are described in Table 21.

TABLE 21

Reaction of organocobalt(III) compounds with olefins in the presence of palladium(II) salts

R	L_n	*B*	*Olefin*	*Ratio* R(Co)/olefin/ $PdCl_4^{2-}$	*Product*	*Yield* (%)
Me	$(dmgH)_2$	aq	styrene	1/4/2	propenylbenzene	64
Me	$(dmgH)_2$	py	styrene	1/4/3	propenylbenzene	76
Me	$(dmgH)_2$	py	1-octene	1/2/1	2-nonene	20
Me	$(dmgH)_2$	py	cyclohexene	1/2/1	1-methylcyclohexene	1
Me	salen	aq	styrene	1/4/2	propenylbenzene	41
Ph	$(dmgH)_2$	py	styrene	1/4/2	*trans*-stilbene	4

One other example which apparently involves electrophilic attack of one cobalt(III) species on the α-carbon of an organocobalt(III) compound is of particular interest and merits further study. Thus, several aquocobalt(III) chelate species react slowly with methylcobalt(III)-chelate species, with transfer of the methyl group from one cobalt to the other (eqs. 153–155)[261]. Irrespective of the mechanism of these reactions, they give a useful measure of the relative carbon-acidity of the respective cobalt-chelate cations. The mechanism of these reactions is also of interest, because of the much more rapid displacement of cobalt(I) from alkylcobalt(III) compounds by the corresponding cobalt(I) chelates, and the reported exchange of methyl groups between cobalt(II) chelates and alkylcobalt(III) chelates; (p. 60–62 and p. 92, respectively). It is possible that all these processes proceed through the same intermediates.

$$MeCo(acacen)aq + Co(salen)aq^{+} \rightleftharpoons MeCo(salen)aq + Co(acacen)aq^{+} \quad (153)$$

$$MeCo(salen)aq + Co(dotnH)aq^{2+} \rightleftharpoons MeCo(dotnH)aq^{+} + Co(salen)aq^{+} \quad (154)$$

$$MeCo(salphen)aq + cobalamin\text{-}aq \rightleftharpoons Mecobalamin + Co(salphen)aq^{+} \quad (155)$$

(d) Reaction with nitrosating species

Several other electrophiles are also effective towards saturated carbon. Nitrosating agents, such as nitrosyl chloride and acidic solutions of nitrous acid give the corresponding aldoximes on reactions with benzyl- and pyridiniomethyl-pentacyanocobaltates[215] (eq. 156). The reactions obey the rate law shown in eq. 157.

$$ArCH_2Co(CN)_5^{3-} + NOX \longrightarrow Co(CN)_5^{3-} + X^{-} + ArCH_2NO \longrightarrow ArCH{=}NOH \quad (156)$$

(Ar = Ph, Hpy^{+}; X = Cl, H_2O^{+})

$$-d[ArCH_2Co(CN)_5^{3-}]/dt = [ArCH_2Co(CN)_5^{3-}][HNO_2][H^{+}](k_3 + k_4[Cl^{-}]) \quad (157)$$

This rate law is the same as that observed for the diazotisation of aromatic amines, and indicates that nitrosyl chloride and the nitrous acidium ion are the reactive species. Indeed, the rate at which these species attack the α-carbon of the pyridiniomethylpentacyanocobaltates is comparable with the rate of diazotisation of nitroanilines, under the same conditions.

The reaction of nitrosyl chloride with methylcobalamin in glacial acetic acid takes place preferentially on the equatorial ligand at C(10) to give the *C*-nitroso derivative, together with 5% of the ring B lactone derivative[84]. On the other hand, the reaction of 5′-deoxyadenosylcobalamin with nitrous acid causes diazotisation of the amino group of the adenine with the formation of the corresponding hypoxanthene derivative[222].

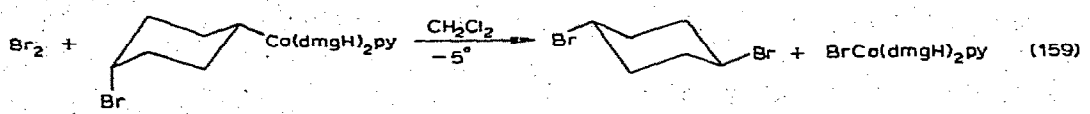
The reaction of nitrosyl sulphuric acid with benzylcobaloxime does not proceed via an electrophilic attack on the α-carbon, instead it behaves as an oxidising agent as described for halogens on p. 81. Nitrosyl chloride also reacts as an oxidising agent with benzyl- and

alkyl-cobaloximes to give mixtures of products which include the alkyl nitrate and the alkyl chloride[260].

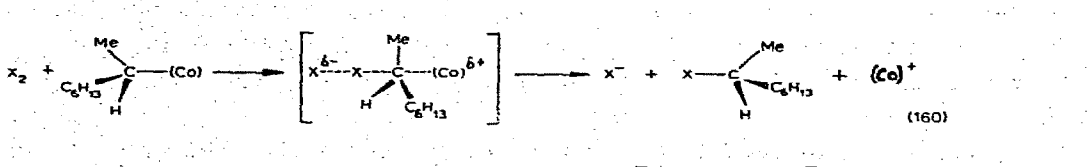
(e) Halogenation

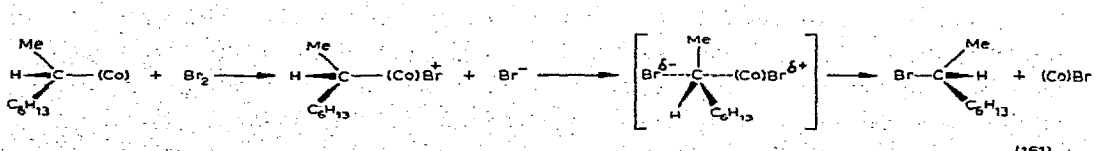
The reactions of organocobalt(III) compounds with the halogens have not been studied in as much detail as those described above, but the initial results show that they are more complicated and more interesting than was expected. Two features stand out: first, that the reactions frequently give a variety of products[108,262], secondly, that the alkyl halide may be formed predominantly by a process which involves inversion of configuration at the α-carbon[108,109], *e.g.*:

$$S\text{-}(+)\text{-}C_6H_{13}CHMeCo(dmgH)_2py + Br_2 \longrightarrow R\text{-}(-)\text{-}C_6H_{13}CHMeBr + \\ + BrCo(dmgH)_2py + C_6H_{13}CHBrCH_2Br + C_5H_{11}CHBrCHMeBr \qquad (158)$$



Two explanations have been put forward for the inversion of configuration at the α-carbon in these reactions. (i) That direct electrophilic substitution (eq. 160) may occur with either retention or inversion of configuration, depending upon the size and character of the incoming and outgoing electrophiles[109] (shown here with inversion of configuration). (ii) That the electrophilic attack takes place at the metal or at other ligands on the metal, thereby oxidising the complex such that attack at the α-carbon is a subsequent nucleophilic reaction with bromide ion or other nucleophilic species present in the solution (eq. 161). The latter reaction requires that the attack on the metal causes a large increase in the nucleofugal character of the cobalt, which, as is seen below, may have additional consequences.

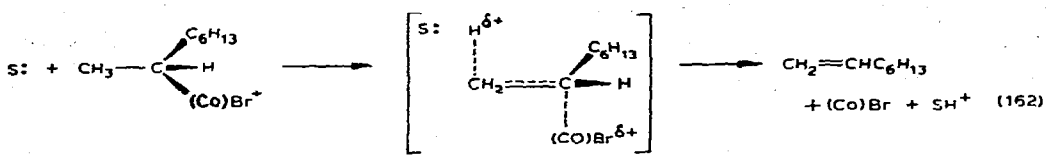




Though it is possible that each mechanism may operate in appropriate cases, several factors favour the attack of the halogen on other than the α-carbon. (a) The low yields of alkyl halides that are formed in many reactions. Thus, the reaction between sec-octyl-

cobaloxime and bromine in acetic acid gives only about a 30% yield of sec-octyl bromide, together with mainly the dibromides of 1-octene and 2-octene[108,262]. The latter would be expected if the solvent is sufficiently basic to assist in the removal of a β-proton from the sec-octyl group with synchronous displacement of the enhanced nucleofugal cobalt (*e.g.*, eq. 162). The octenes formed would immediately be brominated in the presence of an excess of bromine to form the observed octene dibromides[263].

(b) The reaction of electrophiles with benzylcobaloximes in the presence of added nucleophiles results in the formation of the benzyl derivatives of the nucleophiles as well as of the electrophiles. For example, the reaction of benzylcobaloxime with iodine chloride in the presence of added chloride ion gives mainly benzyl chloride together with the *O*-benzyl ether of dimethylglyoxime, but little benzyl iodide. This reaction is not due to the presence of the more reactive chlorine, because a chlorine scavenger such as anisole is recovered unchanged at the end of the reaction[262].



(162)

$$PhCH_2Co(dmgH)_2aq + X_2 \xrightarrow[AcOH]{Cl^-} PhCH_2X + PhCH_2Cl + PhCH_2dmgH + \\ + XCo(dmgH)_2aq \qquad (163)$$

(c) Still further support for an oxidatively induced nucleophilic substitution mechanism for halogenation comes from the reaction of the hexachloroiridate(IV) ion with benzylcobaloxime in the presence of halide ion. The transient benzylcobalt(IV) compound[264] (p. 89) is readily attacked at the α-carbon by bromide or chloride ion to give mainly the benzyl halide together with the benzyl ether of dimethylglyoxime. Indeed, the products of oxidation by $IrCl_6^{2-}$ and by ICl, in the presence of chloride ion, are almost identical. Still more convincing is the fact that (*S*)-(+)-sec-octylcobaloxime reacts with $IrCl_6^{2-}$ in the presence of bromide ion (2*M*) to give (*R*)-(−)-sec-octyl bromide in 37% yield; *i.e.*, with inversion of configuration observed in all S_N2 reactions and in the bromination of the same substrate.

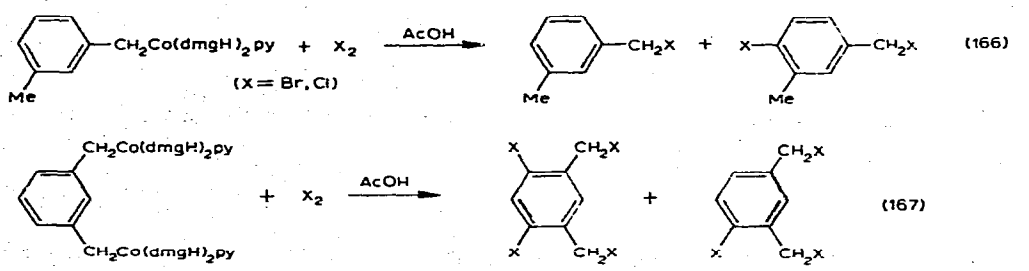
$$PhCH_2Co^{III}(dmgH)_2aq + IrCl_6^{2-} \longrightarrow [PhCH_2Co^{IV}(dmgH)_2aq]^+ + IrCl_6^{3-} \qquad (164)$$

$$[PhCH_2Co^{IV}(dmgH)_2aq]^+ + X^- \longrightarrow PhCH_2X + Co^{II}(dmgH)_2aq \qquad (165)$$

The character of the halogenations may also be particularly solvent dependent. For example, in methylene chloride, the absence of an appropriate base may mean that the

product alkyl halide is accompanied by little elimination. The reaction of cyclohexyl-(pyridine)cobaloxime with bromine in methylene chloride is reported to give largely cyclohexyl bromide and unchanged cyclohexylcobaloxime[109]. In trifluoroacetic acid on the other hand, the solvent is sufficiently nucleophilic that some alkyl trifluoroacetate is found in the reaction products[262].

Methylenecobalt(III) groups as substituents in aromatic substitution. In the reaction of benzyl- and substituted benzyl-cobaloximes with halogens, the course of the reaction is also influenced by competition between the cleavage reaction described above and electrophilic substitution in the aromatic ring. Benzylcobaloxime in acetic acid undergoes almost complete carbon–cobalt bond fission in the reaction with dilute halogen solutions[35]. However, *meta*-methylbenzylcobaloxime, in which the aromatic ring is activated by both the methyl group and the group $-CH_2Co(dmgH)_2py$, undergoes appreciable ring bromination prior to carbon–cobalt bond fission in acetic acid (eq. 166). In the bromination of the *meta*-xylylenedicobaloxime XXXI which has two activating $CH_2Co(dmgH)_2py$ groups, appreciable dibromination precedes the carbon–cobalt bond fission (eq. 167).



In all cases in which the reagent is iodine, only carbon–cobalt bond cleavage is observed. In these reactions, as in the reactions with chlorine and bromine, varying amounts of the corresponding benzyl ether of dimethylglyoxime are also obtained. Competition reactions, in which a mixture of a substituted benzylcobaloxime and the corresponding toluene are allowed to react with a limited quantity of bromine or chlorine, show that the ring substitution is activated more by the group $-CH_2Co(dmgH)_2B$ than by the methyl group, particularly in positions *ortho* and *para* to that group. This is further evidence for the σ–π-conjugation interaction between the metal and the ring.

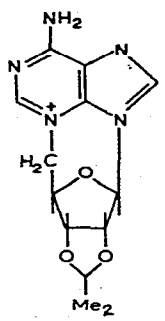
Protonation of the dimethylglyoxime ligands reduces the rate of carbon–cobalt bond cleavage more than it reduces the rate of ring halogenation such that, in 20–60% sulphuric acid where the monoprotonated benzylcobaloxime is the reactive species, ring substitution and carbon–cobalt bond cleavage proceed at almost equal rates[265]. In more concentrated sulphuric acid where the diprotonated benzylcobaloxime is the reactive species, ring substitution preceeds carbon–cobalt bond cleavage (eq. 170).

$$PhCH_2Co(dmgH)_2B + Br_2 \longrightarrow PhCH_2Br + BrCo(dmgH)_2B \quad (168)$$

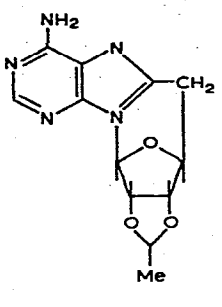
$$[PhCH_2Co(dmgH)(dmgH_2)aq]^+ + Br_2 \longrightarrow BrC_6H_4CH_2Br + C_6H_5CH_2Br + Br(Co) \quad (169)$$

$$[PhCH_2Co(dmgH_2)_2aq]^{2+} + Br_2 \longrightarrow BrC_6H_4CH_2Br + Br(Co) \quad (170)$$

Halogenation of the cobalamins may also take place at sites other than the cobalt–carbon bond and without cleavage of that bond. For example, methylcobalamin reacts with *N*-bromosuccinimide in glacial acetic acid to give 88% methyl(10-bromo)cobalamin and 12% of the methylcobalamin derivative having a lactone on ring B. In aqueous acetic acid, the proportion of the lactone is higher[84]. Chlorination of methylcobalamin with chloramine-T gives the 10-chloro derivative. In contrast to the 10-bromo derivative, the 10-chloro derivative cannot be dehalogenated by treatment with sodium borohydride. Aerobic iodination of methylcobalamin in methanol in the dark gives iodocobalamin and 5′-iodo-5′-deoxyadenosine[266]. The corresponding 2′,3′-isopropylidene-5′-deoxyadenosylcobalamin reacts with iodine in the dark to give 2′,3′-isopropylidene-5′-deoxyadenosine, together with the cationic cyclic nucleoside XXXII, derived from the former product. When the same reaction is carried out under anaerobic conditions in the presence of light, the same cyclic nucleoside XXXII and another cyclic species XXXIII are formed[266]. The latter probably arises by cyclisation of the intermediate organic radical.

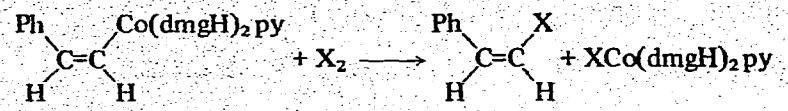


(XXXII)



(XXXIII)

Reaction of halogen with unsaturated organocobalt(III) compounds. The reactions of *cis*- and *trans*-β-styryl(pyridine)cobaloximes with chlorine, bromine, and iodine in acetic acid involve a rapid and stereospecific cleavage of the carbon–cobalt bond, comparable with that observed in the reaction of the same cobaloximes with mercury(II) species (p. 77)[257,267]. As the yield is quantitative and the *cis*-β-styrylcobaloxime may be prepared stereospecifically in reasonable yield from phenyl acetylene, this reaction provides a convenient synthesis of stereochemically pure *cis*-β-halogenostyrenes.



(171)

(X = Cl, Br, I)

This reaction is, however, not indicative of the mechanism, as both nucleophilic and electrophilic cleavage of vinyl–metal compounds are expected to proceed with retention of configuration with or without some loss of stereospecificity. A number of other substituted vinylcobaloximes do show a considerable loss of stereospecificity during the cleavage with halogens[257].

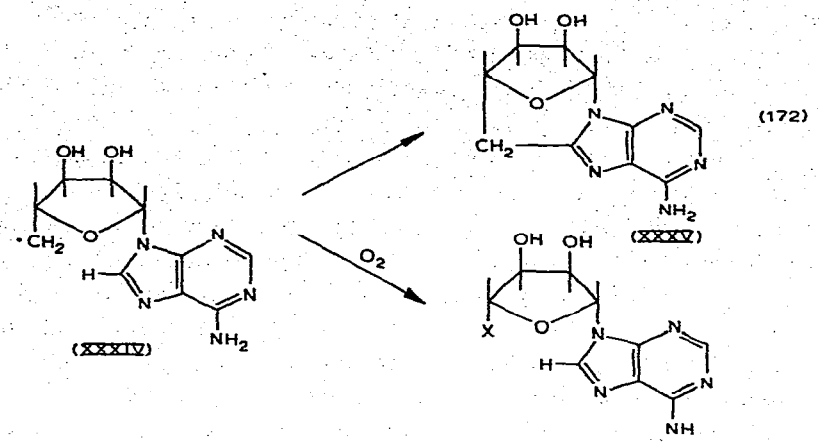
(III) Homolytic reactions

Homolytic cleavage of the carbon–cobalt bond occurs under a variety of conditions, notably on electrolytic reduction, on oxidation, on heating, and on irradiation.

(a) Photolysis

The instability of the coenzyme in the presence of light was one of the factors which complicated the problem of its purifications and identification[268]. As with the majority of organocobalt(III) compounds, the absorption of light results in the homolysis of the carbon–cobalt bond, but in no case is the reaction completely straight-forward. The main factors of interest are: (i) the character of the light absorption process and the causes of the carbon–cobalt bond fission; (ii) the nature of the organic and inorganic radicals formed on homolysis; and (iii) the fate of these species.

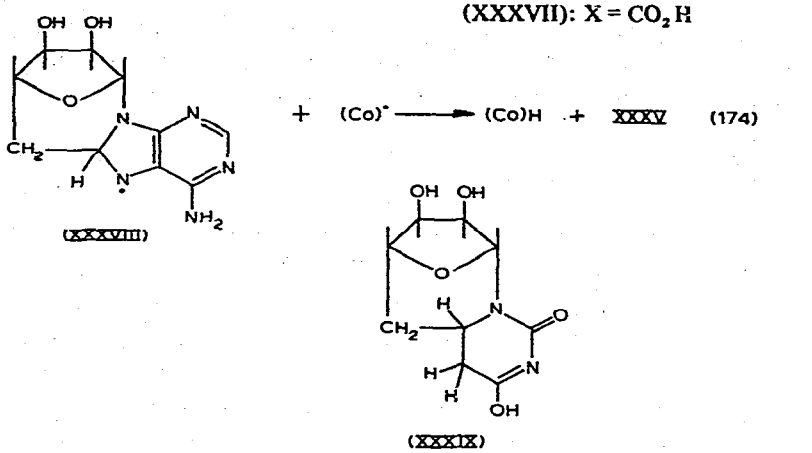
There is some uncertainty about the nature of the activation process. The aerobic photolysis of methylcobalamin is reported[269] to have a high quantum yield (0.2–0.5) at wavelengths in the region 490–550 nm, and to be due to π–π^*-transitions of the corrinoid ring. σ–π-Transitions have also been invoked[65]. However, the quantum yields in the photolysis of the alkylcobaloximes are much lower in the region 400–475 mm[65]. The minimum threshold energy in the photolysis of the alkylcobaloximes coincides with what is believed to be the carbon–cobalt charge transfer σ–σ^*-transition, indicating that the carbon–cobalt excitation occurs by transfer of a ligand electron to the metal. The rates of most of these reactions are increased by the presence of oxygen, though that of the coenzyme is not[270]. This is a result of the competition between rapid recombination of initially formed radical fragments, reaction of radical fragments with other reagents, and recombination of radical fragments after intramolecular rearrangement. Photolysis of the coenzyme gives the organic radical (XXXIV)[271] which, in the absence of oxygen cyclises to the nucleoside (XXXV)[87,217] (termed nucleoside A or peak 2 in the early work prior to its identification)[217,272] and in the presence of oxygen gives the



(172)

(XXXIV) (XXXV)

(XXXVI) : X = CHO (173)
(XXXVII): X = CO_2H



(174)

(XXXVIII) (XXXIX)

aldehydic (XXXVI)[273,274] or acidic (XXXVII)[217] nucleoside depending upon the degree of oxidation.

An interesting feature of the cyclisation reaction is the loss of the heteroaromatic hydrogen atom. It seems probable that this is removed from a cyclic radical intermediate (XXXVIII) by the cobalt(II) fragment, though not necessarily at the metal atom of the latter. The cyclised product is also formed, but in lower yield, in the presence of oxygen [273,274]. The uridine analogue of the coenzyme undergoes intramolecular reaction in the absence of oxygen, but the initially formed radical rearranges first to a cyclic nucleoside which is then reduced to the dihydro derivative (XXXIX)[216] possibly by the cobalt species involved in, or available for, the hydrogen abstraction. The presence of cobalt(I) species in the products of these photolysis is evident from the fact that some methylcobalamin is formed during the photolysis of other alkylcobalamins in the presence of methyl iodide[275].

Another interesting reaction which appears to involve hydrogen abstraction, occurs in the photolysis of the coenzyme in the presence of a thiol such as homocysteine or cysteine[229,230,276]. The intermediate alkyl radical would be expected to abstract a hydrogen atom from the thiol, yet the product is the corresponding thioether, *S*-adenosylhomocysteine (42% yield) or *S*-adenosylcysteine[276], respectively. Similarly, the photolysis of methylcobalamin in the presence of homocysteine gives methionine in 58% yield[276]. This suggests two possible mechanisms; either (i) the hydrogen abstraction from the thiol may be performed by the cobalt fragment rather than by the organic radical, or (ii) the reaction may be a photochemically induced nucleophilic displacement of cobalt(I) by the attack of the sulphur nucleophile on the α-carbon of the photochemically activated organocobalt compound. Such a reaction would be analogous to the oxidatively induced nucleophilic displacements by even weak nucleophiles like chloride ion, p. 81.

Hydrogen abstraction from the organic fragment (*cf.*, eqn. 39; p. 20) appears to control the formation of ethylene[204,277,278] following the production of the ethyl radical on photolysis of several ethylcobalt(III) complexes. The observation that some deuterated ethylene is present in the product formed from the photolysis of ethylcobalt(III) compounds in D_2O suggests that the hydrogen abstraction is reversible (eq. 175)[67].

$$C_2H_5(Co) \rightleftharpoons C_2H_5^{\cdot} + (Co)^{\cdot} \rightleftharpoons (Co)H + C_2H_4 \qquad (175)$$

Higher alkylcobalt(III) compounds also lose the β-hydrogen and give olefinic products, but in the photolysis of methylcobalt(III) compounds[204,216,275,276,277] there is no available β-hydrogen, and other radical reactions predominate, notably dimerisation, the abstraction of a hydrogen atom from the solvent or from other ligands, and combination with other methyl radicals that may have come from the equatorial ligands. Thus, the methane formed from the photolysis of methylcobalamin in D_2O gives 66% CH_3D and 34% CH_4 at pH 7 under anaerobic conditions[65]. The hydrogen abstraction is therefore in part from the corrin ring or its side chains. Similar abstraction from dimethylglyoximinato ligands appears to be more favourable. The proportion of CH_3D and CH_4 in the product is dependent upon the pH and upon the axial base, as is the proportion of ethane in the products, and the rate of the decomposition.

The use of $^{14}CH_3$cobalamin[277] and $^{2}H_3C$cobalamin[67] and $^{2}H_3C$cobaloxime[67] in D_2O and in H_2O indicates that, though most of the ethane formed in the reaction arises from the dimerisation of methyl radicals formed by direct fission of the carbon–cobalt bond, a small proportion arises by dimerisation of methyl radicals, some of which come from the equatorial ligands. It is unlikely, in view of the absence of known free radical displacements at saturated carbon[279], that such products come from a direct attack of methyl radicals on the equatorial methyl groups. It seems more likely that some homolytic dissociation of carbon–methyl bonds takes place in the cobalt(II) fragment.

There are a number of other interesting reactions of the substituted alkylcobalamins which occur on photolysis, but which have not been investigated in detail. For example,

TABLE 22

Kinetics of photolysis of organocobalt(III) compounds [a]

R	L_n	*B*	*Conditions*	10^3k [b]	*Ref.*
Me	$(dmgH)_2$	aq	300W, absorbance ≤ 0.5	2.1	65
Et	$(dmgH)_2$	aq	300W, absorbance ≤ 0.5	5.8	65
i-Bu	$(dmgH)_2$	aq	300W, absorbance ≤ 0.5	56	65
Me	$(dmgH)_2$	py	300W, absorbance ≤ 0.5	1.7	65
Me	$(dmgH)_2$	CN^-	300W, absorbance ≤ 0.5	0.2	65
Et	$(dmgH)_2$	CN^-	300W, absorbance ≤ 0.5	1.2	65
Et	$(dmgH)_2$	py	300W, absorbance ≤ 0.5	3.5	65
Et	cobinamide	py	300W, absorbance ≤ 0.5	10.8	65
Me	cobinamide	aq	300W, absorbance ≤ 0.5	12.1	65
Me	cobalamin		300W, absorbance ≤ 0.5	43	65
Me	$(dpgH)_2$	aq	300W, absorbance ≤ 0.5	5.8	65
Me	cobinamide	aq	200W, 60 cm	1.01 [c]	191
Me	cobinamide	CN^-	200W, 60 cm	2.1	191
Me	cobinamide	imidazole	200W, 60 cm	0.55	191
Me	cobalamin		200W, 60 cm	0.94 [d]	191
Me	cobalamin		200W, 60 cm	1.25 [e]	191
HO_2CCH_2	cobalamin		200W, 45 cm	32	192
MeO_2CCH_2	cobalamin		200W, 45 cm	45	192
$HO_2CCH_2CH_2$	cobalamin		200W, 45 cm	27	192
$NCCH_2CH_2$	cobalamin		200W, 45 cm	36	192
$HOCH_2CH_2$	cobalamin		200W, 45 cm	36	192
Me	cobalamin		200W, 45 cm	19	192

[a] Other rate coefficients in references. [b] s^{-1}. [c] pH 1–8. [d] pH 1. [e] pH 8.

photolysis of α-carboxymethylcobalamin[280] in the presence of oxygen gives carbon dioxide, formaldehyde, etc., but anaerobic photolysis of concentrated solutions gives acetate ion, some succinic acid, and several other acids. Anaerobic photolysis in dilute solution gives acetate and CO_2. The anaerobic photolysis of α,β-dihydroxypropylcobalamin gives glycerol[285a].

Other molecules which serve as radical traps[281,282] or sources of hydrogen atoms also have an effect on the rate and product proportions of the photolysis. Thus, isopropanol, from which the α-hydrogen is readily abstracted, increases the rate of photolysis of methylcobalamin (eq. 176) more than do other alcohols. Pinacol is found among the products of this reaction and, though it is usually assumed that the abstraction is performed by the methyl radical, it seems possible that abstraction may also take place by the fresh five-coordinate inorganic fragment. In methanolic solution the solvent is partially oxidised to formaldehyde and, in the presence of carbon monoxide, the main inorganic product is the methyl ester $MeOCOCoL_nB$[17,18,283–285], *e.g.*:

$$\text{Mecobalamin} \rightleftharpoons B_{12r} + \cdot CH_3 \xrightleftharpoons{Me_2CHOH} CH_4 + Me_2\dot{C}OH \qquad (176)$$

The rates of photolysis[65,192] depend upon the nature of the organic group, the axial base, and the equatorial ligands. Some examples of the relative rates are shown in Table 22, though comparison between different sets of results is generally inadvisable, because of the difficulties in comparing the different conditions. In particular, the cobalamins and cobinamides photolyse about ten times more readily than the cobaloximes; secondary alkylcobalt(III) compounds photolyse more readily than primary alkylcobalt(III) compounds, and the methylcobaloximes with some nitrogenous axial bases are surprisingly light stable under anaerobic conditions. The kinetics of such reactions are, however, greatly complicated by the reversibility and multiple reaction paths. Further discussion of photolysis of alkylcobaloximes in the presence of oxygen is included on p. 95.

Substituted alkylcobalt(III) complexes also undergo photolysis, though few reactions have been studied in detail[285a]. Hydroxyethyl radicals from the photolysis of β-hydroxyethylCo(aetpor)[286] undergo the expected hydrogen atom transfer to give acetaldehyde, and this reaction has been compared with possible steps in the dioldehydrase reactions (p. 101). An unusual reaction involves the formation of chlorocarbene in the photolysis of monochloromethylcobalamin impregnated in polystyrene[286a].

(b) Thermolysis

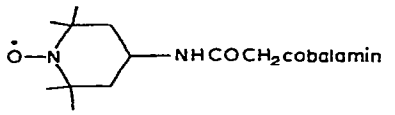
Most organocobalt(III) compounds decompose on heating without melting. The decomposition temperature depends upon the nature of the organic group; in general, the more stable the incipient organic radical, the lower the decomposition temperature[39]. For example, α-phenylethylcobaloxime decomposes at ca. 90°, but the β-phenylethylcobaloxime decomposes at ca. 175°. The principal organic product is styrene and the inorganic product from the former is the hydridocobalt(III) species. Hydridotriphenylphosphinebis(dimethylglyoximato)cobalt(III) is formed as a solid on pyrolysis in vacuo of β-cyanoethylbis(dimethylglyoximato)triphenylphosphinecobalt(III)[44]. The organic products from such reactions are usually the corresponding olefin or substituted alkane, depending upon whether there is a β-hydrogen available for abstraction. An unusual example is the formation of cyclopropane from the pyrolysis of the trimethylenedi-

cobaloxime XL[39]. Thermolysis of RCo(salen)aq in vacuo at 200° gives a quantitative yield of Co^{II}(salen)[17].

$$py(dmgH)_2CoCH_2CH_2CH_2Co(dmgH)_2py \longrightarrow 2Co(dmgH)_2py + (CH_2)_3 \quad (177)$$
(XL)

Thermolysis may also be induced at low temperatures by chemical reaction. For example, the protonation, particularly the diprotonation of benzylbis(dimethylglyoximato)-pyridinecobalt(III) greatly increases the rate of homolysis in solution at room temperature (*cf.* p. 66)[235]. It is interesting to note that despite the fact that such protonation decreases the stability of the carbon–cobalt bond, it also increases its resistance to reaction with mercury(II)[200,235,235a], and halogens[265].

An interesting method of studying the homolysis of the carbon–cobalt bond of alkylcobalamins has been developed by synthesising compounds with spin-labelled alkylsubstituents (*e.g.* XLI)[287] and with a nitroxyl compound as the axial base[287a], and using these as probes for electron spin resonance studies.



(XLI)

(c) Chemical oxidation

Oxidation of organocobalt(III) compounds can be achieved by a variety of oxidants [264,264a] to give the corresponding organocobalt(IV) compounds which may decompose homolytically[264]. For example, oxidation by the hexachloroiridate(IV) ion (eq. 164) is extremely sensitive to the character of the organic group and of the equatorial ligand. The influence of substituents in the *para*-position of benzylcobaloximes is enormous, with $> 10^6$ fold difference between 4-MeO- and 4-NO_2-benzyl cobaloxime. Protonation of the equatorial ligand also causes a very large drop in the rate of electron transfer, such that a rate expression of the form shown in eq. 144 (with $[IrCl_6^{2-}]$ in place of $[Hg^{2+}]$) is appropriate. Some rate coefficients are shown in Table 23.

When only one equivalent of the hexachloroiridate(IV) ion is used in aqueous solution, benzylaquocobaloxime is converted almost quantitatively into the *O*-benzyl ether of dimethylglyoxime (eq. 178). When an excess of the oxidant is used, the product is benzyl alcohol. The latter has been ascribed to an oxidation of the benzyl radical formed on homolysis of the intermediate benzylcobalt(IV) compound (eq. 179–180).

$$[PhCH_2Co(dmgH)_2aq]^+ \longrightarrow PhCH_2dmgH + Co^{2+} + dmgH_2 \quad (178)$$

$$[PhCH_2Co(dmgH)_2aq]^+ \longrightarrow Ph\dot{C}H_2 + [Co(dmgH)_2aq]^+ \quad (179)$$

$$PhCH_2 + H_2O + IrCl_6^{2-} \longrightarrow PhCH_2OH + H^+ + IrCl_6^{3-} \quad (180)$$

(d) Polarographic reduction and oxidation

Much useful information has been provided by polarographic studies of organocobalt (III) compounds. Detailed comparison of different sets of data are difficult because of the variety of conditions used, but broad comparisons about the ease of reduction of the several cobalt–chelate systems may be drawn.

In most cases, several one-electron transfer steps are observed in the reduction process, corresponding to the reduction of the organocobalt(III) compound to the organocobalt(I) compound via the organocobalt(II) compound. In some cases, depending upon the conditions used, only a single two-electron reduction is observed. For example, in 0.1*M* aqueous potassium sulphate solution at 25°, dilute solutions of alkylcobaloximes show a single irreversible wave[288] due to the reduction:

$$MeCo(dmgH)_2B + 2e^- \longrightarrow MeCo^{I}(dmgH)_2B^{2-} \quad (181)$$

Whereas in acetonitrile most of the same compounds show two or more waves[118], the first two being due to the reduction to the cobalt(I) state, the third being due to the reduction of other species such as the axial pyridine ligand. Several such half-wave potentials are shown in Table 24.

The reduction of most other alkyl and aryl cobalt chelates are reversible and give rise to relatively stable, though short lived, organocobalt(II) and organocobalt(I) species. The stability of many of these species may be clearly demonstrated by the reversibility of the system found in cyclic voltammetry studies. In particular, phenylCo(salen) and phenylCo(dotnH)$^+$ complexes are readily reduced to observable cobalt(I) species[289,290,291], *e.g.*:

$$PhCo(salen) \rightleftharpoons PhCo^{II}(salen)^- \rightleftharpoons PhCo^{I}(salen)^{2-} \quad (182)$$

$$PhCo(dotnH)^+ \rightleftharpoons PhCo^{II}(dotnH) \rightleftharpoons PhCo^{I}(dotnH)^- \quad (183)$$

(XLIII) (XLII)

The phenylcobalt(I) species (XLII) is stable for several hours and may be reoxidised to the cobalt(III) species (XLIII). The corresponding methylcobalt(II)(dotnH) and methylcobalt(I)(dotnH)$^-$ species are less stable, though some reactions of the latter, and of MeCo(salen)$^-$, have been characterised. For example, MeCo(salen)$^-$ decomposes according to eq. 184, and the cobalt(III) species MeCo(dotnH)$^+$ reacts with the cobalt(I) species MeCo(dotnH)$^-$ in aqueous solution to give the novel dimethylcobalt(III) compound XLIV[237] (eq. 185).

$$MeCo^{II}(salen) \longrightarrow Me\cdot + Co^{I}(salen)^- \quad (184)$$

$$\underset{\text{(XLV)}}{MeCo^{I}(dotnH)^{-}} + \underset{\text{(XLVI)}}{MeCo^{III}(dotnH)^{+}} \rightarrow \underset{\text{(XLIV)}}{Me_2Co^{III}(dotnH)} + \underset{\text{(XLVII)}}{Co^{I}(dotnH)} \qquad (185)$$

The mechanism of reaction 185 might involve a nucleophilic attack of the cobalt(I) species XLV on the methyl group of the methylcobalt(III) species XLVI with the displacement of the cobalt(I) species XLVII (*cf.* p. 61) or it might involve an electrophilic attack of the cobalt(III) species XLVI on the methyl group of the cobalt(I) species XLV (*cf.* p. 79). Unfortunately, because of the ready electron transfer between XLV and XLVI it will be difficult to distinguish between these two distinct mechanisms. In the absence of other reagents, the methylcobalt(I) species such as XLV decompose in protic solvents by electrophilic attack at the α-carbon (eq. 186). Such reaction is analogous to reductive cleavages with thiols in protic solvents. It is doubtful whether carbanions are formed except in exceptional circumstances where the carbanion would be stabilised by strongly electron-withdrawing groups.

$$MeCo(salen)^{2-} + H_2O \longrightarrow CH_4 + Co(salen)^{-} + OH^{-} \qquad (186)$$

For many organocobalt compounds, the half-wave potentials for the first stage of the reduction [$E_{1/2}$(I); for Co^{III}–Co^{I}] tends to parallel that for the second stage of the reduction [$E_{1/2}$(II); for Co^{II}–Co^{I}]. They are both very sensitive to changes in the equatorial ligand. For example, the ease of reduction [$E_{1/2}$(I)] increases in the following order: (all in dimethylformamide, relative to SCE)[289,291] EtCo(acacen)(−1.97V) < EtCo(Me_2-salen)(−1.80V) < EtCo(salenO(−1.71V) < EtCo(salphen)(−1.54V) < Methylcobalamin (−1.4V) < EtCo(dotnH)$^{+}$(−0.93V).

The reduction potentials are less sensitive to, but are influenced by, the basicity of the axial ligand. Thus, the two electron reduction potential of methylbis(dimethylglyoximato) cobalt(III) compounds increases with the basicity of the axial ligand, though this relationship is not linear. The change of the two electron half-wave potential on changing the axial ligand from water to more basic ligands ($\Delta E_{1/2}$) has also been shown to be proportional to the shift in frequency ($\Delta\nu$) of the charge-transfer band in the ultraviolet spectrum of the organocobalt(III) species on making the same changes in the axial ligand[288].

The first reduction potential is also dependent upon the character of the organic ligand. For example, the first reduction potential [$E_{1/2}$(I)] of RCo(salen) and [RCo(dotnH)]$^{+}$ is an inverse linear function of the acidity of the parent hydrocarbon, *i.e.* [289, 291,292]: EtCo(chelate)› MeCo(chelate)› PhCo(chelate)› $PhCH_2$Co(chelate). In most cases, the increase in the ease of reduction of the several cobalt chelates also parallels the acidity of the coordinated water and the decrease in the tendency towards five coordination, as well as other physical properties of the compounds[289,290,291]. It is also interesting to compare these results with the ease of oxidation by the outer sphere electron transfer mechanism (p. 89 and Table 23); thus the most difficult species to reduce are the easiest to

TABLE 23

Kinetics of reaction of organoaquocobaloximes with the hexachloroiridate (IV) ion at 25° and $\mu = 1.0$, in aqueous solution[264]

R	k^a
Me	1
Et	2
n-Pr	2
i-Pr	8×10^4
$PhCH_2$	8×10^3
$4\text{-}MeOC_6H_4CH_2$	4×10^6
$4\text{-}MeC_6H_4CH_2$	2×10^5
$4\text{-}FC_6H_4CH_2$	1.5×10^4
$4\text{-}O_2NC_6H_4CH_2$	ca. 2

[a] $M^{-1} \cdot s^{-1}$.

oxidise. Much less is known about the polarographic oxidation of organ cobalt(III) compounds, though it has been observed[289] that, just as the difference between the first reduction potential and the second reduction potential for ethylcobalt(III) compounds containing a variety of equatorial ligands is approximately constant [i.e., $E_{1/2}(I) - E_{1/2}(II) = ca.\ 0.45V$] so the difference between the first oxidation potential and the first reduction potential is also constant [*i.e.*, $E_{1/2}(ox) - E_{1/2}(I) = ca.\ 2.28V$].

The products from the decomposition of reduced cobalamins are rather difficult to determine[94,293], but there have been several sets of determinations of the appropriate half-wave potentials for the organocobalamins. The variation of absolute values between one set and another suggests that comparison should be restricted to within any one particular set. The interesting features that emerge are (i) the high value of $E_{1/2}(II)$ for vinylcobalamin, and (ii) the influence of ionisation and protonation, respectively, on the half wave potentials for the carboxyl- and aminoethyl-cobalamins.

(e) Miscellaneous free radical reactions

One of the problems in the study of the chemistry of the organic compounds of cobalt (III) is that free radical reactions are liable to intrude under almost any circumstances, whether as a side reaction or as the predominant reaction. For example, in the oxidation of formaldehyde [194] and in the decomposition of formic acid[296] catalysed by organocobalt(III) compounds, free radical reactions are believed to dominate. In halogenation, though the main reactions appear to be either electrophilic or nucleophilic, it is very difficult to rule out at least partial free radical reactions of the type:

$$RCo(chelate) + Br^{\cdot} \rightleftharpoons [RCo(chelate)Br]^{\cdot} \qquad (187)$$

$$[R\dot{C}o(chelate)Br]^{\cdot} \rightarrow R^{\cdot} + Co(chelate)Br \quad (188)$$

$$R^{\cdot} + Br_2 \rightarrow RBr + Br^{\cdot} \quad (189)$$

Indeed, the slight loss in stereospecificity in the halogenation of optically active organocobalt(III) compounds may be due to the intrusion of such a process[108].

Another reaction is of particular interest because of its relevance to other displacements and to metal–metal exchanges, and because of the very interesting mechanistic problems that it poses. Thus, on mixing MeCo(acacen) with Co^{II}(F-acacen), the equilibrium between these two species and those formed by transfer of a methyl radical from one to the other (eq. 190) is complete within ca. 2 min at 0° in dimethyl sulphoxide[297]. A similar rapid exchange occurs with the ethyl derivatives.

$$RCo(acacen) + \cdot Co(F\text{-}acacen) \rightleftharpoons RCo(F\text{-}acacen) + \cdot Co(acacen) \quad (R = Me, Et) \quad (190)$$

$$^{\cdot}(Co) + R(Co') \rightleftharpoons [\delta^{\cdot}(Co)\text{-----}R\text{----}(Co')\delta^{\cdot}] \rightleftharpoons (Co)R + (Co')^{\cdot} \quad (191)$$

If this reaction proceeds by a direct homolytic attack of the inorganic cobalt(II) species on the methyl group, then it is of very special interest, because it would represent the first clear cut case of a bimolecular homolytic attack at saturated carbon[279] or, in inorganic terminology, the first case of an electron transfer reaction via a saturated carbon bridge (eqn. 191). Unfortunately, it is extremely difficult to verify the mechanism of this reaction, and several alternatives involving the formation of transient species in different oxidation states cannot be ruled out.

In the corresponding reaction of the dioximatocobalt species, there is little doubt that there is a mechanism which proceeds through cobalt(I) species. For example, bis(cyclohexanedionedioximato)pyridinecobalt(II) reacts with methylbis(dimethylglyoximato) pyridinecobalt(III) in alkaline methanolic solution at 0° to give a very rapid exchange of the methyl group from one cobalt to the other (eq. 192)[223]. However, under these conditions the cobalt(II) species are largely disproportionated to a mixture of the cobalt(I) and cobalt(III) species and it is the former which is the reactive species. Consequently the rate sequence: Me > Et > n-octyl ≫ isobutyl ~ sec-octyl is the same as is observed in the nucleophilic displacement reactions (eq. 102; p. 61), and the rate of reaction of the n-octyl derivative is approximately one half of that observed in the reaction of the cobalt(I) species, in accord with the proportion of cobalt(II) species which has been converted into the reactive cobalt(I) species.

$$MeCo(dmgH)_2py + \cdot Co^{II}(c\text{-}hgH)_2py \rightleftharpoons MeCo(c\text{-}hgH)_2py + \cdot Co^{II}(dmgH)_2py \quad (192)$$

$$2\,Co^{II}(xgH)_2py \overset{OH^-}{\rightleftharpoons} [Co^{I}(xgH)_2py]^- + [Co^{III}(xgH)_2py]^+ \quad x = dm, c\text{-}h \quad (193)$$

TABLE 24

Half-wave potentials[a] in the polarographic reduction of some organocobalt(III) compounds

Compound	$E_{1/2}(V)$			*Solvent*	*Ref.*
	I	*II*	*III*		
$MeCo(dmgH)_2aq$	−1.7 [b]	−2.42 [b]		MeCN	118
$MeCo(dmgH)_2py$	−1.75 [b]	−2.44 [b]	−3.01 [b]	MeCN	118
$MeCo(dmgH)_2PPh_3$		−2.12 [b,c]		MeCN	118
$MeCo(dmgH)_2aq$		−1.26 [c]		H_2O/0.1*M* K_2SO_4	288
$MeCo(dmgH)_2$nicotinamide		−1.28 [c]		H_2O/0.1*M* K_2SO_4	288
$MeCo(dmgH)_2$-*p*-toluidine		−1.28 [c]		H_2O/0.1*M* K_2SO_4	288
$MeCo(dmgH)_2py$		−1.31 [c]		H_2O/0.1*M* K_2SO_4	288
$MeCo(dmgH)_2$-4-Mepy		−1.33 [c]		H_2O/0.1*M* K_2SO_4	288
$MeCo(dmgH)_2$imidazole		−1.40 [c]		H_2O/0.1*M* K_2SO_4	288
Mecobalamin		−1.20 [c]		H_2O/0.1*M* K_2SO_4	288
$EtCo(dmgH)_2py$		−1.31 [c]		H_2O/0.1*M* K_2SO_4	288
$i\text{-}PrCo(dmgH)_2py$		−1.30 [c]		H_2O/0.1*M* K_2SO_4	288
$MeCH(OH)CH_2Co(dmgH)_2py$		−1.24 [c]		H_2O/0.1*M* K_2SO_4	288
$PhCH_2Co(dmgH)_2py$		−1.20 [c]		H_2O/0.1*M* K_2SO_4	288
$MeCo(dotnH)dmf^+$	−0.86	−1.44	−2.05 [d]	dmf/0.2*M* Et_4NClO_4 [e]	291
MeCo(dotnH)Me	−2.05			dmf/0.2*M* Et_4NClO_4 [e]	29[illegible]
MeCo(salen)dmf	−1.57	−2.17	−2.26	dmf/0.2*M* Et_4NClO_4 [e]	291
PhCo(salen)dmf	−1.42	−2.11	−2.25	dmf/0.2*M* Et_4NClO_4 [e]	291
EtCo(salen)dmf	−1.71	−2.27		dmf/0.2*M* Et_4NClO_4 [e]	290
$PhCH_2Co$(salen)dmf	−1.25	−2.08		dmf/0.2*M* Et_4NClO_4 [e]	290
$EtCo(dotnH)dmf^+$	−0.93			dmf/0.2*M* Et_4NClO_4 [e]	290
$PhCo(dotnH)dmf^+$	−0.83	−0.93		dmf/0.2*M* Et_4NClO_4 [e]	290
$PhCH_2Co(dotnH)dmf^+$	−0.74	−1.44		dmf/0.2*M* Et_4NClO_4 [e]	290
CH_2=CHCo(salen)dmf	−1.54			dmf/0.2*M* Et_4NClO_4 [e]	290
CH_2=CHCo(7,7'-Me-salen)dmf	−1.59			dmf/0.2*M* Et_4NClO_4 [e]	290
CH_2=CHCo(acacen)dmf	−1.77			dmf/0.2*M* Et_4NClO_4 [e]	290
Mecobalamin		−1.39 [c]		H_2O/0.1*M* K_2SO_4 [f]	293
Mecobalamin		−1.55 [c]		H_2O/0.1*M* K_2SO_4 [f]	294
Etcobalamin		−1.37 [c]		H_2O/0.1*M* K_2SO_4 [f]	293
Etcobalamin		−1.37 [c]		H_2O/0.1*M* K_2SO_4 [f]	293
$HOCH_2CH_2$cobalamin		−1.39 [c]		H_2O/0.1*M* K_2SO_4 [f]	293
$MeOCH_2CH_2$cobalamin		−1.38 [c]		H_2O/0.1*M* K_2SO_4 [f]	293
CH_2=CHcobalamin		−1.53 [c]		H_2O/0.1*M* K_2SO_4 [f]	293
5'-Deoxyadenosylcobalamin		−1.37 [c]		H_2O/0.1*M* K_2SO_4 [f]	293
$H_2NCH_2CH_2$cobalamin		−1.35 [c]		H_2O/0.1*M* K_2SO_4 [f]	293
$H_2NCH_2CH_2$cobalamin		−1.52 [c]		H_2O/0.1*M* K_2SO_4 [f]	294
$^-O_2CCH_2$cobalamin		−1.40 [c]		H_2O/0.1*M* K_2SO_4 [f]	293
HO_2CCH_2cobalamin		−0.84 [c]		H_2O/0.1*M* K_2SO_4 [f]	293

(Table continued)

TABLE 24 (continued)

Compound	$E_{1/2}$(V)			Solvent	Ref.
	I	II	III		
MeO_2CCH_2cobalamin		−1.14 [c]		H_2O/0.1M K_2SO_4 [f]	293
Mecobinamide-aq	−1.17	−1.44 [c]		H_2O/0.1M K_2SO_4 [f]	293
Mecobinamide-imidazole	−1.19			H_2O/0.1M K_2SO_4 [f]	293
Mecobinamide-CN^-	−1.25			H_2O/0.1M K_2SO_4 [f]	293
5'-Deoxyadenosylcobinamide	−1.30			H_2O/0.1M K_2SO_4 [f]	294

[a] *vs.* SCE at 25°, except where stated. [b] *vs.*. Ag/$AgNO_3$ (0.1M) electrode. [c] 2-Electron reductions. [d] Due to MeCo(dotnH)Me formation, see next line. [e] At 0°; dmf = dimethylformamide. [f] At 20°.

(IV) Insertion reactions

(a) Oxygen.

Organocobaloximes undergo both photochemical and thermal insertion of oxygen. Thus, on irradiation of a solution of a simple alkylcobaloxime in the presence of oxygen, a peroxyalkyl product is formed in which the ^{1}H NMR of the α-proton is some 1−2 ppm lower than in the substrate[298]. For example, the α-proton resonance of benzylcobaloxime and of benzylperoxycobaloxime are at τ7.15 and 5.70 respectively. The mechanism of the reaction is not known, but it is believed that the axial base ligand is labilised in the excited state[297a] and that the resulting five-coordinate complex reacts so rapidly with oxygen that the rate determining step is usually the absorption of light[298a]. Consequently, benzyl- and sec-octyl-cobaloxime react at very similar rates. A chain reaction seems improbable, though an initial homolysis of the carbon bond seems probable. An alternative mechanism might be:

$$RCo(dmgH)_2py \xrightarrow{h\nu} RCo(dmgH)_2 + py \quad (194)$$

$$RCo(dmgH)_2 + O_2 \rightleftharpoons RCo(dmgH)_2OO\cdot \ (cis?) \quad (195)$$

$$RCo(dmgH)_2OO\cdot + py \longrightarrow ROOCo(dmgH)_2py \quad (196)$$

The thermal insertion is of special interest because an optically active alkylperoxycobaloxime has been obtained from the thermal insertion reaction of an optically active alkylcobaloxime[299a]. This is in contrast to the other known oxygen insertion reactions of organometallic compounds, in which there is complete loss of optical activity[301]. The thermal reaction is only observed with the less stable organocobaloximes, such as allyl-

and α-phenylethylcobaloximes. For example the latter undergoes almost complete reaction with oxygen within a few minutes in dichloromethane solution[299]. With substituted allylcobaloximes, rearrangement of the allyl group occurs during the insertion (eq. 197). Such a rearrangement might be the result of formation of an allyl fragment or of a six-membered cyclic transition state.

$$MeCH{=}CHCH_2Co(dmgH)_2py + O_2 \longrightarrow CH_2{=}CHCHMeOOCo(dmgH)_2py \quad (197)$$

(b) Sulphur dioxide

Many alkylcobalt(III) compounds react with sulphur dioxide to give the corresponding alkanesulphonylcobalt(III) compounds[13,152,300]. The reactions of the methylcobalt compounds in liquid sulphur dioxide are relatively slow at room temperature (eqs. 198–200) compared with the reaction of the allylcobaloximes (eqs. 202 and 201). No reaction is observed with vinylcobaloximes, even over several months in liquid sulphur dioxide[73].

$$RCo(dmgH)_2py + SO_2 \longrightarrow R(SO_2)Co(dmgH)_2py \quad (198)$$

$$MeCo(salen) + SO_2 \longrightarrow Me(SO_2)Co(salen) \quad (199)$$

$$MeCo(CN)_5^{3-} + SO_2 \longrightarrow Me(SO_2)Co(CN)_5^{3-} \quad (200)$$

In the reaction of allylcobaloximes either complete rearrangement, or no rearrangement, is usually observed (eqs. 201 and 202, respectively). On the basis of the relative rates of reaction, the rearrangement of the allyl groups, and the low yields of normal insertion products obtained from the 6-hexenyl- and 4-butenyl-cobaloximes, a free radical mechanism for the insertion has been postulated.

The alkanesulphonylcobaloximes are stable under a wide range of conditions and are believed to contain the Co–S–R linkage, whereas the allylsulphonylcobaloximes, which are readily hydrolysed by wet sulphur dioxide (eq. 203) to the corresponding olefin, are believed to contain the Co–O–S-allyl linkage[73].

$$MeCH{=}CHCH_2Co(dmgH)_2py + SO_2 \longrightarrow CH_2{=}CHCHMeSO_2Co(dmgH)_2py \quad (201)$$

$$PhCH{=}CHCH_2Co(dmgH)_2py + SO_2 \longrightarrow PhCH{=}CHCH_2SO_2Co(dmgH)_2py \quad (202)$$

$$PhCH{=}CHCH_2SO_2Co(dmgH)_2py + H_2O \xrightarrow{SO_2} PhCH{=}CHCH_3 + {}^{+}{}^{-}O_3SCo(dmgH)_2py \quad (203)$$

(c) Carbon monoxide

The photochemical decomposition of organocobalt(III) compounds in alcoholic solution in the presence of carbon monoxide does not give the acylcobalt(III) species. Instead, the alkoxycarbonylcobalt(III) species is formed in which the alkoxy group is derived

from the solvent, (eq. 204)[18,283,285]. The reaction is believed to involve an initial homolysis of the carbon–cobalt bond (eq. 205) followed by further reactions of the radical species with the solvent and with oxygen.

$$RCo(chelate)L + CO \xrightarrow[h\nu]{R'OH} R'OCOCo(chelate)L \qquad (204)$$

(R = alkyl, aryl; Chel = acacen, salen; L = aq, py; R′ = Me, Et, i-Pr).

Oxidation of the solvent also takes place, presumably via the abstraction of a hydrogen atom from the α-carbon (rather than from the hydroxyl group) (eq. 206). The cobalt(II) fragment does not react with carbon monoxide, but the cobalt(III) species formed after reaction with molecular oxygen does coordinate to carbon monoxide and the product reacts with the solvent or with alkoxide ion to give the observed alkoxycarbonylcobalt (III) species, which has been prepared independently from the reaction of alkoxycobalt (III) species with carbon monoxide, and from the reaction between cobalt(I) species and chloroformates (eq. 209).

$$RCo(salen)aq \rightleftharpoons R\cdot + Co^{II}(salen) + H_2O \qquad (205)$$

$$R\cdot + MeOH \longrightarrow RH + \cdot CH_2OH \qquad (206)$$

$$Co^{II}(salen) + MeOH \xrightarrow{O_2} MeOCo(salen) \qquad (207)$$

$$MeOCo(salen) + CO \longrightarrow MeOCOCo(salen) \qquad (208)$$

$$MeOCOCl + Co^{I}(salen)^- \longrightarrow MeOCOCo(salen) + Cl^- \qquad (209)$$

CHEMICAL ASPECTS OF BIOLOGICALLY IMPORTANT REACTIONS

The importance of cobalt corrinoids in a number of biochemical reactions has been known for some time, but it was not until 1958 that a B_{12} derivative was shown to be an obligatory cofactor; in the fermentation of glutamate by *Clostridium tetanomorphum*. Barker isolated the adenyl coenzyme (I; with adenine as the axial ligand) and showed that it was an essential requirement in the catalysis of the rearrangement of glutamic acid to β-methylaspartic acid by cell-free extracts of *C. tetanomorphum*[302,311]. When the same bacteria are grown in the presence of 5,6-dimethylbenzimidazole, vitamin B_{12} coenzyme (I) is formed and may be isolated by appropriate extraction techniques carried out in the absence of light[303]. A lack of appreciation of the light sensitivity of these compounds, and an early realisation that stable materials could be more readily isolated from the extracts after treatment with cyanide ion, were two factors which delayed the isolation of the pure coenzyme[302,304,308].

There is little doubt that the coenzyme is the most abundant naturally occurring

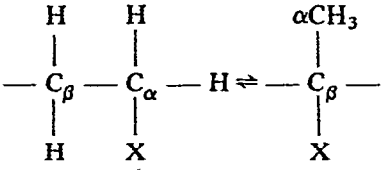
cobalt corrinoid. It has been isolated from a number of sources, including both micro-organisms and mammalian tissues. However, the other organocobalt corrinoids which occur naturally are manifold and a number of these have been isolated and at least partially characterised; these are described in Table 1. Numerous different derivatives may also be present in a single source. For example, sixteen different organocobalt(III) compounds have been identified in extracts from *C. thermoaceticum*. In humans, 5,6-dimethylbenzimidazole-5′deoxyadenosylcobalamin is found in the liver[309], whereas the corresponding methylcobalamin is the main cobalt-containing component in blood plasma[310].

The biosynthesis of the coenzyme from cobalt precursors is catalysed by extracts of *C. tetanomorphum* and *Propionobacterium shermanii*[305–307], but also requires the presence of a reducing system and ATP. It is believed that the reducing system converts the cobalt species to the nucleophilic cobalt(I) state which then attacks the 5′-carbon of the enzyme-bound ATP to form the coenzyme and inorganic tripolyphosphate, pyrophosphate, or orthophosphate. The analogous chemical synthesis has not been achieved directly from ATP, but requires a protected derivative such as 2′,3′-isopropylidene-5′-deoxyadenosyl-*p*-toluenesulphonate (p. 73). Reduced flavin, thioprotein and reduced ferredoxin are believed to be effective naturally occurring reducing agents.

(a) Rearrangement reactions catalysed by B_{12} coenzyme

The first reaction which was shown to be catalysed by the B_{12} coenzyme was the rearrangement of glutamic acid to β-methylaspartate (eq. 210)[312,313]. Subsequently, the coenzyme has been found to be required in a wide range of similar skeletal 1,2-rearrangements. These rearrangements all have the general form shown in eq. 211 in which the group X on C_α exchanges with a hydrogen on C_β. Thus, in the rearrangement of glutamic acid and in the rearrangement of β-methylaspartic acid, the migrating group X is carboxyl.

$$HO_2CCH_2CH_2CH(NH_2)CO_2H \rightleftharpoons HO_2CCHMeCH(NH_2)CO_2H \qquad (210)$$



(211)

Other examples in which the migrating group is carboxyl (or a carboxyl derivative) are: (i) the rearrangement of methylmalonyl coenzyme A to succinyl coenzyme A (eq. 212)[315–316] and (ii) the rearrangement of α-methyleneglutarate (eq. 213)[317]. The migrating group is underlined in the equations.

$$HO_2CCH_2CH_2\underline{COScoA} \rightleftharpoons HO_2CCHMe\underline{COScoA} \qquad (212)$$

$$\underline{HO_2C}CH_2CH_2C(=CH_2)CO_2H \rightleftharpoons \underline{HO_2C}CHMeC(=CH_2)CO_2H \quad (213)$$

Examples in which the amino group migrates from C_α to C_β are (i) reversible rearrangement of L-β-lysine[317] (eq. 214); (ii) the reversible rearrangement of D-α-lysine[318] (eq. 215); (iii) the reversible rearrangement of ornithine[319–320] (eq. 216); and (iv) the deamination of ethanolamine[1,322] (eq. 217).

$$\underline{H_2N}CH_2CH_2CH(NH_2)CH_2CO_2H \rightleftharpoons \underline{H_2N}CHMeCH_2CH(NH_2)CH_2CO_2H \quad (214)$$

$$\underline{H_2N}CH_2CH_2CH_2CH(NH_2)CO_2H \rightleftharpoons \underline{H_2N}CHMeCH_2CH_2CH(NH_2)CO_2H \quad (215)$$

$$\underline{H_2N}CH_2CH_2CH(NH_2)CO_2H \rightleftharpoons \underline{H_2N}CHMeCH_2CH(NH_2)CO_2H \quad (216)$$

$$\underline{H_2N}CH_2CH_2OH \longrightarrow CH_3CHO + NH_3 \quad (217)$$

In the latter reaction, as in the dehydrations described below, the migrations are believed to precede the actual loss of ammonia or water, respectively[325,326]. For example, the first stage in the reaction shown in eq. 217 would be:

$$\underline{H_2N}CH_2CH_2OH \rightleftharpoons CH_3CH(OH)(\underline{NH_2}) \quad (218)$$

In the dehydration of diols, catalysed by diol dehydrase[220,324], the migrating group X is hydroxyl, *i.e.*:

$$RCH(\underline{OH})CH_2OH \longrightarrow RCH_2CHO + H_2O \quad (R = H, Me, HOCH_2) \quad (219)$$

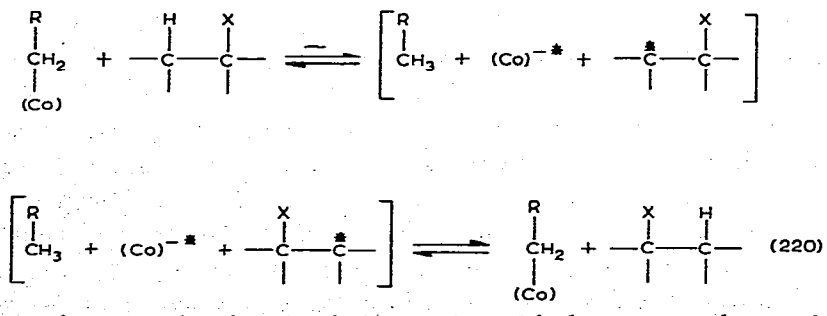
The mechanisms of these reactions and the part played by the cobalt species present a formidable challenge, and the knowledge of organocobalt chemistry described in the preceding sections is of assistance only in understanding the chemical processes which may occur. The way in which these may be controlled and modified by the enzyme system is much more difficult to ascertain, especially as the structures of the relevent enzymes and the role of other cofactors have not yet been determined. However, a number of experiments, particularly those involving the use of isotopic tracers with crude and partially purified enzymes, have provided information about the stereochemical course and other features of the rearrangements, which allow broad conclusions to be drawn about the role of organocobalt compounds.

For example, the absence of exchange of the migrating β-proton with the medium has been demonstrated in the isomerisation of β-methylaspartate[314,327], in the rearrangement of methylmalonyl coenzyme A[328,325], the dehydration of propanediol[329,330] (eq. 219; R = Me), and in the deamination of ethanolamine[323,331]. The absence of exchange of the

migrating amino group with ammonium ion in solution has been demonstrated in the rearrangement of β-lysine[332] and of glutamic acid[327]. Similarly, the aldehydic oxygen of the acetaldehyde formed in the deamination of ethanolamine comes from the substrate and not from the solvent[323,326].

By the use of deuterium and tritium tracers on the β-carbon of the substrate and on the 5′-carbon of the coenzyme, it has been shown that the β-hydrogen removed from the substrate is first transferred to the 5′-carbon of the coenzyme during the rearrangement of glutamic acid[333], β-methylaspartic acid[313], and methylmalonyl coenzyme A[334], and in the dehydration and deamination of diols[335] and ethanolamine[331], respectively. Moreover, careful examination of the distribution in the products, of the severally-labelled hydrogen atoms of substrate and coenzyme, has shown that, in these cases, the hydrogen which is transferred from the coenzyme to the product is not necessarily that which was first transferred to the 5′-carbon of the coenzyme from the substrate. In fact, in most cases, the hydrogen which is transferred to the 5′-carbon of the coenzyme becomes effectively equivalent to the two hydrogen atoms already on that carbon such that, apart from kinetic isotope effects, it has a one-in-three chance of being transferred to the product[220,313,336]. Such observations are complicated by the extent of the reverse reaction and the appreciable kinetic isotope effects.

The mechanism postulated to account for these observations involves the cleavage of the 5′-carbon to cobalt bond with the formation of 5′-deoxyadenosine and a substrate fragment which may or may not be bound to the cobalt. We formulate the reaction as follows:



(220)

where the square brackets imply interaction with the enzyme, the asterisk implies a positive or negative charge, or an unpaired electron, and the negative asterisk (—*) implies a negative or positive charge, or an unpaired electron respectively. We use asterisks because it is not known whether the reaction involves formally charged fragments, radical fragments, or intermediate organocobalt species involving bond formation between the rearranging fragment and the cobalt fragment.

Some support for the formation of 5′-deoxyadenosine comes from the observation that some free 5′-deoxyadenosine is formed when certain analogue-substrate/coenzyme/enzyme conbinations are allowed to react. For example, substantial quantities of 5′-

-deoxyadenosine have been obtained from partially reacted mixtures of ethylene glycol with ethanolamine ammonia lyase in the presence of vitamin B_{12} coenzyme[337]. Moreover, tracer studies showed that one of the hydrogens in the isolated 5′-deoxyadenosine was derived from a CH group of the glycol. Similarly, 5′-deoxyinosine has been obtained from incomplete reaction mixtures of propane-1,2-diol and dioldehydrase in the presence of 5′-deoxyinosylcobalamin[338]. However, added labelled 5′-deoxyadenosine is not a participant in these reactions, indicating that any nucleoside which is formed, except for that which is aborted, remains within the enzyme complex.

Clearly, the main uncertainty lies in the character of the hydrogen transfer steps, because migrations of functional groups (X) are well established for ionic and free radical species. There is some evidence for free radical species present during the reactions and some evidence that cobalt(I) species may also be formed, but it is unwise to assume that exactly the same mechanism operates in all the rearrangements. For example, spectrophotometric measurements during the reaction of propanediol with glycerol dehydrase in the presence of B_{12} coenzyme[339] show that the concentration of B_{12r} increases to a maximum during the reaction and then decreases. The maximum concentration coincides with the maximum rate of product formation and the level of unpaired electrons at this maximum is very high (*i.e.* ca. 0.5 e^- per mole of B_{12} coenzyme employed). Though the electron spin resonance spectrum almost disappears towards the end of the reaction, it reappears on the addition of more substrate.

The evidence for a free radical mechanism is less clear in the reaction of ethanolamine with ethanolamine ammonia lyase in the presence of B_{12} coenzyme. In this reaction, though free radicals have been detected[339a], their concentrations are rather low and the time of attainment of maximum radical concentration does not coincide with the maximum rate of product formation. It is possible therefore that some of these observations indicate that free radical side reactions may take place.

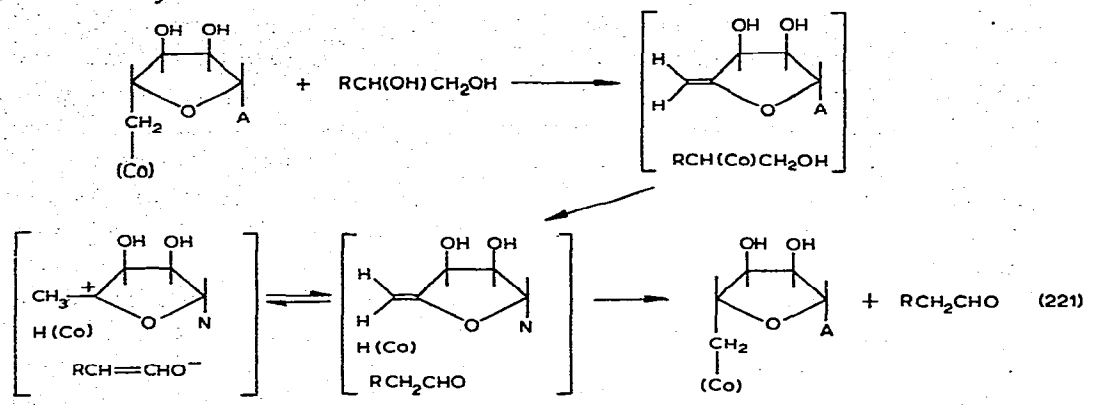
Evidence for the formation of cobalt(I) species during the diol dehydrase reactions comes from the observation that nitrous oxide, which reacts rapidly with cobalt(I) but not with cobalt(II), inhibits this reaction[341]*. In contrast, it has been reported that the rearrangement of methylmalonyl coenzyme A is not inhibited by nitrous oxide[313].

An alternative mechanism has been put forward for the diol dehydrase reactions which involves the formation of an intermediate β-hydroxyethylcobalamin (eq. 221)[138,341], which breaks down to form acetaldehyde and a cobalt(I) species. The coenzyme is believed to have two functions in this mechanism; first, to supply cobalt(I) species for the formation of the β-hydroxyethylcobalamin, and secondly, to allow hydrogen exchange between the product acetaldehyde and the nucleoside fragment. It has been estimated[138] that the variation of hydrogen transfer as a function of time, for this mechanism, is similar to that proposed for the mechanism shown in eq. 220, but there is some disagreement over these conclusions[340,220].

These disagreements illustrate the problems of using solely details of reactants and products for verification of the subtleties of mechanism. Indeed, the calculations do

* See, however, ref. 595.

depend markedly on the choice of kinetic isotope effects for the transfer of hydrogen, deuterium, and tritium. Approximations must be made, for few if any direct measurements of isotope effects of single steps can be made. Some of the isotope effects that have been deduced are remarkably large; for example, a value $k_H/k_T = 160$ has been estimated for the transfer of hydrogen and tritium from the 5′-carbon of the coenzyme to the product in the deamination of ethanolamine[342]. Experience of simple organic reactions involving hydrogen transfer steps suggests that such a high value may only be achieved if quantum mechanical tunnelling is taking place[343]. Whilst this cannot be completely ruled out, a more rigorous examination of the system might prove fruitful, with detailed consideration of possible additional steps which may serve to exaggerate the isotope effects by, for example, multiple isotopic fractionation. Similar high isotope effects have been deduced for the diol dehydrase reactions[340].

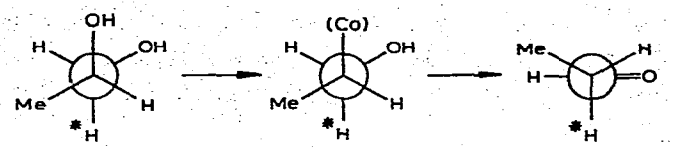


(221)

The mechanisms must also account for the stereospecificity which has been demonstrated for these processes. For example, elegant isotopic labelling experiments have shown that the rearrangement of β-methylaspartic acid[344] and the rearrangement involved in the dehydration of propane-1,2-diol[345,346] occur with inversion of configuration at the α-carbon to which the hydrogen migrates. Whilst such inversion is probably consistent with the mechanism for the diol dehydrase reaction according to equation 220, it is only consistent with the mechanism of equation 221 if the intermediate β-hydroxyethylcobalamin is formed from the diol with retention of configuration (eq. 222). In view of the fact that the known nucleophilic displacements of ester groups from saturated carbon by metal nucleophiles takes place with inversion of configuration, the required retention seems unlikely.

Moreover, in the diol dehydrase reaction and in the deamination of ethanolamine, only one of the two diastereotopic β-hydrogens is transferred from the substrate to the coenzyme[334,342]. If hydrogen transfer were from preformed acetaldehyde to the 5′-carbon of the nucleoside fragment (eq. 221), then the enantiotopic hydrogens of the acetaldehyde would have an equal chance of being transferred, even in the asymmetric environment of

the enzyme, unless the carbonyl carbon were made asymmetric by some appropriate prior carbonyl addition reaction.



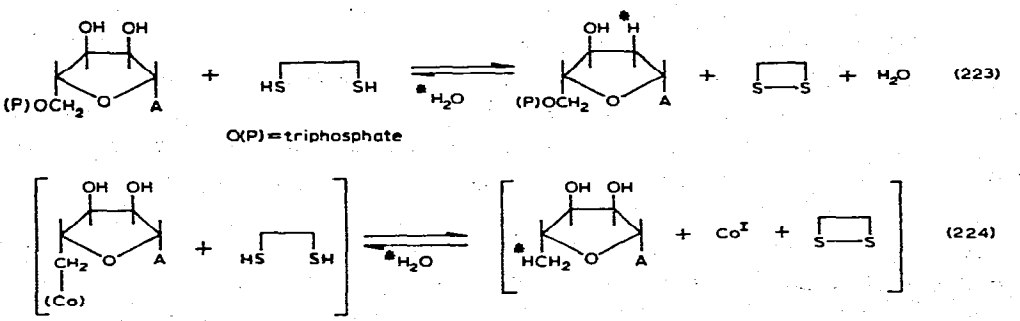
(222)

The dangers of considering that all of these reactions proceed via a common mechanism are further exemplified by the fact that the rearrangement of methylmalonyl coenzyme A occurs with retention of configuration[347] at the α-carbon to which the hydrogen is transferred.

(b) Other reactions catalysed by B_{12} coenzyme

One further reaction is known which requires B_{12} coenzyme as an obligatory cofactor, but does not involve a 1,2-rearrangement. This is a reduction of ribonucleoside triphosphates to 2′-deoxyribonucleoside triphosphates[348–350]. This reaction differs from the rearrangement reactions in that exchange of hydrogens does occur between solvent water and the 5′-hydrogens of the coenzyme. Consequently, hydrogens from the solvent appear in the product (eq. 223). This has been ascribed to the fact that the dithiol reductant undergoes rapid proton exchange with the solvent prior to reduction of the coenzyme. However, reduction of the coenzyme by a dithiol probably involves attack of solvent protons directly on the 5′-carbon (eq. 224).

Both 1,4- and 1,3-dithiols, such as dihydrolipoate, are effective reductants[351] and the reduction is stereospecific; the incoming hydrogen has the same configuration as the outgoing hydroxyl group[351a], but the detailed mechanism of the reduction process is obscure. The specificity of B_{12} coenzyme is fairly complete, even 2′,5′-dideoxyadenosylcobamides are ineffective[352], and enzymic activity has been demonstrated in extracts of *C. tetanomorphum, C. Sticklandii,* and *Lactobacillus acidophilus.* Free radical species have been detected during the course of the reduction process[353].



(223)

(224)

(c) Reactions catalysed by other cobalt(III) species

A third class of reactions do not involve the B_{12} coenzyme, but do require the presence of other organocobalt cobamides. In these reactions it is probable that methylcobamides are important intermediates. The reactions are as follows: (i) the biosynthesis of methionine; (ii) the biosynthesis of methane from a variety of one-carbon precursors; (iii) the biosynthesis of acetate.

The biosynthesis of methionine[354,355] is probably the best understood of these reactions, though many of the finer details of the mechanism require to be elucidated. It has been known for some time that an important stage of this reaction involves the transfer of a methyl group from N^5-methyltetrahydrofolate to homocysteine[356], and that this requires the presence of *S*-adenosylmethionine[357], the methyl transferase, and a B_{12} derivative[358] (eq. 225). A similar reaction, catalysed by the same enzyme[359], involves the direct transfer of the methyl group from methylcobalamin to homocysteine[229] (eq. 226).

$$\text{Me-THFA} + \text{HSCH}_2\text{CH}_2\text{CH(NH}_2\text{)CO}_2\text{H} \longrightarrow \text{MeSCH}_2\text{CH}_2\text{CH(NH}_2\text{)CO}_2\text{H} + \text{H-THFA} \quad (225)$$

(Me-THFA = N^5-methyltetrahydrofolate)

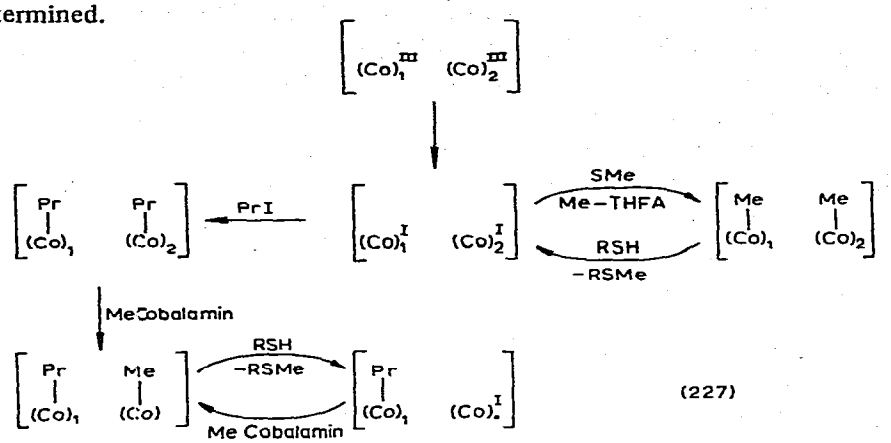
$$\text{Mecobalamin} + \text{HSCH}_2\text{CH}_2\text{CH(NH}_2\text{)CO}_2\text{H} \longrightarrow \text{MeSCH}_2\text{CH}_2\text{CH(NH}_2\text{)CO}_2\text{H} + \text{B}_{12\text{S}} \quad (226)$$

Kinetic studies[360] on the reactions of unlabelled and $^{14}CH_3$-labelled N^5-methyltetrahydrofolate and *S*-adenosylmethionine with homocysteine catalysed by partially purified enzymes have shown that the initial methylation of the cobamide takes place much more rapidly with *S*-adenosylmethionine than with N^5-methyltetrahydrofolate. Once the cobamide has been methylated by the *S*-adenosylmethionine (SMe), exchange of the cobalt-bound methyl groups with those of N^5-methyltetrahydrofolate takes place readily. Studies of the effect of propyl iodide on these reactions indicate that there is more than one cobamide site on the enzyme[359] and that one of these binds a cobamide firmly, the other binds a cobamide only weakly. When the cobamide-enzyme complex is treated with propyl iodide, the firmly bound cobamide is propylated and hence is completely deactivated. The weakly bound cobamide is also propylated but, as it can readily be replaced by added methylcobalamin, the propylated enzyme-cobamide complex is still capable of catalysing reaction 226 (eq. 227). In contrast, methylation of homocysteine by N^5-methyltetrahydrofolate, which appears to involve only the tightly bound cobamide, is greatly inhibited by propylation. The activity of both sites can be restored by photolysis, which causes homolytic cleavage of the propyl carbon–cobalt bond and regeneration of the active bound cobamide species.

The need for added reducing agents in the reactions catalysed by partially purified enzymes clearly suggests that the enzyme bound cobamide is reduced, probably to the

cobalt(I) state, which behaves as a nucleophile towards *S*-adenosylmethionine, N^5-methyltetrahydrofolate, methylcobalamin, or added reagents such as propyl iodide. The order of effectiveness for inhibition by RI (*i.e.*, R = Pr ≫ Et > Me)[361] suggests a parallel with the ease of nucleophilic displacement by and of cobalt(I) from the corresponding alkyl esters and alkylcobalt(III) compounds, respectively. The inhibition by propyl iodide is also greatly reduced in the presence of *S*-adenosylmethionine because the latter succesfully competes with the propyl iodide for the reduced cobamide, thereby bringing about methylation rather than propylation of the cobalt.

The transfer of the methyl groups to the sulphur from the cobalt would appear to involve nucleophilic attack of the sulphur species on the α-carbon of the methylcobamide in a manner discussed on p. 58. However, the subtele role of the enzyme in promoting this displacement, and the exact priming role of the *S*-adenosylmethionine, remain to be determined.



(227)

The biosynthesis of methane. The biological formation of methane from carbon dioxide formate ion, methanol, the methyl carbon of acetate and the β-carbon of serine is also catalysed by cobamide compounds. Indeed, the bacteria *Methanosarcina barkerii* contain so much cobalt that the cells are pink-red[362]. The predominant cobamides in these bacteria and in *Methanobacillus omelianskii*[363] contain a 5-hydroxybenzimidazole group in place of the more common 5,6-dimethylbenzimidazole (shown in I). Several enzyme systems have been investigated. For example, in the conversion of methanol to methane catalysed by *Methanosarcina barkerii*, the methyl group has been shown, by tracer studies, to be transferred intact (eq. 228). Though methylcobamides have not been isolated from these bacteria, it has been demonstrated that ^{14}C-labelled methylcobalamin[233] is formed when ^{14}C-methanol is treated with electrolytically prepared B_{12s} in the presence of extracts of *M. barkerii* and potassium phosphate under an atmosphere of hydrogen.

$$4MeOH \longrightarrow 3CH_4 + CO_2 + 2H_2O \qquad (228)$$

$$^{14}CH_3OH + B_{12s} \longrightarrow {}^{14}CH_3\text{cobalamin} \quad (229)$$

The role of methylcobamides in these processes can only be surmised from the plausibility of the reactions involved, the amount of cobamide species present, and the fact that methylcobamides can be isolated from other systems, such as *Clostridium thermoaceticum*[364]. As in the case of methionine synthesis, the cobamide activity is reduced on treatment with propyl iodide[365] but can be regenerated by photolysis. ATP is also required, but its role has not been elucidated.

The biosynthesis of acetate. The anaerobic synthesis of acetate presents even greater mechanistic problems because of the larger number of reaction steps which must be involved. The acetate may be formed from a number of one-carbon precursors; for example, *Clostridium thermoaceticum* converts a mixture of carbon dioxide and hydrogen into acetic acid[364]. Experiments using labelled carbon dioxide show that both of the acetate carbon atoms may be derived from the carbon dioxide. Cell-free extracts of *C. thermoaceticum* also convert $^{14}CH_3$cobalamin and $^{14}CH_3$-N^5-methyltetrahydrofolate into $^{14}CH_3$-acetate. That the carbon dioxide may be converted into intermediate methylcobamides has been demonstrated by the isolation of $^{14}CH_3$cobamides from *C. thermoaceticum* which has been exposed to $^{14}CO_2$.

These cobamides have been shown to contain 5-methoxybenzimidazole in place of the 5,6-dimethylbenzimidazole shown in (I).

$$4H_2 + 2CO_2 \longrightarrow CH_3CO_2H + 2H_2O \quad (230)$$

$$^{14}CH_3\text{cobalamin} + CO_2 \longrightarrow {}^{14}CH_3CO_2H \quad (231)$$

$$\text{Me-THFA} + CO_2 \longrightarrow CH_3CO_2H \quad (232)$$

It seems probably therefore that methylcobamides are also intermediates in these reactions, but the way in which they are formed from carbon dioxide presents further mechanistic problems. A possible route is via formate ion, and it has been demonstrated that appropriately labelled acetate is formed when labelled formate is used as the one-carbon precursor[366]. A second problem involves the conversion of the methylcobamide species into the acetate ion, *i.e.*, whether the process involves an intermediate α-carboxymethylcobamide or whether cleavage of the carbon–cobalt bond and reaction with carbon dioxide occur synchronously or sequentially. The type of experiment carried out so far only indicates which processes may be possible. For example, labelled α-carboxymethylcobalamin is converted into acetate by extracts of *C. thermoaceticum* and pyruvate[367]. However, it is possible that electrophilic displacement of cobalt by attack of carbon dioxide on the methyl group might be specifically activated by appropriate reducing proteins. Indeed, treatment of methylcobaloxime with carbon dioxide in the presence of a dithiol does give a small yield of acetate[367a].

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TABLE 1.

THE ORGANIC COMPOUNDS OF COBALT(III) (Listed according to the equatorial ligands L_n)

1. Main section headings (repeated on new pages) refer to the equatorial ligand(s) described in Table 2.
2. *Organic Ligands (R)* are arranged in order of increasing carbon chain and increasing unsaturation. *E.g.*, methyl, substituted methyl, ethyl, substituted ethyl, n-propyl, substituted n-propyl, etc., (cycloalkyl follows each alkyl), benzyl, substituted benzyl, miscellaneous cyclic ligands and some unsaturated ligands, vinyl, alkynyl, aryl, alkoxycarbonyl, unspecified ligands. Dicobalt complexes are placed last. As the 'top' and 'bottom' of the corrin ring are not the same, there are some examples in which the organic ligand and the axial base are interchanged. In these cases, the organic group is placed in the 'B' column and the axial base in the 'R' column.
3. *Axial bases (B)* are arranged in the order Hal, N, O, 'none', P, S, C. Ambidentate ligands appear in only one group unless separate complexes have been isolated. Bridged complexes containing bidentate ligands are described in one group only.
4. *Reagent* refers to the main source of R. Other reagents are referred to under method. Alternative reagents are indicated in brackets.
5. *Method.* The preparative method is usually described in the following sequence: a roman numeral referring to Table 3, the inorganic reagent(s), the solvent (/ indicates a mixed solvent or solvent/reagent), and other details. In other cases, especially where no carbon–cobalt bond is formed in the preparation, the method is spelled out.
6. *References.* An asterisk next to a reference number implies that the compound has only been identified in solution.
7. *Variants.* Reference to Fig. 1 and Table 2 will assist in understanding the nature of the variants. The letters a–j refer to the side-chains on the corrin ring (see figures in table 2). The terms *lactam* and *lactone* involve the side-chain (c) and C-8. 10-X refers to substitution by X at C-10. In some cases the side chain has been spelled out, in others, especially where the longest side chain (f) of the corrin has been modified close to the corrin ring, the side-chain is spelled out from the corrin to the end of the modification and terminates with "etc.".
8. Table 1 is essentially complete, except for the two sections headed 'other complexes' and 'natural sources'. The latter includes positive identifications and compounds isolated. It includes the main preparative routes and provides a useful indication of the wide occurrence of these compounds, including those which have not been synthesised chemically.
9. *Abbreviations.* Limitations of the computer necessitate some abbreviations such as NH4Cl for NH_4Cl, a for α, b for β, X(–) for X^-, TRI(X) for X_3, DI(X) for X_2, BH4 for BH_4^-, etc.

Other abbreviations are as follows:

(Co)	a cobalt complex having the same equatorial ligand(s) as are described in the section heading. If no other ligands are shown the species is cobalt(II).
?	insufficient information
A (in notes column)	full analysis in ref.
(A) (in notes column)	partial analysis in ref.
'none'	the complex in which no axial base is apparent. This may include complexes in which the equatorial ligand(s) or the organic group act as an axial base.

ADDITION TO 'NONE' addition of an axial base to 'none'

UNSPEC	unspecified in ref.	BIPY	2,2'-bipyridyl
DISP	displacement	PHEN	*o*-phenanthroline
ALK	alkaline	Gly	glycine; other amino acid abbreviations are standard
NEUT	neutral		
IMID	imidazole	OTs	*p*-toluenesulphonate
BENZIMID	benzimidazole	CPR	controlled potentiometric reduction
c-Hex	cyclohexyl	DISPROP	disproportionation
en	ethylenediamine		

Abbreviations for bacteria:

P	*Propionibacterium*	E	*Escherichia*
C	*Clostridium*	M	*Methanobacillus*

R	REAGENT	METHOD	NOTES	REF
METHYL	RI	IIA; AQ/MeOH OR AQ	(A)	19,20
METHYL	RI	IIA; AQ UNDER HYDROGEN	(A)	20
METHYL-(4-PYRIDYL)	RBr	IIA; AQ	A K SALT	209
METHYL-(3-PYRIDYL)	RBr	IIA; AQ	(A)	369,45
METHYL-(2-PYRIDYL)	RBr	IIA; AQ	A K SALT	369,45
METHYL-CARBOXY	RI(Br,Cl)	IIA; AQ		98
METHYL-METHOXYCARBONYL	RI(Br,Cl)	IIA; AQ		98
METHYL-AMINOCARBONYL	RI(Br,Cl)	IIA; AQ		98
METHYL-SULPHITO	RI	IIA; AQ		98
METHYL-CYANO	RCl	IIA; AQ	(A)	20
METHYL-CYANO	RCl	IIA; AQ UNDER HYDROGEN		46
ETHYL	RI	IIA; AQ/MeOH OR AQ		19,20
ETHYL-2-PHENYL	RI	IIA; AQ		51
ETHYL-2-(PHENYL-4-FLUORO)	RI	IIA; AQ/MeOH		47
ETHYL-2-CHLORO	RI	IIA; AQ		51
ETHYL-2-HYDROXY	RI	IIA; AQ		51
ETHYL-2-ETHOXY	RI	IIA; AQ		51
ETHYL-2-CARBOXY	RI(Br)	IIA; AQ		98
ETHYL-2-METHOXYCARBONYL	RI	IIA; AQ		98,51
ETHYL-2-CYANO	RI	IIA; AQ		51
ETHYL-1-METHYL	RI	IIA; AQ (LOW YIELD)		46,568
ETHYL-1-PHENYL	STYRENE	IIIC; H2 AQ/MeOH		115*
ETHYL-1-PHENYL	STYRENE	IIIC; (Co)/AQ/HEXA(NC)Cr(II) AQ/MeOH		556*
ETHYL-1-(2-PYRIDYL)	2-VINYLPYRIDINE	IIIC; H2 AQ		51,46,114* 115

R	REAGENT	METHOD	NOTES	REF
ETHYL-1-(2-PYRIDYL)	RBr	IIA; AQ		114*
ETHYL-1-(2-PYRIDYL)	2-VINYLPYRIDINE	IIIC; (Co)/AQ/HEXA(NC)Cr(II) AQ/MeOH		556*
ETHYL-1-(4-PYRIDYL)	4-VINYLPYRIDINE	IIIC; H2 AQ		173*
ETHYL-1-CARBOXY	RBr	IIA; AQ		98
ETHYL-1-CARBOXY	ACRYLATE ION	IIIC; H2 AQ		51,115*
ETHYL-1-CARBOXY	ACRYLATE ION	IIIC; AGE IN AQ AQ		120*
ETHYL-1-METHOXYCARBONYL	RBr	IIA; AQ		51
ETHYL-1-METHOXYCARBONYL	METHYL ACRYLATE	IIIC; H2 AQ		51
ETHYL-1-CYANO	RBr	IIA; AQ OR AQ UNDER H?		46
ETHYL-1-CYANO	ACRYLONITRILE	IIIC; H2 AQ	(A)	20
ETHYL-1-CYANO	ACRYLONITRILE	IIIC; H2 AQ/ACETONE(ALK)	A K SALT	115
ETHYL-1-CYANO	ACRYLONITRILE	IIIC; (Co)/AQ/HEXA(NC)Cr(II) AQ/MeOH		556*
ETHYL-1-(PHENYL-4-CYANO)	4-CYANOSTYRENE	IIIC; H2 AQ		51,46
ETHYL-2,2-DIETHOXY	RI	IIA; AQ		51
ETHYL-2-PHENYL-2-KETO	RBr	IIA; AQ	(A)	20
ETHYL-2-PHENYL-2-KETO-1-METHYL	RBr	IIA; AQ		20
ETHYL-2-PHENYL-2-KETO-1-METHYL	VINYL PHENYL KETONE	IIIC; H2 AQ		20
ETHYL-2-PHENYL-1-CYANO	CINNAMONITRILE	IIIC; H2 AQ		51
ETHYL-1,2-DIALKOXYCARBONYL(UNSPEC)	DIALKYLMALEATE	IIIC; H2 AQ		51
ETHYL-1,2-DIALKOXYCARBONYL(UNSPEC)	DIALKYLFUMARATE	IIIC; H2 AQ		51
ETHYL-1,2-DICARBOXY	RBr	IIA; AQ		98
ETHYL-1,2-DICARBOXY	MALEATE ION	IIIC; AGE IN AQ AQ		120*
ETHYL-1,2-DICARBOXY	FUMARATE ION	IIIC; AGE IN AQ AQ		120*
ETHYL-1,2-DICARBOXY-2-D-THREO	FUMARATE ION	IIIC(D(Co)); AGE IN D2O D2O		120*

R	REAGENT	METHOD	NOTES	REF
ETHYL-1,2-DICARBOXY-2-D-ERYTHRO	MALEATE ION	IIIC(D(Co)); AGE IN D2O D2O		120*
ETHYL-1-METHYL-1-CYANO	RI(Cl)	IIA; AQ OR AQ UNDER H2		46
ETHYL-1-METHYL-1-CYANO	PROP-1-ENE-2-CYANO	IIIC; H2 AQ OR AQ/MeOH		46,115*
ETHYL-1-METHYL-1-CYANO	PROP-1-ENE-2-CYANO	IIIC; (Co)/AQ/HEXA(NC)Cr(II) AQ/MeOH		556*
ETHYL-1-METHYL-1-METHOXYCARBONYL	METHYL METHACRYLATE	IIIC; H2 AQ		51,46
ETHYL-1-CARBOXY-2,2-DI(D)	ACRYLATE ION	IIIC(D(Co)); AGE IN D2O D2O		120*
ETHYL-1,1,2,2-TETRAFLUORO	TETRAFLUOROETHYLENE	IIIC; K(Hg) AQ	A K SALT (X-RAY)	25,372 (162)
PROPYL	RI	IIA; AQ/MeOH OR AQ	(A)	19,20
PROPYL-2-METHYL	RI	IIA; AQ		20
PROPYL-2-KETO	RBr	IIA; AQ		51
PROPYL-1-CYANO	CROTONONITRILE	IIIC; H2 AQ		51
PROPYL-1-CARBOXY	TRANS-CROTONATE ION	IIIC; AGE IN AQ AQ		120*
PROPYL-2-D-1-CARBOXY	TRANS-CROTONATE ION	IIIC(D(Co)); AGE IN D2O D2O		120*
PROPYL-2,2-DIMETHYL	RI	IIA; AQ		46
PROPYL-2-PHENYL-2-METHYL	RI	IIA; AQ		46
PROPYL-2-KETO-1-METHYL	RBr	IIA; AQ		51
PROPYL-2-KETO-1-METHYL	BUT-1-ENE-3-KETO	IIIC; H2 AQ		51
CYCLOPROPYL	RBr	IIA; AQ (LOW YIELD)		51
BUTYL	RI	IIA; AQ		20
BUTYL-4-IODO?	RI	IIA; AQ/MeOH		100a*
PENTYL-5-IODO?	RI	IIA; AQ/MeOH		100a*
CYCLOHEXYL-1-CYANO	1-CYANOCYCLOHEXENE	IIIC; H2 AQ		51
1-ADAMANTYL	RI	IIA; AQ/MeOH	A K SALT	570
BENZYL	RBr(I,Cl)	IIA; AQ/MeOH OR AQ	A Na,K SALTS	19,20,368 100a*

R	REAGENT	METHOD	NOTES	REF
BENZYL	RBr	IIA; AQ UNDER HYDROGEN	(A)	20
BENZYL-4-METHYL	RBr(I)	IIA; AQ		51
BENZYL-4-METHOXY	RI	IIA; AQ		51
BENZYL-4-CARBOXY	RBr	IIA; AQ		98
BENZYL-4-FLUORO	RBr	IIA; AQ/MeOH		47
BENZYL-4-BROMO	RBr	IIA; AQ/MeOH		100a*
BENZYL-4-NITRO	RBr	IIA; AQ/MeOH		100a*
BENZYL-a-CYANO	RBr	IIA; AQ OR AQ UNDER H2		46
6-(2-OXONORBORNYL)	2-NORBORNENONE	IIIC; H2 AQ		51
PROP-2-ENYL	RI(Br)	IIA; AQ		370,20
BUT-2-ENYL	RBr	IIA; AQ		370,20
BUT-2-ENYL	1,3-BUTADIENE	IIIC; H2 AQ OR AQ/MeOH		371,370,20, 115*,567
BUT-2-ENYL-4-HYDROXY	RCl	IIA; AQ		51
BUT-2-ENYL-3-METHYL	ISOPRENE	IIIC; H2 AQ/ACETONE(ALK)		115
BUT-2-ENYL-3-METHYL	ISOPRENE	IIIC; H2 AQ		567
VINYL	RCl(Br)	IIIC; H2 AQ	(A)	20,51
PROP-1-ENYL	RBr	IIIC; H2 AQ		51
VINYL-1-PHENYL-2-CARBOXY	PHENYLPROPIOLATE ION	IIIC; H2 AQ		51
VINYL-1-PHENYL	PHENYLACETYLENE	IIIC; H2 AQ		51
ALLENYL	3-Cl-2-Br-PROP-1-ENE	IIA; AQ		51
ALLENYL	3-Br(Cl)-PROP-1-YNE	IIA; AQ		51
VINYL-1,2-DIMETHOXYCARBONYL-TRANS?	DI(METHOXYCARBONYL)-ACETYLENE	IIIC; H2 AQ		24
ETHYNYL?	TRANS-DICHLOROETHYLENE	IIIC; H2 AQ		51
2-PYRIDYL	RI	IIA; AQ	A Na SALT	98

PENTACYANO

R	REAGENT	METHOD	NOTES	REF
PHENYL	PHENYLDIAZONIUM CHLORIDE	IID; AQ		20
(Co)C(=S)-S(Co)	CARBON DISULPHIDE	IIC; AQ	A K SALT	590,591
ETHANE-TETRA(F)-1,2-DI(Co)	TETRAFLUOROETHYLENE	IIC; AQ	A K SALT	25,372
ETHYLENE-1,2-DI(Co)-TRANS?	ACETYLENE	IIC; AQ	A K SALT	4
ETHYLENE-1,2-DI(CN)-1,2-DI(Co)-TRANS?	DICYANOACETYLENE	IIC; AQ		24
ETHANE-TETRA(CN)-1,2-DI(Co)	TETRA(CN)-ETHYLENE	IIC; AQ		24
ETHYLENE-1,2-DI(MeO.CO)-1,2-DI(Co)-TRANS	DI(MeO.CO)ACETYLENE	IIC; AQ	A K SALT	24
ETHYLENE-1,2-DI(EtO.CO)-1,2-DI(Co)-TRANS	DI(EtO.CO)ACETYLENE	IIC; AQ		24
ETHYLENE-1-(MeO.CO)-1,2-DI(Co)-TRANS?	METHYL PROPIOLATE	IIC; AQ		24

TETRACYANO

R	B	REAGENT	METHOD	NOTES	REF
METHYL	CNH	PENTA(CN) ANALOGUE	PROTONATION IN ACID AQ		45*
ETHYL-1-IMINO	AQ?	MeCoPENTA(CN)	ACID CATALYSED INSERTION AQ		45*
ETHYL-1-KETO?	AQ?	1-IMINOETHYL ANALOGUE	ACID HYDROLYSIS		45*
METHYL-(2-PYRIDIO)	CNH	PENTA(CN) ANALOGUE	PROTONATION IN ACID AQ		45
METHYL-(3-PYRIDIO)	CNH	PENTA(CN) ANALOGUE	PROTONATION IN ACID AQ		45
METHYL-(4-PYRIDIO)	CNH	PENTA(CN) ANALOGUE	PROTONATION IN ACID AQ		45
METHYL-(2-PYRIDIO)	AQ	PENTA(CN) ANALOGUE	DISP OF AXIAL CN(-) IN DILUTE ACID AQ		45
METHYL-(3-PYRIDIO)	AQ	PENTA(CN) ANALOGUE	DISP OF AXIAL CN(-) IN DILUTE ACID AQ		45
METHYL-(4-PYRIDIO)	AQ	PENTA(CN) ANALOGUE	DISP OF AXIAL CN(-) IN DILUTE ACID AQ		209
ETHYL-1-(2-PYRIDIO)	CNH	PENTA(CN) ANALOGUE	PROTONATION IN ACID AQ (A SECOND CN(-) IS PROTONATED IN CONC ACID)		114*

R	B	REAGENT	METHOD	NOTES	REF
ETHYL-2-PHENYL-1-IMINO	AQ?	BENZYLCoPENTA(CN)	ACID CATALYSED INSERTION	AQ	238
ETHYL-1-(2-PYRIDIO)	AQ	PENTA(CN) ANALOGUE	DISP OF AXIAL CN(-) IN DILUTE ACID AQ		114*
ETHYL-2-(2-PYRIDIO)-1-IMINO	AQ?	2-PY-MeCoPENTA(CN)	ACID CATALYSED INSERTION	AQ (A)	369,45
ETHYL-2-(3-PYRIDIO)-1-IMINO	AQ?	3-PY-MeCoPENTA(CN)	ACID CATALYSED INSERTION	AQ	45*
ETHYL-2-(4-PYRIDIO)-1-IMINO	AQ?	4-PY-MeCoPENTA(CN)	ACID CATALYSED INSERTION	AQ	45
ETHYL-2-(X-PYRIDIO)-2,2--DIDEUTERIO-1-DEUTERIOIMINO?	D2O?	X-PY-MeCoPENTA(CN) (X = 2,3,4)	ACID CATALYSED INSERTION	D2O	45*
PROPYL-2-(2-PYRIDIO)--1-IMINO	AQ?	1-(2-PY)-EtCoPENTA(CN)	ACID CATALYSED INSERTION	AQ (A)	114
BUTYL-1-IMINO	AQ?	PROPYLCoPENTA(CN)	ACID CATALYSED INSERTION	AQ	238

BIS(GLYOXIMATO)

R	B	REAGENT	METHOD	NOTES	REF
METHYL	PY	RI	IIIA; BH4 MeOH	A	118
CYCLOHEXYL-2,2-DIDEUTERIO	PY	RX	IIIA; BH4? MeOH	A	107

BIS(DIMETHYLGLYOXIMATO)

R	B	REAGENT	METHOD	NOTES	REF
METHYL	PY		ADDITION TO NONE		136*
METHYL	PY	TRI(Me)PbBr	IIIA; BH4 MeOH		97a
METHYL	PY	MeHgCl	IIIA; BH4 MeOH		97a
METHYL	PY	DI(Me)SULPHATE OR MeI	IIIA; BH4 MeOH	A	118,50
METHYL	PY	MeI	IIIA; BH4 AQ/EtOH	A	129

R	B	REAGENT	METHOD	NOTES	REF
METHYL	PY	MeI	IIIA; MeSH MeOH?,THEN PY (LOW YIELD)		79
METHYL	PY	1,1-DI(Me)PIPERIDINIUM IODIDE	IIIA; BH4 MeOH		29
METHYL	PY	1-MePIPERIDINE/DI(METH-OXYCARBONYL)ACETYLENE	IIIA; BH4 MeOH		29
METHYL	PY	MeI	IIIA; NaOH + TRI(R)Sn(Co) MeOH		97a
METHYL	PY		DISP OF AXIAL AQ	A	74,566*
METHYL	PY	MeI	IIIA; NaOH + 2-NC-Et(Co) MeOH		39
METHYL	PY	MONO- OR DI-(X)Me(Co)	EXCESS BH4 MeOH (X=Cl,Br)		32
METHYL	PY-4-Br	MeI?	IIIA?; BH4? MeOH?	A	132a
METHYL	PY-4-Me	MeI	IIIA; ALK DISPROP MeOH	A	74
METHYL	PY-4-Me	RI?	IIIA; BH4 MeOH		571
METHYL	PY-4-Me		DISP OF AXIAL AQ		74,374*,566*, 571*
METHYL	PY-4-Et		DISP OF AXIAL AQ	A	386
METHYL	PY-4-OEt	MeI?	IIIA?; BH4? MeOH?	A	132a
METHYL	PY-4-MeO.CO	MeI?	IIIA?; BH4? MeOH? (B=PY-4-CN?)	A	132a
METHYL	PY-4-AMINOCARBONYL		DISP OF AXIAL AQ		566*
METHYL	PY-4-CN		DISP OF AXIAL AQ		374*,132a,566*, 571
METHYL	PY-4-AMINO	RI?	IIIA; BH4 MeOH		571
METHYL	PY-4-AMINO		DISP OF AXIAL AQ		374*,566*,571*
METHYL	PY-3-Br	MeI?	IIIA?; BH4? MeOH?	A	132a
METHYL	PY-3-Me	MeI?	IIIA?; BH4? MeOH?	A	132a
METHYL	PY-3-OEt		DISP OF AXIAL AQ?		132a
METHYL	PY-3-MeO.CO	MeI	IIIA; BH4 MeOH (B=PY-3-CN; + ONE PROD)	A	132a

R	B	REAGENT	METHOD	NOTES	REF.
METHYL	PY-3-CN	MeI	IIIA; BH4 MeOH (+ ONE PROD)	A	132a
METHYL	NICOTINAMIDE	MeI	IIIA; BH4 OR ALK DISPROP MeOH	A	74
METHYL	PY-2-Me		IIIA?; BH4? MeOH?	A	65
METHYL	PY-2,4,6-TRI(Me)		DISP OF AXIAL AQ?		375
METHYL	ISOQUINOLINE	MeI	IIIA; BH4 MeOH		152
METHYL	PYRAZINE-2-Me		DISP OF AXIAL AQ?		375
METHYL	PYRAZOLE		DISP OF AXIAL AQ?	A	132a
METHYL	IMID	MeI	IIIA; BH4 OR ALK DISPROP MeOH	A	65,74
METHYL	1-MeIMID	MeI?	IIIA?; ALK DISPROP? MeOH?	A	132a
METHYL	BENZIMID	MeI	IIIA; BH4 MeOH	A	118
METHYL	AMMONIA		DISP OF AXIAL AQ	A	184*,65
METHYL	PIPERIDINE	MeI?	IIIA?; BH4? MeOH?	A	132a
METHYL	MORPHOLINE		DISP OF AXIAL AQ?		132a
METHYL	TRI(Me)N		ADDITION TO NONE		137*,136*
METHYL	ANILINE	MeI	IIIA; BH4 MeOH	A	118
METHYL	ANILINE-4-Me	MeI	IIIA; BH4 OR ALK DISPROP MeOH	A	74
METHYL	2-MeO-ETHYLAMINE		DISP OF AXIAL AQ		566*
METHYL	2,2-DI(MeO)ETHYLAMINE		DISP OF AXIAL AQ		566*
METHYL	2,2,2-TRI(F)ETHYLAMINE		DISP OF AXIAL AQ		566*
METHYL	PROPYLAMINE		DISP OF AXIAL AQ		566*
METHYL	3-MeO-PROPYLAMINE		DISP OF AXIAL AQ		566*
METHYL	BENZYLAMINE		DISP OF AXIAL AQ	A	140,132a
METHYL	BENZYLAMINE		DISP OF AXIAL NITROGEN BASES		132a*
METHYL	BENZYL-NHMe		DISP OF AXIAL AQ	A	140,132a

BIS(DIMETHYLGLYOXIMATO)

A	B REAGENT	METHOD	NOTES	REF
METHYL	Gly-Et ESTER	DISP OF AXIAL AQ		140*,140a*
METHYL	Leu-Me ESTER	DISP OF AXIAL AQ	A	140
METHYL	L-Phe-Me ESTER	DISP OF AXIAL AQ	A	140,140a
METHYL	L-Try-Me ESTER	DISP OF AXIAL AQ	A	140,140a
METHYL	L-Glu-DI(Me)ESTER	DISP OF AXIAL AQ	A	140,140a
METHYL	SARCOSINE-Et ESTER	DISP OF AXIAL AQ		140a*
METHYL	L-Ala-Me ESTER	DISP OF AXIAL AQ	A	140a
METHYL	L-Val-Me ESTER	DISP OF AXIAL AQ	A	140a
METHYL	L-Thr-Me ESTER	DISP OF AXIAL AQ	A	140a
METHYL	L-Asp-Me,t-Bu ESTER	DISP OF AXIAL AQ		140a*
METHYL	L-Phe-BENZYL ESTER	DISP OF AXIAL AQ	A	140a
METHYL	L-His-Me ESTER	DISP OF AXIAL AQ		140a*
METHYL	L-Val-Me ESTER-N-DI(D)	EXCHANGE OF PROTONS IN D2O		140a*
METHYL	L-Phe-BENZYL ESTER-N-DI(D)	EXCHANGE OF PROTONS IN D2O		140a*
METHYL	L-His-Me ESTER-N-DI(D)	EXCHANGE OF PROTONS IN D2O		140a*
METHYL	AZIDE(-)	DISP OF AXIAL AQ	A AsPh4 SALT	184*,123
METHYL	NCS(-)	DISP OF AXIAL AQ	A AsPh4 SALT	184*,185*,123
METHYL	NCO(-)	DISP OF AXIAL AQ	A AsPh4 SALT	123
METHYL	AZIDE(Co)Me(-)	DISP OF AXIAL AQ	A AsPh4 SALT	123
METHYL	NC(Co)Me(-)	DISP OF AXIAL AQ	A NBu4 SALT	123
METHYL	NC(Co)CN(-)	DISP OF AXIAL AQ		123*
METHYL	NCCoBIS(c-hgH)Me(-)	DISP OF AXIAL AQ		123*
METHYL	NC(Co)CN(Co)Me(-)	DISP OF AXIAL AQ	A AsPh4 SALT	123
METHYL	NC(Co)-n-OCTYL(-)	DISP OF AXIAL AQ		123*
METHYL	NC(Co)-s-OCTYL(-)	DISP OF AXIAL AQ		123*

R	B	REAGENT	METHOD	NOTES	REF
METHYL	NC(Co)-c-HEXYL(-)		DISP OF AXIAL AQ		123*
METHYL	NC(Co)BENZYL(-)		DISP OF AXIAL AQ		123*
METHYL	NC(Co)BENZYL-3-MeO(-)		DISP OF AXIAL AQ		123*
METHYL	NC(Co)VINYL(-)		DISP OF AXIAL AQ		123*
METHYL	NC(Co)-i-PROPENYL(-)		DISP OF AXIAL AQ		123*
METHYL	NC(Co)VINYL-2-Ph(-)-TRANS		DISP OF AXIAL AQ		123*
METHYL	NC(Co)VINYL-2-Ph(-)-CIS		DISP OF AXIAL AQ		123*
METHYL	NC(Co)VINYL-1-Ph(-)		DISP OF AXIAL AQ		123*
METHYL	NC(Co)ETHYNYL-Ph		DISP OF AXIAL AQ		123*
METHYL	NCCo(dmgH)-(dmgH2)Me	RCoBIS(dmgH)CN(-)	ACIDIFICATION OF AQ. SOLN.	A	373
METHYL	SCN(Co)Me(-)		DISP OF AXIAL AQ		121*
METHYL	MeCN		ADDITION TO NONE		137*, 136
METHYL	MeCN-TRI(D)		DISP OF AXIAL AQ		136*
METHYL	4-AMINO-2,2,6,6-TETRA(Me)-PIPERIDINE-N-OXYL		DISP OF AXIAL AQ?		297a*
METHYL	DMF		ADDITION TO 'NONE'		575*
METHYL	NITRITO(-)		DISP OF AXIAL AQ	A AsPh4 SALT	373
METHYL	AQ		DISP OF AXIAL SCN(-) WITH Ag(+)		184*
METHYL	AQ		DISP OF AXIAL DI(Me)S	A	118,50
METHYL	AQ	MeI	IIIA; H2 MeOH		118,50
METHYL	AQ		DISP OF AXIAL PY ON ACIDIC RESIN AQ/MeOH		118
METHYL	AQ		DISP OF AXIAL PY BY METHYLATION WITH DIMETHYL SULPHATE MeOH		118
METHYL	AQ		DISP OF RS(-) IN ACIDIC AQ		205a*
METHYL	AQ	MeCo(acacen)AQ	IA; AQ/MeOH		290

A	B	REAGENT	METHOD	NOTES	REF
METHYL	AQ	MeCo(salen)AQ	IA; AQ/MeOH		290
METHYL	AQ	MeI	IIIA; ALK DISPROP MeOH	A	74
METHYL	AQ	MeCo(salphen)AQ	IA; AQ/MeOH		290
METHYL	AQ		DISP OF AXIAL PY BY IRRADIATION IN MeOH		297a
METHYL	AQ		DISP OF AXIAL PY IN ACID AQ.		584*
METHYL	OH(-)?		AQ COMPLEX IN ALKALI (POSS. dagH IONISATION?)		184*,205i*,566
METHYL	NONE		REMOVAL OF AXIAL AQ	A	118,376,141,575
METHYL	NONE		REMOVAL OF AXIAL DI(Me)S		376
METHYL	TRI(Ph)P	MeMgI	IA; THF	A	12
METHYL	TRI(Ph)P	DIAZOMETHANE	IIIC; BH4 MeOH/ETHER	A	12
METHYL	TRI(Ph)P	MeI	IIIA; BH4 MeOH	A	118
METHYL	TRI(Ph)P	MeI	IIIA; BH4 AQ/EtOH	A	129
METHYL	TRI(Ph)P		DISP OF AXIAL PY		118
METHYL	TRI(Ph)P		ADDITION TO NONE		137*,136*
METHYL	DI(Ph)PH		DISP OF AXIAL AQ?		128
METHYL	DI(Ph)PCl		DISP OF AXIAL AQ?		128
METHYL	TRI(Bu)P	TRI(Me)S(+) I(-)	IIIA; H2 MeOH		79
METHYL	TRI(Bu)P	S-ADENOSYLMETHIONINE(+) I(-)	IIIA; BH4 MeOH		79
METHYL	TRI(Bu)P		ADDITION TO NONE?		136*
METHYL	TRI(Bu)P	MeI(Br,Cl)	IIIA; BH4 MeOH	A	118,191*
METHYL	TRI(Bu)P		DISP OF AXIAL PY		118
METHYL	TRI(Me)P		DISP OF AXIAL AQ?		128
METHYL	TRI(MeO)P	MeI	IIIA; BH4 MeOH	A	118
METHYL	TRI(MeO)P		ADDITION TO NONE		137*,136*

R	B	REAGENT	METHOD	NOTES	REF
METHYL	TRI(EtO)P		ADDITION TO NONE		136*
METHYL	TRI(PhO)P	MeI	IIIA; BH4 MeOH		67
METHYL	TRI(Ph)As	MeI	IIIA; BH4 MeOH	A	67
METHYL	TRI(Ph)Sb	MeI	IIIA; BH4 MeOH	A	67
METHYL	DI(Me)S	MeI	IIIA; BH4 MeOH	A	118,50
METHYL	DI(Me)S		ADDITION TO NONE		137*,136*
METHYL	DI(Et)S	MeI	IIIA; BH4 MeOH	A	118
METHYL	ETHANOL-2-SH		DISP OF AXIAL AQ		205a*
METHYL	ETHANOL-2-SMe		DISP OF AXIAL AQ		205a*
METHYL	ETHANOL-2-S(-)		DISP OF AXIAL AQ		205a*
METHYL	MeACETATE-2-S(-)		DISP OF AXIAL AQ		205a*
METHYL	ACETATE(-)-2-S(-)		DISP OF AXIAL AQ		205a*
METHYL	DI(Ph)SO		ADDITION TO NONE	A	137*,136
METHYL	DMSO		ADDITION TO NONE	A	137*,136
METHYL	DMSO-HEXA(D)		DISP OF AXIAL AQ		136*
METHYL	TETRA(METHYLENE)SO		ADDITION TO NONE	A	136
METHYL	THIOXANE		ADDITION TO NONE		137*,136*
METHYL	c-HexNC	MeI	IIIA; BH4 MeOH	A	67
METHYL	MeNC		ADDITION TO NONE	A	130
METHYL	CN(-)		DISP OF AXIAL AQ	A AsPh4 SALT	67*,184*,123
METHYL	CN(-)		DISP OF AXIAL AQ	A NEt4 SALT	123
METHYL	CN(-)		DISP OF AXIAL PY	AsPh4 SALT	67*,123
METHYL	CO		ADDITION TO NONE		130*
METHYL-[^{14}C]	AQ	MeI-[^{14}C]?	VIA DISP OF AXIAL DI(Me)S?		377
METHYL-MONO(D)	PY	MONO(X)-Me(Co)	BH4 MeOD (X=Cl,Br)		32

BIS(DIMETHYLGLYOXIMATO)

R	B	REAGENT	METHOD	NOTES	REF
METHYL-MONO(D)	PY	MONO(D)-DI(Cl)-Me(Co)	BH4 MeOH		32
METHYL-TRI(D)	PY	MeI-TRI(D)	IIIA; BH4 MeOH	A	118,67
METHYL-TRI(D)	PY	MeI-TRI(D)	IIIA; BH4 AQ EtOH	A	129
METHYL-TRI(D)	TRI(Ph)P	MeI-TRI(D)	IIIA; BH4 EtOH	A	129
METHYL-CYCLOPENTYL	PY	RCl	IIIA; BH4 MeOH		73
METHYL-CYCLOPENTYL--1-ETHOXYCARBONYL-2-OXO	PY	RBr	IIIA; BH4 MeOH	A	560
METHYL-CHLORO	PY	DICHLOROMETHANE	IIIA; BH4 MeOH(MILDLY ALK)	A	39,21
METHYL-CHLORO	PY	DI(Cl)-Me(Co)	BH4(NOT EXCESS) MeOH		32
METHYL-CHLORO	DI(Me)S	DICHLOROMETHANE	IIIA; BH4 MeOH	A	39
METHYL-CHLORO	NONE		REMOVAL OF AXIAL AQ	A	39,141
METHYL-CHLORO	THIOXANE		ADDITION TO 'NONE'		141*
METHYL-BROMO	PY	DIBROMOMETHANE	IIIA; BH4 MeOH(MILDLY ALK)	A	32,21
METHYL-BROMO	PY	DI(Br)-Me(Co)	BH4(NOT EXCESS) MeOH		32
METHYL-IODO	PY	DI-IODOMETHANE	IIIA; BH4 MeOH(MILDLY ALK)	A	39,21
METHYL-CHLORO Hg(2+) COMPLEX	AQ	Cl-Me(Co)AQ	Hg(2+) AQ PERCHLORIC ACID		200*
METHYL-METHOXY	PY	Hal-Me(Co) (VIA RHal)	NaOMe MeOH (VIA IIIA)	A	21
METHYL-METHOXY	TRI(Bu)P	RCl	IIIA; BH4 MeOH		101*
METHYL-(N-ANILINO)	ANILINE	ANILINE/FORMALDEHYDE	IIIA; H2 MeOH	A	383
METHYL-CYANO	PY	RCl	IIIA; BH4 MeOH	A	39
METHYL-CYANO	TRI(Bu)P	RCl	IIIA; BH4 MeOH		101*
METHYL-METHOXYCARBONYL	PY	RHal	IIIA; BH4 AQ EtOH	A	379
METHYL-METHOXYCARBONYL	PY	RCl	IIIA; BH4 MeOH	A (X-RAY)	39 (164)
METHYL-METHOXYCARBONYL	BENZIMID		DISP OF AXIAL PY	A	39
METHYL-ETHOXYCARBONYL	PY	RCl	IIIA; BH4 EtOH		380
METHYL-HYDROXYCARBONYL	PY	MeO.CO-Me(Co)	ACID HYDROLYSIS	A	39

R	B	REAGENT	METHOD	NOTES	REF
METHYL-CARBOXY	TRI(Bu)P	RBr(I)	IIIA; BH4 MeOH		101*
METHYL-AMINOCARBONYL	TRI(Bu)P	RCl	IIIA; BH4 MeOH		101*
METHYL(1-NAPHTHYL)	TRI(Bu)P	RCl	IIIA; BH4 MeOH		101*
METHYL-DIFLUORO	AQ	RHal?	IIIA; BH4? MeOH?	A	141
METHYL-DIFLUORO	THIOXANE		ADDITION TO 'NONE'		141*
METHYL-DIFLUORO	NONE		REMOVAL OF AXIAL AQ	A (UNSTABLE)	141
METHYL-DICHLORO	PY	CHLOROFORM	IIIA; BH4 MeOH(MILDLY ALK)	A	32,21
METHYL-DICHLORO-DEUTERIO	PY	DEUTERIOCHLOROFORM	IIIA; BH4? MeOH	A	32
METHYL-DIBROMO	PY	BROMOFORM	IIIA; BH4 MeOH(MILDLY ALK)	A	32,21
METHYL-DIIODO	PY	IODOFORM	IIIA; BH4? MeOH(MILDLY ALK)	A	21
METHYL-DIPHENYL?	TRI(Bu)P	RCl(Br)	IIIA; BH4 MeOH		101*
METHYL-TRIFLUORO	PY	RI	IIA; MeOH	A	118
METHYL-TRIFLUORO	PY	RI	IIIA; BH4 MeOH		21
METHYL-TRICHLORO	PY	RCl	IIA; DICHLOROMETHANE	A	21
METHYL-TRIBROMO	PY	RBr	IIA; DICHLOROMETHANE	A	21
METHYL-TRIIODO	PY	RI	IIA; DICHLOROMETHANE	A	21
ETHYL	PY	EtI(Br)	IIIA; BH4 MeOH	A	119
ETHYL	PY	EtI	IIIA;1-Ph-2-HO-Et(Co)PY AT 40° (VIA H(Co)) METHANOL		69
ETHYL	PY	TRI(Et)N + DI(METHOXY -CARBONYL)ACETYLENE	IIIA; BH4 MeOH		29
ETHYL	PY	EtMgBr	IA; ETHER/BENZENE		47
ETHYL	PY-4-CN(?)	EtBr	IIIA; BH4 MeOH		101*
ETHYL	PY-4-Me	EtHal?	IIIA?; BH4? MeOH?	A	132a
ETHYL	PY-3-Br	EtHal?	IIIA?; BH4? MeOH?	A	132a
ETHYL	PY-3-CN		DISP OF AXIAL AQ?	A	378,132a

BIS(DIMETHYLGLYOXIMATO)

R	B	REAGENT	METHOD	NOTES	REF
ETHYL	PY-2-Me	EtBr	IIIA; BH4 MeOH		101*
ETHYL	PY-2,6-DI-METHYL	EtBr	IIIA; BH4 MeOH		101*
ETHYL	PY-2,4,6,TRI(Me)		DISP OF AXIAL AQ?		378,132a
ETHYL	PYRAZOLE		DISP OF AXIAL AQ?	A	132a
ETHYL	IMID	EtHal?	IIIA?; ALK DISPROP? MeOH?	A	378,132a
ETHYL	1-MeIMID	EtHal?	IIIA?; ALK DISPROP? MeOH?	A	132a
ETHYL	BENZIMID		DISP OF AXIAL AQ?	A	65
ETHYL	AMMONIA		DISP OF AXIAL AQ?	A	378,132a
ETHYL	METHYLAMINE		DISP OF AXIAL AQ?	A	378,132a
ETHYL	c-HEXYLAMINE	EtBr	IIIA; BH4 MeOH		101*
ETHYL	BENZYLAMINE		DISP OF AXIAL AQ?	A	378,132a
ETHYL	PIPERIDINE		DISP OF AXIAL AQ?	A	378,132a
ETHYL	MORPHOLINE		DISP OF AXIAL AQ?	A	378,132a
ETHYL	ANILINE	EtHal?	IIIA?; BH4? MeOH?	A	378,132a
ETHYL	L-His-Me ESTER		DISP OF AXIAL AQ		132a*
ETHYL	AZIDE(-)		DISP OF AXIAL AQ		184*
ETHYL	NCS(-)		DISP OF AXIAL AQ		184*
ETHYL	AQ		DISP OF AXIAL DI(Me)S	A	118
ETHYL	AQ	EtI	IIIA; ALK DISPROP MeOH	A	74
ETHYL	AQ	EtBr	IIIA; BH4 MeOH		101*
ETHYL	AQ		DISP OF AXIAL PY IN ACID AQ.		584*
ETHYL	NONE		REMOVAL OF AXIAL AQ	A	118
ETHYL	TRI(Bu)P	EtHal	IIIA; BH4 MeOH	A	67
ETHYL	TRI(Bu)P	EtBr	IIIA; BH4 EtOH,PrOH OR AQ/MeOH		101*
ETHYL	TRI(Ph)P	EtI	IIIA; BH4 MeOH	A	134,135

R	B	REAGENT	METHOD	NOTES	REF
ETHYL	TRI(Ph)P	EtMgHal	IA; THF	A	12
ETHYL	TRI(EtO)P		DISP OF AXIAL PY?	A	132a
ETHYL	TRI(Ph)As	EtHal	IIIA; BH4 MeOH	A	152,65
ETHYL	TRI(Ph)Sb		DISP OF AXIAL AQ?	A	65
ETHYL	DI(Me)S	EtHal	IIIA; BH4 MeOH		118
ETHYL	DI(Et)S	EtHal	IIIA; BH4 MeOH	A	378,132a
ETHYL	CN(-)		DISP OF AXIAL AQ		65*
ETHYL	CN(-)		DISP OF AXIAL PY OR TRI(Bu)P		67*
ETHYL	CN(-)	EtBr	IIIA; BH4 MeOH		101*
ETHYL	c-HexNC	EtBr	IIIA; BH4 MeOH		101*
ETHYL-2-HYDROXY	PY	ETHYLENE OXIDE	IIIA; H2 MeOH (NEUTRAL)	A	33
ETHYL-2-HYDROXY	BENZIMID		DISP OF AXIAL AQ	A	33
ETHYL-2-HYDROXY	AQ	ETHYLENE OXIDE	IIIA; H2 MeOH (NEUTRAL)	A	33
ETHYL-2-HYDROXY	TRI(Bu)P		DISP OF AXIAL AQ?		33
ETHYL-2-HYDROXY	TRI(Bu)P	RBr	IIIA; BH4 MeOH		101*
ETHYL-2-HYDROXY	TRI(Ph)P		DISP OF AXIAL AQ	A	33
ETHYL-2-OH-2-D	PY	RCl	IIIA; H2 MeOH(NEUTRAL)		104
ETHYL-2-METHOXY	PY	2-AcO-Et(Co)PY	MeOH SOVOLYSIS	A	240
ETHYL-2-MeO-2,2-DI(D)	PY	2-AcO-2,2-DI(D)-Et(Co)	MeOH SOLVOLYSIS (50% OF PROD)	A(MIX)	240a,565
ETHYL-2-MeO-1,1-DI(D)	PY	2-AcO-2,2-DI(D)-Et(Co)	MeOH SOLVOLYSIS (50% OF PROD)	A(MIX)	240a,565
ETHYL-(2-^{13}C)-2-METHOXY	PY	2-MeCO.O-(2-^{13}C)-Et(Co)	METHANOLYSIS MeOH (50% OF PROD)		504
ETHYL-(1-^{13}C)-2-METHOXY	PY	2-MeCO.O-(2-^{13}C)-Et(Co)	METHANOLYSIS MeOH (50% OF PROD)		504
ETHYL-2-ETHOXY	PY	EBr	IIIA; BH4 MeOH	A	33
ETHYL-2-ETHOXY	PY	2-AcO-Et(Co)PY	EtOH SOLVOLYSIS	A	240

R	B	REAGENT	METHOD	NOTES	REF
ETHYL-2-ETHOXY	TRI(Ph) P	RBr	IIIA; BH4? EtOH/DIOXAN?	A	240a
ETHYL-2-ETHOXY	CN(-)		DISP OF AXIAL PY		33*
ETHYL-2-ACETOXY	PY	2-HO-Et(Co)PY	ACETYLATION DI(Ac)O/PY	A	240
ETHYL-2-ACETOXY	TRI(Ph) P	2-HO-Et(Co)TRI(Ph) P	ACETYLATION DI(Ac)O/ DI(i-Pr)NEt/PhH	A	240a
ETHYL-2-ACETOXY-2,2-DI(D)	PY	RBr	IIIA; BH4? EtOH/DIOXAN?	A	240a,565
ETHYL-2-ACETOXY-1,1-DI(D)	PY	2,2-DI(D) ANALOGUE	OBSERVED DURING METHANOLYSIS		565*
ETHYL-(2-^{13}C)-2-ACETOXY	PY	RBr	IIIA; BH4 MeOH		504
ETHYL-2-METHOXYCARBONYL	PY	Me ACRYLATE	IIIB; H2 MeOH	A	39
ETHYL-2-METHOXYCARBONYL	TRI(Bu) P		DISP OF AXIAL PY	A	39
ETHYL-2-HYDROXYCARBONYL	PY	2-MeO.CO-Et(Co)PY	ACID HYDROLYSIS	A	39
ETHYL-2-ETHOXYCARBONYL	PY	Et ACRYLATE	IIIB; ALK DISPROP MeOH	A	39
ETHYL-2-ALKOXYCARBONYL	PY	R ACRYLATE (R UNSPEC)	IIIB; NaOH + 2-NC-Et(Co)	MeOH	39
ETHYL-2-CYANO	PY	ACRYLONITRILE	IIIB; BH4 MeOH	A	12
ETHYL-2-CYANO	PY	RBr	IIIA; BH4 MeOH	A	381
ETHYL-2-CYANO	PY	ACRYLONITRILE	IIIB; H2 MeOH	A	39
ETHYL-2-CYANO	AQ	ACRYLONITRILE?	IIIB?; H2? MeOH?		110
ETHYL-2-CYANO	TRI(Bu) P		DISP OF AXIAL AQ?		110
ETHYL-2-CN-TETRA(D)	PY	2-NC-Et(Co)PY	NaOD D2O/THF (pH>12.5)		110
ETHYL-2-PHENYL	PY	RBr	IIIA; BH4 MeOH	A	39
ETHYL-2-KETO	PY	2,2-DI(MeO)-Et(Co)PY	ACID HYDROLYSIS	A	39
ETHYL-1-METHYL	PY	RI	IIIA; NEUT DISPROP OR IIA; METHANOL	A	118
ETHYL-1-METHYL	PY	RBr(I)	IIIA; BH4 MeOH		118
ETHYL-1-METHYL	PY	PROPENE	IIIC; H2 EtOH		118
ETHYL-1-METHYL	PY-2,4,6-TRI(Me)		DISP OF AXIAL AQ?		375

R	B	REAGENT	METHOD	NOTES	REF
ETHYL-1-METHYL	PYRAZINE-2-Me		DISP OF AXIAL AQ?		375
ETHYL-1-METHYL	IMID		DISP OF AXIAL AQ	A	65
ETHYL-1-METHYL	ANILINE		DISP OF AXIAL AQ?		375
ETHYL-1-METHYL	AZIDE(-)		DISP OF AXIAL AQ		184*
ETHYL-1-METHYL	NCS(-)		DISP OF AXIAL AQ		184*
ETHYL-1-METHYL	AQ		DISP OF AXIAL DI(Me)S	A	184,65
ETHYL-1-METHYL	AQ	RI	IIIA; ALK DISPROP MeOH	A	74
ETHYL-1-METHYL	AQ		DISP OF AXIAL PY IN ACID AQ.		584*
ETHYL-1-METHYL	TRI(Bu)P	RCl(Br)	IIIA; BH4 MeOH		101*
ETHYL-1-METHYL	DI(Me)S	RHal	IIIA; BH4 MeOH		118
ETHYL-1-ACETOXY	PY	VINYL ACETATE	IIIC; H2 MeOH (LOW YIELD)	A	39
ETHYL-1-CYANO	PY	ACRYLONITRILE	IIIC; H2 MeOH	A	39
ETHYL-1-CYANO	PY	ACRYLONITRILE	IIIC; BH4 MeOH	A	381
ETHYL-1-CYANO	ANILINE	ACRYLONITRILE	IIIC; H2 MeOH	A	39
ETHYL-1-CYANO	TRI(Bu)P	ACRYLONITRILE	IIIC; H2 MeOH	A	39
ETHYL-1-CYANO	TRI(Bu)P	ACRYLONITRILE	IIIC(CRYST H(Co)); AQ MeOH(pH7-9)		44
ETHYL-1-HYDROXYCARBONYL	PY	ACRYLIC ACID	IIIC; H2 MeOH	A	39
ETHYL-1-HYDROXYCARBONYL	AQ	ACRYLIC ACID	IIIC; H2 MeOH	A	39
ETHYL-1-METHOXYCARBONYL	PY	METHYL ACRYLATE	IIIC; H2 MeOH	A	39
ETHYL-1-METHOXYCARBONYL	AQ	METHYL ACRYLATE	IIIC; H2 MeOH	A	39
ETHYL-1-METHOXYCARBONYL	TRI(Bu)P	METHYL ACRYLATE	IIIC; H2 MeOH	A	39
ETHYL-1-ETHOXYCARBONYL	PY	ETHYL ACRYLATE	IIIC; H2 MeOH	A	39
ETHYL-1-ETHOXYCARBONYL	AMMONIA		DISP OF AXIAL PY	A	39
ETHYL-1-ALKOXYCARBONYL	TRI(Bu)P	R ACRYLATE(UNSPEC)	IIIC; CRYST H(Co) AQ/MeOH(pH7-9)		44
ETHYL-1-HYDROXYMETHYL	PY	RBr	IIIA; ALK DISPROP OR BH4 MeOH	A	74

R	B	REAGENT	METHOD	NOTES	REF
ETHYL-1-HYDROXYMETHYL-2-Cl	PY	1,2-EPOXY-3-Cl-PROPANE	IIIA; BH4 AQ/EtOH	A	129
ETHYL-1-PHENYL	PY	STYRENE	IIIB OR IIIC; H2 MeOH	A	39
ETHYL-1-PHENYL	PY	STYRENE	IIIB; BH4 MeOH	A	12
ETHYL-1-PHENYL	PY	RBr	IIA; BENZENE		99*,99a*
ETHYL-1-PHENYL	AQ	STYRENE	IIIB OR IIIC; H2 MeOH	A	39
ETHYL-1-PHENYL	TRI(Bu)P	RCl	IIIA; BH4 MeOH		101*
ETHYL-1-(3-FLUOROPHENYL)	PY	3-F-STYRENE	IIIB OR IIIC; H2? AQ/MeOH	A	299a
ETHYL-1-(4-FLUOROPHENYL)	PY	4-F-STYRENE	IIIB OR IIIC; H2? AQ/MeOH	A	299
ETHYL-1-(3-CHLOROPHENYL)	PY	3-Cl-STYRENE	IIIB OR IIIC; H2? AQ/MeOH	A	299a
ETHYL-1-(4-CHLOROPHENYL)	PY	4-Cl-STYRENE	IIIB OR IIIC; H2? AQ/MeOH	A	299
ETHYL-1-(2-BROMOPHENYL)	PY	2-Br-STYRENE	IIIB OR IIIC; H2? AQ/MeOH		299a
ETHYL-1-(3-BROMOPHENYL)	PY	3-Br-STIRENE	IIIB OR IIIC; H2? AQ/MeOH	A	299a
ETHYL-1-(4-BROMOPHENYL)	PY	4-Br-STYRENE	IIIB OR IIIC; H2? AQ/MeOH	A	299
ETHYL-1-(4-METHOXYPHENYL)	PY	4-MeO-STYRENE	IIIB OR IIIC; H2? AQ/MeOH	A	299
ETHYL-1-(4-METHYLPHENYL)	PY	4-Me-STYRENE	IIIB OR IIIC; H2? AQ/MeOH	A	299
ETHYL-1-KETO	1-MeIMID	ROR	IIIA; BH4 MeOH	A	16
ETHYL-2-KETO-2-PHENYL	PY	RBr	IIIA; BH4 MeOH	A	39
ETHYL-2,2-DIMETHOXY	PY	RBr	IIIA; ALK DISPROP MeOH	A	39
ETHYL-1,2-DICYANO	PY	FUMARONITRILE	IIIC; H2 MeOH	A	39
ETHYL-1,2-DICYANO	TRI(Bu)P		DISP OF AXIAL PY?		110
ETHYL-1,2-DI(CN)-TRI(D)	PY	1,2-DI(CN)-Et(Co)PY	D2O PY		110*
ETHYL-1,2-DI(ETHOXY-CARBONYL)	PY	DIETHYLFUMARATE (MALEATE)	IIIC; H2 MeOH	A	39
ETHYL-1,2-DI(ETHOXY-CARBONYL)	AQ	DIETHYLFUMARATE (MALEATE)	IIIC; H2 MeOH	A	39
ETHIL-1-ETHOXICARBONYL-2-HYDROXICARBONYL	PY	1,2-DI(EtO.CO)-Et(Co)	ACID HYDROLYSIS	A	39

R	B	REAGENT	METHOD	NOTES	REF
ETHYL-2-HYDROXY-1-PHENYL	PY	STYRENE OXIDE	IIIA; H2 MeOH	A	33,69
(+)-ETHYL-2-HYDROXY-1-Ph	PY	(-)-STYRENE OXIDE	IIIA; H2? MeOH		299a
ETHYL-2-OH-2,2-DI(D)-1-Ph	PY	1-Ph-2,2-DI(D)-ETHYL-ENE OXIDE	IIIA; H2 MeOH	A	69,299a
ETHYL-2-CYANO-1-PHENYL	PY	CINNAMONITRILE?	IIIB; H2? MeOH?		110
ETHYL-2-ACETOXY-1-METHYL	PY	RBr	IIIA; NEUT DISPROP OR IIA; MeOH	A	39
ETHYL-2,2,2-TRIFLUORO	PY	RI	IIIA; BH4 MeOH	A	135
ETHYL-2,2,2-TRIFLUORO	AQ		DISP OF AXIAL PY IN ACID AQ.		584*
ETHYL-2,2,2-TRIFLUORO	TRI(Ph)P	RI	IIIA; BH4 MeOH	A	134,135
PROPYL	PY	PrI(Cl)	IIIA; BH4 MeOH	A	118,135
PROPYL	PY	PrI	IIIA; NEUT DISPROP MeOH	A	118
PROPYL	PY	PrBr	IIIA; BH4 AQ EtOH	A	379
PROPYL	PY-4-Me		DISP OF AXIAL AQ?	A	74
PROPYL	BENZIMID		DISP OF AXIAL AQ?	A	65
PROPYL	AQ		DISP OF AXIAL DI(Me)S	A	118
PROPYL	AQ	PrI	IIIA; ALK DISPROP MeOH	A	74
PROPYL	AQ	PrCl	IIIA; BH4 MeOH		101*
PROPYL	AQ		DISP OF AXIAL PY IN ACID AQ.		584*
PROPYL	TRI(Ph)P	PrI	IIIA; BH4 MeOH	A	134,135
PROPYL	TRI(Bu)P	PrCl(Br)	IIIA; BH4 MeOH		101*
PROPYL	DI(Me)S	PrHal	IIIA; BH4 MeOH		118
PROPYL	TRI(Ph)As		DISP OF AXIAL AQ?	A	65
PROPYL	TRI(Ph)Sb		DISP OF AXIAL AQ?	A	65
PROPYL	c-HexNC		DISP OF AXIAL AQ?	A	65
PROPYL-1-METHYL	TRI(Bu)P	RI	IIIA; BH4 MeOH		101*

R	B	REAGENT	METHOD	NOTES	REF
PROPYL-1-METHYL	PY	RBr(I)	IIIA; BH4 OR ALK DISPROP MeOH	A	223
(+)-PROPYL-1-METHYL	PY	(-)ROTs	IIIA; BH4 MeOH	A	109
PROPYL-1-CYANO	PY	CROTONONITRILE	IIIC; H2 MeOH (LOW YIELD)	A	39
PROPYL-1-PHENYL	PY	1-Ph-PROP-1-ENE	IIIB; H2 OR BH4 MeOH	A	140
PROPYL-3-BROMO	PY	RBr	IIIA; BH4 MeOH	A	118
PROPYL-3-HYDROXY	PY	RBr	IIIA; H2 MeOH (NEUTRAL)	A	33
PROPYL-3-HYDROXY	PY	TRIMETHYLENE OXIDE	IIIA; H2 MeOH (NEUTRAL)		33
PROPYL-3-HYDROXY	PY	ALLYL ALCOHOL	IIIB?; H2 MeOH? (LOW YIELD)		33
PROPYL-2-METHYL	PY	RHal	IIIA; BH4 MeOH	A	118
PROPYL-2-METHYL	AQ	RHal?	IIIA?; BH4? MeOH?	A	65
PROPYL-2-METHYL	IMID		DISP OF AXIAL AQ?		65*
PROPYL-2-METHYL	BENZIMID		DISP OF AXIAL AQ?		65*
PROPYL-2-METHYL	TRI(Bu)P	RCl(Br,I)	IIIA; BH4 MeOH		101*
PROPYL-2-CYANO	PY	METHACRYLONITRILE	IIIB OR IIIC; H2 MeOH(NEUT)	A	39
PROPYL-2-CYANO	ANILINE	METHACRYLONITRILE	IIIB OR IIIC; H2 MeOH(NEUT)	A	39
PROPYL-2-METHOXYCARBONYL	PY	Me METHACRYLATE	IIIB; H2 MeOH (LOW YIELD)	A	39
PROPYL-2-ETHOXYCARBONYL	PY	RBr	IIIA; BH4 MeOH	A	39
PROPYL-2-KETO	PY	ALLENYL(Co)PY	HCl AQ MeOH		382
PROPYL-2-KETO	PY	PROPARGYLBr (VIA PROP-ARGYL(Co))	IIIA; NEUT DISPROP MeOH (0.1M IN HOAc)		73
PROPYL-2-HYDROXY	PY	PROPANE-1,2-EPOXY	IIIA; H2 MeOH(NEUTRAL)	A	33
PROPYL-2-HYDROXY	PY	RBr	IIIA; ALK DISPROP OR BH4 MeOH	A	74
PROPYL-2-HYDROXY	PY-4-Me	PROPANE-1,2-EPOXY?	IIIA?; H2? MeOH(NEUTRAL)?		573
PROPYL-2-METHOXY	PY	2-AcO-Pr(Co)PY	MeOH SOLVOLYSIS		565
PROPYL-2-ETHOXY	PY	2-AcO-Pr(Co)PY	EtOH SOLVOLYSIS	A	240

R	B	REAGENT	METHOD	NOTES	REF
PROPYL-2-ACETOXY	PY	2-HO-Pr(Co)PY	ACETYLATION DI(MeCO)O PY	A	240
(S)-PROPYL-2-ACETOXY	PY	(S)-RBr	IIIA; BH4 EtOH/DIOXAN	A	240a,565
(S)-PROPYL-2-BENZYLOXY	PY	(S)-ROTs	IIIA; BH4? EtOH/DIOXAN?	A	240a,565
(S)-PROPYL-2-BENZYLOXY	PY	(S)-2-AcO-Pr(Co)PY	BENZYL ALCOHOL SOLVOLYSIS	A	240a,565
PROPYL-2-HYDROXY-3-PHENYL	PY	PROPANE-3-Ph-1,2-EPOXY	IIIA; H2 OR BH4 MeOH	A	140
PROPYL-2,3-DIHYDROXY	PY	PROPANE-1-OH-2,3-EPOXY	IIIA; H2 MeOH(NEUTRAL)	A	33
PROPYL-2,3-DIHYDROXY	PY	RCl	IIIA; ALK DISPROP OR BH4 MeOH	A	74
PROPYL-2,2-DIMETHYL	PY	RHal	IIIA; BH4 MeOH	A	118
PROPYL-2,2-DIMETHYL	TRI(Bu)P	RBr	IIIA; BH4 MeOH		101*
PROPYL-2-METHYL-2-HYDROXY	PY	PROPANE-2-Me-1,2-EPOXY	IIIA; H2 MeOH(NEUTRAL)	A	384,104
PROPYL-2-KETO-1-METHYL	PY	VINYL.CO.Me	IIIC; H2 MeOH	A	39
CYCLOPROPYL	TRI(Bu)P	RBr	IIIA; BH4 MeOH		101*
BUTYL	PY	TRI(Bu)B	IA; BENZENE	A	118
BUTYL	PY	RBr(I)	IIIA; BH4 MeOH	A	12,118
BUTYL	PY	RHal	IIIA; BH4 AQ EtOH	A	379
BUTYL	PY	RLi	IA; ETHER		47
BUTYL	PY-4-Me		DISP OF AXIAL AQ?	A	74
BUTYL	DMF		ADDITION TO 'NONE'		575*
BUTYL	AQ	RI	IIIA; ALK DISPROP MeOH	A	74
BUTYL	AQ	RBr?	IIIA?; BH4? MeOH?	A	575
BUTYL	NONE		REMOVAL OF AXIAL AQ		575
BUTYL	TRI(Bu)P	RCl	IIIA; BH4 MeOH		101*
BUTYL-4-CHLORO	TRI(Bu)P	RBr	IIIA; BH4 MeOH		101*
BUTYL-4-BROMO	PY	RBr	IIIA; ALK DISPROP MeOH	A	33
BUTYL-4-BROMO	TRI(Bu)P	RBr	IIIA; BH4 MeOH		101*

BIS(DIMETHYLGLYOXIMATO)

R	B	REAGENT	METHOD	NOTES	REF
BUTYL-4-HYDROXY	PY	RBr	IIIA; H2 MeOH (NEUTRAL)	A	33
BUTYL-3-METHYL	PY	RHal	IIIA; BH4 MeOH		203
BUTYL-3-METHYL	TRI(Bu)P	RBr	IIIA; BH4 MeOH		101*
BUTYL-1-METHYL	TRI(Bu)P	RBr	IIIA; BH4 MeOH		101*
CYCLOBUTYL	TRI(Bu)P	RBr	IIIA; BH4 MeOH		101*
PENTYL	PY	RHal	IIIA; BH4 MeOH		298
PENTYL	TRI(Bu)P	RCl	IIIA; BH4 MeOH		101*
PENTYL-2,5-DIHYDROXY	PY	1-Cl-2-AcO-PENTAN-5-OL/ 1-AcO-2-Cl-PENTAN-5-OL	IIIA; BH4? MeOH?		577
CYCLOPENTYL	TRI(Bu)P	RBr	IIIA; BH4 MeOH		101*
CYCLOPENTYL-2-Me-3,3,4,4--TETRACYANO	PY	CROTYL(Co)PY	TETRACYANOETHYLENE DICHLOROMETHANE	A	588
HEXYL	PY	RHal	IIIA; BH4 MeOH	A	118
HEXYL	TRI(Bu)P	RCl	IIIA; BH4 MeOH		101*
HEXYL-1-METHYL?	PY	HEPT-1-ENE	IXIC; H2 EtOH (TRACES ONLY)		118
CYCLOHEXYL	PY	RBr	IIIA; BH4 MeOH	A	107
CYCLOHEXYL	TRI(Bu)P	RBr	IIIA; BH4 MeOH		101*
CYCLOHEXYL	CN(-)		DISP OF AXIAL AQ	A AsPh4 SALT	123
CYCLOHEXYL-2-HYDROXY	PY	CYCLOHEXENE OXIDE	IIIA; H2 MeOH(NEUTRAL)	A	33
TRANS-CYCLOHEXYL-2-OH	PY	CIS-CYCLOHEXENE OXIDE	IIIA; BH4 MeOH	A	107
CIS-CYCLOHEXYL-2-OMe	PY	TRANS-RBr	IIIA; BH4 MeOH	A	107
ETHYL-2-ACETOXY-1-Ph	PY	2-HO-1-Ph-Et(Co)PY?	ACETYLATION? DI(MeCO)O? PY?		299a
CIS-CYCLOHEXYL-4-BROMO	PY	TRANS-RBr	IIIA; BH4 MeOH	A	107
TRANS-CYCLOHEXYL-4-BROMO	PY	CIS-RBr	IIIA; BH4 MeOH	A	107
CIS-CYCLOHEXYL-4-HYDROXY	PY	TRANS-ROTs	IIIA; BH4 MeOH	A	107
TRANS-CYCLOHEXYL-4-HYDROXY	PY	CIS-ROTs	IIIA; BH4 MeOH	A	107

R	B	REAGENT	METHOD	NOTES	REF
HEPTYL-1-METHYL	PY	RHal	IIIA; BH4 MeOH		152
HEPTYL-1-METHYL	AQ	RI	IIIA; ALK DISPROP MeOH		380
(+)HEPTYL-1-METHYL	PY	(-)RBr	IIIA; BH4 MeOH		108
HEPTYL-1-METHYL	CN(-)		DISP OF AXIAL PY	AsPh4 SALT	123
CYCLOHEPTYL	TRI(Bu)P	RBr	IIIA; BH4 MeOH		101*
OCTYL	PY	RBr	IIIA; BH4 MeOH	A	223
OCTYL	AQ	RBr	IIIA; ALK DISPROP MeOH	A	373
OCTYL	TRI(Ph)P		DISP OF AXIAL AQ	A	373
OCTYL	CN(-)		DISP OF AXIAL PY	A AsPh4 SALT	123
OCTYL-2-HYDROXY	PY	OCTANE-1,2-EPOXY	IIIA; H2 MeOH(NEUTRAL)	A	33
CYCLOOCTYL	TRI(Bu)P	RBr	IIIA; BH4 MeOH		101*
BENZYL	PY	RMgHal	IA; THF	A	12
BENZYL	PY	RCl	IIIA; Na OR K THF	A	12
BENZYL	PY	RCl(Br)	IIIA; BH4 MeOH	A	12,99
BENZYL	PY	RCl	IIIA; BH4 AQ/EtOH	A	385,379
BENZYL	PY	TRI(Me)N-BENZYL(+)I(-)	IIIA; BH4 MeOH		29
BENZYL	PY	DI(Me)N-BENZYL/DI(METH-OXYCARBONYL)ACETYLENE	IIIA; BH4 MeOH		29
BENZYL	PY	RBr	IIA; PhH OR ACETONE		99*,99a*
BENZYL	PY	a-Cl-BENZYL(Co)	BH4 MeOH		32
BENZYL	PY-4-Me	RBr	IIIA; BH4 MeOH		99a
BENZYL	PY-4-Me	RBr	IIA; PhH OR ACETONE		99*,99a*
BENZYL	NICOTINAMIDE	RBr	IIA; ACETONE		99*,99a*
BENZYL	PY-2,4,6-TRI(Me)		DISP OF AXIAL AQ?		375
BENZYL	ISOQUINOLINE	RHal	IIIA; BH4 MeOH		152
BENZYL	2-Me-PYRAZINE		DISP OF AXIAL AQ?		375

R	B	REAGENT	METHOD	NOTES	REF
BENZYL	1-Me-IMID	RBr	IIA; PhH OR ACETONE		99a*
BENZYL	PIPERIDINE	RBr	IIA; PhH OR ACETONE		99a*
BENZYL	ANILINE		DISP OF AXIAL AQ?		375
BENZYL	ANILINE-2,4--DIMETHYL	RHal	IIIA; BH4 MeOH?		133
BENZYL	NCCo(dmgH)-(dmgH2)R	RCoBIS(dmgH)CN(-)	ACIDIFICATION OF AQ. SOLN.	A	373
BENZYL	AQ	RBr	IIIA; ALK DISPROP MeOH	A	47
BENZYL	AQ		DISP OF PY ON ACIDIC RESIN	AQ/MeOH	47
BENZYL	AQ	RBr	IIIA; BH4 MeOH (LOW YIELD)		380
BENZYL	AQ		DISP OF AXIAL PY IN ACID AQ.		264*,584*
BENZYL	AQ OR NONE	RBr	IIA; ACETONE		99a*
BENZYL	TRI(Me)P	RBr	IIA; BENZENE		99a*
BENZYL	TRI(Et)P	RBr	IIA; BENZENE		99a*
BENZYL	TRI(Bu)P	RCl	IIIA; BH4 MeOH		101*
BENZYL	TRI(Bu)P	RBr	IIA; BENZENE		99a*
BENZYL	TRI(c-HEX)P	RBr	IIA; ACETONE		99a*
BENZYL	TRI(Ph)P	RMgHal	IA; THF	A	12
BENZYL	TRI(Ph)P	RCl	IIIA; Na OR K THF	A	12
BENZYL	TRI(Ph)P	RCl(Br)	IIIA; BH4 MeOH	A	12,39
BENZYL	TRI(Ph)P	RBr	IIA; PhH OR ACETONE		99*,99a*
BENZYL	TRI(Ph)P	RI	IIA; BENZENE		99a*
BENZYL	TRI(Ph)P		DISP OF AXIAL AQ		380
BENZYL	TRI(4-Cl--Ph)P	RBr	IIA; BENZENE		99a*
BENZYL	TRI(4-MeO--Ph)P	RBr	IIA; BENZENE		99a*

R	B	REAGENT	METHOD	NOTES	REF
BENZYL	TRI(4-Me--Ph)P	RBr	IIA; BENZENE		99a*
BENZYL	TRI(MeO)P	RBr	IIA; BENZENE		99a*
BENZYL	THIOUREA		DISP OF AXIAL AQ	A	386
BENZYL	CN(-)		DISP OF AXIAL AQ	A AsPh4 SALT	123
BENZYL	CN(-)		DISP OF AXIAL AQ	A NEt4 SALT	380
BENZYL-a-D	PY	a-Cl-BENZYL(Co)	BH4 MeOD		32
BENZYL-3-FLUORO	PY	RCl	IIIA; ALK DISPROP MeOH	A	47
BENZYL-3-FLUORO	BENZIMID		DISP OF AXIAL PY	A	47
BENZYL-3-FLUORO	MeCN		DISP OF AXIAL AQ		47*
BENZYL-3-FLUORO	TRI(Ph)P		DISP OF AXIAL PY	A	47
BENZYL-3-FLUORO	TRI(MeO)P		DISP OF AXIAL DI(Me)S		47
BENZYL-3-FLUORO	DI(Me)S	RCl	IIIA; ALK DISPROP MeOH	A	47
BENZYL-3-FLUORO	DMSO		DISP OF AXIAL AQ		47*
BENZYL-3-FLUORO	CN(-)		DISP OF AXIAL PY	A NEt4 SALT	47
BENZYL-4-FLUORO	Br(-)		DISP OF AXIAL AQ	A AsPh4 SALT	373
BENZYL-4-FLUORO	I(-)		DISP OF AXIAL AQ	A PPr4 SALT	373
BENZYL-4-FLUORO	PY		DISP OF AXIAL AQ	A	47
BENZYL-4-FLUORO	PY	RHal	IIIA; BH4 MeOH	A	584
BENZYL-4-FLUORO	BENZIMID		DISP OF AXIAL AQ	A	47
BENZYL-4-FLUORO	TRI(Me)N		DISP OF AXIAL AQ	A	47
BENZYL-4-FLUORO	DMF		DISP OF AXIAL AQ	A	47
BENZYL-4-FLUORO	AZIDE(-)		DISP OF AXIAL AQ	A NEt4 SALT	47
BENZYL-4-FLUORO	MeCN		DISP OF AXIAL AQ		47*
BENZYL-4-FLUORO	NC(Co)Me(-)		DISP OF AXIAL AQ		47*
BENZYL-4-FLUORO	NC(Co)BENZYL-4-F(-)		DISP OF AXIAL AQ		47*

BIS(DIMETHYLGLYOXIMATO)

R	B	REAGENT	METHOD	NOTES	REF
BENZYL-4-FLUORO	NC(Co)BENZYL-4-NITRO(-)		DISP OF AXIAL AQ		47*
BENZYL-4-FLUORO	NCCo(dmgH)-(dmgH2)R	RCoBIS(dmgH)CN(-)	ACIDIFICATION OF AQ. SOLN.	A	373
BENZYL-4-FLUORO	AQ	RCl	IIIA; ALK DISPROP MeOH	A	47
BENZYL-4-FLUORO	AQ		DISP OF AXIAL PY IN ACID AQ.		264*,584*
BENZYL-4-FLUORO	TRI(Ph)P		DISP OF AXIAL AQ	A	47
BENZYL-4-FLUORO	TRI(MeO)P		DISP OF AXIAL AQ	A	47
BENZYL-4-FLUORO	DI(Me)S		DISP OF AXIAL AQ	A	47
BENZYL-4-FLUORO	DMSO		DISP OF AXIAL AQ		47*
BENZYL-4-FLUORO	CN(-)		DISP OF AXIAL AQ	A AsPh4 SALT	47
BENZYL-4-FLUORO	CN(-)		DISP OF AXIAL AQ	A NEt4 SALT	47
BENZYL-4-FLUORO	NCS(-)		DISP OF AXIAL AQ	A NEt4 SALT	47
BENZYL-4-CHLORO	PY	RCl	IIIA; BH4 MeOH	A	380
BENZYL-4-BROMO	PY	RBr	IIIA; BH4 MeOH	A	380
BENZYL-4-BROMO	TRI(Ph)P	RBr	IIA; BENZENE		99a
BENZYL-3-NITRO	PY	RI	IIIA; BH4 MeOH	A	380
BENZYL-4-NITRO	PY	RI	IIIA; BH4 MeOH	A	380,584
BENZYL-4-NITRO	NC(Co)BENZYL-4-F(-)		DISP OF AXIAL AQ		47*
BENZYL-4-NITRO	NC(Co)BENZYL-4-NITRO(-)		DISP OF AXIAL AQ		123*
BENZYL-4-NITRO	NCCoBIS(c-hgH)Me(-)		DISP OF AXIAL AQ		123*
BENZYL-4-NITRO	AQ		DISP OF PY ON ACIDIC RESIN AQ/MeOH		380
BENZYL-4-NITRO	AQ		DISP OF AXIAL PY IN ACID AQ.		264*,584*
BENZYL-4-NITRO	TRI(Ph)P	RBr(Cl)	IIA; BENZENE		99a*
BENZYL-4-NITRO	CN(-)		DISP OF AXIAL PY	A NEt4 SALT	47
BENZYL-4-DIMETHYLAMINO	PY	ROTs	IIIA; H2 MeOH(NEUTRAL)	A	47

R	B	REAGENT	METHOD	NOTES	REF
BENZYL-3-METHOXY	PY	RCl	IIIA; BH4 MeOH	A	380
BENZYL-3-METHOXY	CN(-)		DISP OF AXIAL PY	A AsPh4 SALT	123
BENZYL-4-METHOXY	PY	RCl	IIIA; BH4 MeOH	A	380,584
BENZYL-4-METHOXY	AQ		DISP OF AXIAL PY IN ACID AQ.		264*,584*
BENZYL-4-CYANO	TRI(Ph)P	RBr	IIA; BENZENE		100*,99a*
BENZYL-4-HYDROXYCARBONYL	PY	RBr	IIIA; H2 MeOH(NEUTRAL)	A	47
BENZYL-4-ETHOXYCARBONYL	AQ	RBr	IIIA; H2 EtOH(NEUTRAL)		47
BENZYL-2-METHYL	PY	RBr	IIIA; BH4 MeOH	A	35
BENZYL-3-METHYL	PY	RBr	IIIA; BH4 MeOH	A	35
BENZYL-4-METHYL	PY	RBr	IIIA; BH4 MeOH	A	35
BENZYL-4-METHYL	AQ	RBr	IIIA; ALK DISPROP MeOH	A	47
BENZYL-4-METHYL	AQ		DISP OF AXIAL PY IN ACID AQ.		264*,584*
BENZYL-4-METHYL	TRI(Ph)P	RBr	IIA; BENZENE		99a*
BENZYL-4-t-BUTYL	TRI(Bu)P	RCl	IIIA; BH4 MeOH		101*
BENZYL-2-BROMOMETHYL	PY	RBr	IIIA; BH4 MeOH		35
BENZYL-3,5-DIMETHYL	PY	RBr	IIIA; BH4 MeOH	A	35
BENZYL-2-Cl-3,5-DI(Me)	PY	3,5-DI(Me)-BENZYL(Co)	CHLORINE(1 MOLE) HOAc (+ 1 PROD)	(A) (MIX)	35
BENZYL-4-Cl-3,5-DI(Me)	PY	3,5-DI(Me)-BENZYL(Co)	CHLORINE(1 MOLE) HOAc (+ 1 PROD)	(A) (MIX)	35
BENZYL-4-Br-3,5-DI(Me)	PY	3,5-DI(Me)-BENZYL(Co)	BROMINE(<1 MOLE) HOAc		35
BENZYL-2,4,5-TRI(Me)	PY	RBr	IIIA; BH4 MeOH	A	35
BENZYL-a-CHLORO	PY	RCl	IIIA; BH4? MeOH	A	32
1-INDANYL	PY	INDENE	IIIB; H2 OR BH4 MeOH	A	140,505
1-INDANYL-2-HYDROXY	PY	INDENE OXIDE	IIIA; H2? MeOH?	A	96,505
TETRAHYDROFURFURYL	PY	2-METHYLENE-THF?	IIIB?; BH4? MeOH?	A	96

R	B	REAGENT	METHOD	NOTES	REF
TETRAHYDROFURFURYL	PY	2,5-DI(HO)-PENTYL(Co) PY	CYCLISATION(CATIONIC) SILICIC ACID CHLOROFORM	A	577
TETRAHYDROFURFURYL	PY	RBr	IIIA; BH4? MeOH?	A	577
5'-DEOXYADENOSYL	PY	N⁶-ACETYL-5'-Br-5'-DEO-XYADENOSINE-2',3'-PHE-NYLBORONATE	IIIA; BH4 EtOH		385
5'-DEOXYADENOSYL	PY	5'-O-TOSYLADENOSINE	IIIA; BH4 MeOH	A	104
5'-DEOXYADENOSYL	PY	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS		104
5'-DEOXYADENOSYL	AQ	5'-O-TOSYLADENOSINE	IIIA; BH4 MeOH		104
2'(3')-O-ACETYL-5'-DEOXYADE-NOSYL	PY	N⁶-ACETYL-2'(3')-O-ACE-TYL-5'-Br-5'-DEOXYADE-NOSINE-3'(2')-(HYDRO-GEN PHENYLBORONATE)	IIIA; BH4 AQ/EtOH	A	379
2',3'-O-ISOPROPYLIDENE-5'-DEOXYADENOSYL	PY	2',3'-O-ISOPROPYLIDENE-5'-O-TOSYLADENOSINE	IIIA; BH4 MeOH		104
UNSPECIFIED ALKYL	UNSPEC	TRI(R) PHOSPHATE OR PHOSPHITE	IIIA		118
PROP-2-ENYL	PY	RCl	IIIA; BH4 MeOH	A	298,73
PROP-2-ENYL-3-PHENYL	PY	RCl	IIIA; BH4 MeOH	A	73
PROP-2-ENYL-2-METHYL	PY	RCl	IIIA; BH4 MeOH	(UNSTABLE)	73*
PROP-2-YNYL	PY	RBr(Cl)	IIIA; NEUT DISPROP MeOH	A	73
PROP-2-YNYL	PY	RBr	IIIA; NEUT DISPROP AQ/THF		73
PROP-2-YNYL	PY	RBr	IIIA; BH4 AQ DIOXAN(pH8)		73
BUT-3-ENYL	PY	RBr	IIIA; BH4 MeOH	A	73
BUT-2-ENYL	PY	BUTA-1,3-DIENE	IIIB; H2 EtOH	A	118
BUT-2-ENYL	PY	BUTA-1,3-DIENE	IIIB; BH4 MeOH	A	119
BUT-2-ENYL	PY	RCl	IIIA; BH4 MeOH	A	73
BUT-2-ENYL	PY	3-Me-3-Cl-PROP-1-ENE	IIIA; BH4 MeOH OR AQ/DIOXAN		73
BUT-2-ENYL?	TRI(Bu)P	3-Me-3-Cl-PROP-1-ENE	IIIA; BH4 MeOH		101*

R	B	REAGENT	METHOD	NOTES	REF
BUT-2-ENYL-3-METHYL	PY	BUTA-1,3-DIENE-2-Me	IIIB; BH4 MeOH	A	119
BUT-2-ENYL-3-METHYL	PY	RCl	IIIA; BH4 MeOH	A	73
BUT-2-YNYL	PY	RCl	IIIA; BH4 MeOH	A	234
PENT-4-ENYL	PY	RBr	IIIA; BH4 MeOH	A	73
HEX-5-ENYL	PY	RBr	IIIA; BH4 MeOH	A	73
2-NORBORNENYL	PY	NORBORNADIENE	IIIC; H2 MeOH(+ ONE PROD)	A(MIX)	47
NORTRICYCLYL	PY	NORBORNADIENE	IIIC; H2 MeOH(+ ONE PROD)	A(MIX)	47
2-NORBORNENYL	TRI(MeO)P		DISP OF AXIAL PY(+ 1 PROD)	A(MIX)	47
NORTRICYCLYL	TRI(MeO)P		DISP OF AXIAL PY(+ 1 PROD)	A(MIX)	47
VINYL	PY	ACETYLENE	IIIB; BH4 MeOH	A	12
VINYL	PY	RCl(Br)	IIIA; ALK DISPROP MeOH	A	39
VINYL	ANILINE	RCl	IIIA; ALK DISPROP MeOH	A	69
VINYL	AZIDE(-)		DISP OF AXIAL AQ	A AsPh4 SALT	123
VINYL	NC(Co)Me(-)		DISP OF AXIAL AQ		123*
VINYL	NC(Co)VINYL(-)		DISP OF AXIAL AQ		123*
VINYL	AQ	RBr	IIIA; ALK DISPROP MeOH	A	123
VINYL	TRI(Bu)P	ACETYLENE	IIIB; CPR EtOH		387
VINYL	TRI(MeO)P		DISP OF AXIAL ANILINE	A	69
VINYL	CN(-)		DISP OF AXIAL AQ	A AsPh4 SALT	123
VINYL	CN(-)		DISP OF AXIAL PY	A AsPh4 SALT	123
VINYL-2-ACETYL-TRANS	PY	RCl	IIIA; BH4 MeOH	A	388
VINYL-2-BENZOYL-TRANS	PY	RCl	IIIA; BH4 MeOH	A	388
VINYL-2-METHOXYCARBONYL-CIS	PY	RCl	IIIA; BH4 MeOH	A	37
VINYL-2-METHOXYCARBONYL-CIS	PY	Me PROPIOLATE	IIIB; H2 MeOH		37
VINYL-2-(EtO.CO)-TRANS	PY	RCl	IIIA; BH4 MeOH	A	37

R	B	REAGENT	METHOD	NOTES	REF
VINYL-2-(EtO.CO)-CIS?	AQ	Et PROPIOLATE	IIIC?; H2 MeOH	A	39
VINYL-2-(EtO.CO)-TRANS	TRI(EtO)P		DISP OF AXIAL PY	A	69
VINYL-2-HYDROXYMETHYL-CIS	PY	3-HO-PROP-1-YNE	IIIB; BH4 MeOH (+ 1 PROD)	A(MIX)	37
VINYL-2-HYDROXYMETHYL-CIS	PY	3-HO-PROP-1-YNE	IIIB; BH4 MeOH (ALK)	A	391
VINYL-2-METHOXYMETHYL-TRANS	PY	CIS/TRANS-1,3-DI(Br) -PROP-1-ENE/MeOH	IIIA; BH4? AQ/MeOH	A	389
VINYL-2-METHOXYMETHYL-TRANS	PY	1,1,2,3-TETRA(Br)-PROP-ANE/MeOH (VIA ALKENE)	IIIA; BH4 MeOH	A	592
VINYL-2-METHOXYMETHYL-TRANS	TRI(EtO)P		DISP OF AXIAL PY	A	389
VINYL-2-t-BUTOXYMETHYL--TRANS	PY	CIS/TRANS-1,3-DI(Br) -PROP-1-ENE/tBuOH	IIIA; BH4? AQ/MeOH (+ 1 PROD)	A	389
VINYL-2-HYDROXYMETHYL-TRANS	PY	CIS/TRANS-1,3-DI(Br) -PROP-1-ENE/tBuOH	IIIA; BH4? AQ/MeOH (+ 1 PROD)	A	389
VINYL-2-(2-HYDROXYCARBONYL-ETHYL)-TRANS	PY	CIS/TRANS-5-Br-PENT-4 -ENOIC ACID	IIIA; BH4? AQ/MeOH	A	389
VINYL-2-(2-ETHOXYCARBONYL-ETHYL)-TRANS	PY	CIS/TRANS-5-Br-PENT-4 -ENOIC ACID Et ESTER	IIIA; BH4? AQ/MeOH	A	389
VINYL-2-(2-(9-CARBAZOLYLCAR -BONYL)ETHYL)-TRANS	PY	RBr	IIIA; BH4? AQ/MeOH	A	389
VINYL-2-TRIFLUOROMETHYL-CIS	PY	TRI(F)-Me-ACETYLENE	IIIB OR IIIC; BH4 MeOH	A	69
VINYL-2-TRIFLUOROMETHYL-CIS	TRI(MeO)P		DISP OF AXIAL PY	A	69
VINYL-2-PHENYL-CIS	PY	PHENYLACETYLENE	IIIB; ALK DISPROP MeOH	A	39
VINYL-2-PHENYL-CIS	PY	PHENYLACETYLENE	IIIB; H2 MeOH(pH11)		37
VINYL-2-PHENYL-CIS	PY	PHENYLACETYLENE	IIIB; BH4 MeOH (ALK)		12,38
VINYL-2-PHENYL-CIS	PY	RBr(I)	IIIA; BH4 MeOH	A	37,38,111
VINYL-2-PHENYL-CIS?	IMID	PHENYLACETYLENE	IIIB(AND IIIC?); BH4 MeOH	A	390
VINYL-2-PHENYL-CIS	ANILINE	RBr	IIIA; ALK DISPROP MeOH	A	37
VINYL-2-PHENYL-CIS	AQ	PHENYLACETYLENE	IIIB; ALK DISPROP MeOH	A	39
VINYL-2-PHENYL-CIS	AQ	RBr	IIIA; ALK DISPROP MeOH	A	37

R	B	REAGENT	METHOD	NOTES	REF
VINYL-2-PHENYL-CIS	TRI(MeO)P		DISP OF AXIAL PY	A	69
VINYL-2-PHENYL-CIS	CN(-)		DISP OF AXIAL PY	A AsPh4 SALT	123
VINYL-2-PHENYL-TRANS	PY	RBr	IIIA; BH4 MeOH	A	37
VINYL-2-PHENYL-TRANS	PY	RBr	IIIA; ALK DISPROP MeOH	A	38
VINYL-2-PHENYL-TRANS	ANILINE	RBr	IIIA; ALK DISPROP MeOH	A	37
VINYL-2-PHENYL-TRANS	AQ	RBr	IIIA; ALK DISPROP MeOH	A	37
VINYL-2-PHENYL-TRANS	TRI(MeO)P		DISP OF AXIAL PY	A	69
VINYL-2-PHENYL-TRANS	CN(-)		DISP OF AXIAL PY	A AsPh4 SALT	123
VINYL-1-METHYL	PY	ALLENE	IIIB; BH4 MeOH	A	40
VINYL-1-METHYL	CN(-)		DISP OF AXIAL PY	A AsPh4 SALT	123
VINYL-1-HYDROXYMETHYL	PY	3-HO-PROP-1-YNE	IIIC; BH4 MeOH(+ 1 PROD)		37
VINYL-1-PHENYL	PY	PHENYLACETYLENE	IIIC; H2 MeOH(pH8)	A	39,37
VINYL-1-PHENYL	PY	PHENYLACETYLENE	IIIC; BH4 MeOH(0.2M HOAc)	A	38
VINYL-1-PHENYL	PY	PHENYLACETYLENE	IIIC; 1-Ph-2-HO-Et(Co)PY AT 40° MeOH		69
VINYL-1-PHENYL	TRI(EtO)P		DISP OF AXIAL PY	A	69
VINYL-1-PHENYL	CN(-)		DISP OF AXIAL PY	A AsPh4 SALT	123
VINYL-1-Ph-2-D(D CIS TO Co)	PY	PHENYLACETYLENE	IIIC(D(Co)); D2 MeOH		69
VINYL-1-Ph-2-D(D CIS TO Co)	TRI(MeO)P		DISP OF AXIAL PY		69
VINYL-1-Me-2-(EtO.CO)-CIS	PY	RCl	IIIA; BH4 MeOH	A	69
VINYL-1-Me-2-(EtO.CO)-CIS	TRI(MeO)P		DISP OF AXIAL PY	A	69
VINYL-1-Me-2-(EtO.CO)-TRANS	ANILINE	Me-(EtO.CO)-ACETYLENE	IIIC OR IIIB; H2 EtOH(pH8)	A	69
VINYL-1-Me-2-(EtO.CO)-TRANS	TRI(MeO)P		DISP OF AXIAL ANILINE	A	69
VINYL-1,2-DI(MeO.CO)-TRANS	PY	DI(MeO.CO)-ACETYLENE	IIIC OR IIIB; H2 MeOH(pH8)	A	39,69
VINYL-1,2-DI(MeO.CO)-TRANS	TRI(MeO)P		DISP OF AXIAL PY	A	69
CYCLOPENT-1-ENYL-3,3,4,4--TETRACYANO	PY	PROPARGYL(Co)PY	TETRACYANOETHYLENE DICHLOROMETHANE	A	588

R	B	REAGENT	METHOD	NOTES	REF
CYCLOPENT-1-ENYL-4-OXA--3,3-DI(TRIFLUOROMETHYL)	PY	PROPARGYL(Co)PY	HEXAFLUOROACETONE DEUTERIOCHLOROFORM	(A)	589
ALLENYL	PY	3-Br(Cl)-PROP-1-YNE	IIIA; BH4 MeOH	A	382,234,73
ALLENYL	PY	3-Br-PROP-1-YNE	IIIA; ALK DISPROP OR BH4 AQ/DIOXAN	A	73
ALLENYL	PY	3-Br-PROP-1-YNE	IIIA; BH4 AQ/THF		73
ALLENYL	PY	3-Br-PROP-1-YNE	IIIA; NEUT DISPROP MeOH(HIGH TEMP)		73
ALLENYL	PY	RCl(Br)	IIIA; BH4 MeOH		234,73
ALLENYL-3,3-DIMETHYL	PY	3-Cl-3-Me-BUT-1-YNE	IIIA; BH4 MeOH	A	234
ALLENYL-3-Me-3-Et	PY	3-Cl-3-Me-PENT-1-YNE	IIIA; BH4 MeOH	A	73
CYCLOHEXYL=C=CH	PY	1-Cl-1-ETHYNYL-cHEXANE	IIIA; BH4 MeOH	A	234
ETHYNYL-PHENYL	PY	RMgHal	IA; THF	A	12
ETHYNYL-PHENYL	PY	RBr	IIIA; BH4 MeOH	A	391
ETHYNYL-PHENYL	CN(-)		DISP OF AXIAL PY	A AsPh4 SALT	123
PHENYL	PY	RMgBr	IA; THF	A	12,50,584
PHENYL	TRI(Me)N	RMgBr	IA; THF	A	12
PHENYL	DMF		DISP OF AXIAL PY		13
PHENYL	AQ		DISP OF AXIAL PY IN ACID AQ.		235a*,584*
PHENYL	TRI(Bu)P	RMgBr	IA; THF	A	12
PHENYL	TRI(Ph)P	RMgBr	IA; THF	A	12
PHENYL	TRI(Ph)P	RMgBr	IA; ETHER	A	392,393
PHENYL-4-FLUORO	PY	RMgHal	IA; THF	A	584
PHENYL-4-FLUORO	AQ		DISP OF AXIAL PY IN ACID AQ.		235a*,584*
PHENYL-4-METHOXY	PY	RMgHal	IA; THF	A	12
PHENYL-4-METHOXY	AQ		DISP OF AXIAL PY IN ACID AQ.		235a*,584*
PHENYL-4-METHYL	PY	RMgHal	IA; THF	A	65

R	B	REAGENT	METHOD	NOTES	REF
PHENYL-4-METHYL	AQ		DISP OF AXIAL PY IN ACID AQ.		235a*,584*
METHOXYCARBONYL	PY	CO	IC; MeO(Co) MeOH	A	18
METHOXYCARBONYL	PY	TRICHLOROMETHYL(Co)	METHANOLYSIS NaOMe MeOH	A	21
BENZOYL	TRI(Bu)P	RCl	XIIA; BH4 MeOH	A	39
UNSPECIFIED	UNSPEC	RLi(Na,Al,B,Hg)	IA		118
PROPANE-1,3-DI(Co)	PY	1,3-DIBROMOPROPANE	XIIA; BH4 MeOH	A	118
BUTANE-1,4-DI(Co)	PY	1,4-DIBROMOBUTANE	XIIA; BH4 MeOH	A	118
BENZENE-1,3-DI(METHY-LENE(Co))	PY	BrRBr	XIIA; BH4 MeOH	A	35
BENZENE-1,4-DI(METHY-LENE(Co))	PY	BrRBr	XIIA; BH4 MeOH	A	35,47
BENZENE-1,4-DI(METHY-LENE(Co))	AQ	BrRBr	XIIA; BH4 MeOH	A	47
BENZENE-5-Me-1,3-DI(METH-YLENE(Co))	PY	BrRBr	XIIA; BH4 MeOH		35
BENZENE-5-BROMOMETHYL-1,3-DI(METHYLENE(Co))	PY	BrRBr	XIIA; BH4 MeOH		35
BENZENE-4-BROMO-1,3-DI(METHYLENE(Co))	PY	1,3-DI(PY(Co)-Me)-PhH	BROMINE(1 MOLE) HOAc(+ 1 PROD)		35
BENZENE-4,6-DI(Br)-1,3-DI(METHYLENE(Co))	PY	1,3-DI(PY(Co)-Me)-PhH	BROMINE(1 MOLE) HOAc(+ 1 PROD)		35
BENZENE-4,6-DI(Br)-5-Me-1,3-DI(METHYLENE(Co))	PY	5-Me-1,3-DI(PY(Co)-Me)-BENZENE	BROMINE(1 MOLE) HOAc	(A)	35
(Co).CH=CH.(Co)-TRANS?	PY	ACETYLENE	IIC; ETHANOL	A	39
(Co).CH=CH.(Co)-TRANS?	AQ	ACETYLENE	IIC; METHANOL	A	39

BIS(DIMETHYLGLYOXIMATO) - VARIANTS (SOLUTION SPECIES OMITTED)

R	B	REAGENT	METHOD	NOTES	REF
METHYL	SO2	MeCoBIS(dmgH)AQ	PY IN LIQUID SO2	A L = (dmgH)(dmg)? H-PY SALT	152
METHYL	NCS(-)	MeCoBIS(dmgH)AQ?	NCS(-) IN ACID AQ?	(A) L = (dmgH2)(dmgH)	200
HEPTYL-1-METHYL	TRIFLUORO-ACETATE(-)	RCoBIS(dmgH)AQ	TRI(F)ACETIC ACID,THEN + AQ	A L = (dmgH2)(dmgH)	380
BENZYL	TRIFLUORO-ACETATE(-)	RCoBIS(dmgH)AQ	TRI(F)ACETIC ACID,THEN + AQ	A L = (dmgH2)(dmgH)	380
BENZYL-4-FLUORO	TRIFLUORO-ACETATE(-)	RCoBIS(dmgH)AQ	TRI(F)ACETIC ACID,THEN + AQ	A L = (dmgH2)(dmgH)	47

BIS(DIPHENYLGLYOXIMATO)

R	B	REAGENT	METHOD	NOTES	REF
METHYL	PY	RI?	IIIA; BH4 MeOH	A	67
METHYL	IMID		DISP OF AXIAL AQ?	A	65
METHYL	BENZIMID		DISP OF AXIAL AQ?	A	65
METHYL	AMMONIA		DISP OF AXIAL AQ?	A	65
METHYL	AQ	RI?	IIIA?; BH4? MeOH?	A	377,6
METHYL	TRI(Bu)P	RI	IIIA; BH4 MeOH	A	65
METHYL	TRI(Ph)P		DISP OF AXIAL AQ OR PY?	A	65
METHYL	c-HexNC		DISP OF AXIAL AQ?	A	65
METHYL	CN(-)		DISP OF AXIAL AQ?		65a
ETHYL	PY	RHal?	IIIA?; BH4? MeOH?	A	65
ETHYL	IMID		DISP OF AXIAL AQ?	A	65
ETHYL	BENZIMID		DISP OF AXIAL AQ?	A	65
ETHYL	AMMONIA		DISP OF AXIAL AQ?	A	65

R	B	REAGENT	METHOD	NOTES	REF
ETHYL	PIPERIDINE		DISP OF AXIAL AQ?		65*
ETHYL	TRI(Et)N		DISP OF AXIAL AQ?		65*
ETHYL	ANILINE		DISP OF AXIAL AQ?		65*
ETHYL	MeCN		DISP OF AXIAL AQ?		65*
ETHYL	AQ	RHal?	IIIA?; BH4? MeOH?	A	65
ETHYL	CN(-)		DISP OF AXIAL AQ		65*
ETHYL-2-CN	PY	ACRYLONITRILE?	IIIA?; BH4? MeOH?		110
ETHYL-1-CN	PY	ACRYLONITRILE	IIIC; BH4 MeOH	A	381
PROPYL	PY	RCl	IIIA; BH4 MeOH		101*
PROPYL	AQ	RCl	IIIA; BH4 MeOH		101*
PROPYL	TRI(Bu)P	RCl	IIIA; BH4 MeOH		101*
PROPYL	DI(Me)S	RCl	IIIA; BH4 MeOH		101*
BENZYL	PY	RBr	IIA; PhH OR ACETONE		99*
6-PYRIMIDYL-2,4-DIHYDROXY--5,6-DIHYDRO	TRI(Ph)P	URACIL	IIIB; BH4 AQ/EtOH	A	394

(REACTIONS WITH URIDINE, 2'-ANHYDROURIDINE & URIDINE-5'-MONOPHOSPHATE ALSO REPORTED ; FOR L = dmgH)

BIS(DI[4-METHOXYPHENYL]GLYOXIMATO)

R	B	REAGENT	METHOD	NOTES	REF
BENZYL	PY	RBr	IIA; PhH OR ACETONE		99*

BIS(DI[4-NITROPHENYL]GLYOXIMATO)

R	B	REAGENT	METHOD	NOTES	REF
BENZYL	PY	RBr	IIA; ACETONE		99*

BIS(CYCLOPENTANE-1,2-DIONEDIOXIMATO)

R	B	REAGENT	METHOD	NOTES	REF
PROPYL	PY	RCl	IIIA; BH4 MeOH		101*
PROPYL	AQ	RCl	IIIA; BH4 MeOH		101*
PROPYL	TRI(Bu)P	RCl	IIIA; BH4 MeOH		101*
PROPYL	DI(Me)S	RCl	IIIA; BH4 MeOH		101*

BIS(CYCLOHEXANE-1,2-DIONEDIOXIMATO)

R	B	REAGENT	METHOD	NOTES	REF
METHYL	PY	MeCoBIS(dmgH)AQ	c-hgH2, PhMe, THEN PY	A	118
METHYL	PY	RI	IIIA; ALK DISPROP MeOH		118
METHYL	PY	DI(R)SULPHATE	IIIA; BH4 MeOH		223
METHYL	NC(Co)Me(-)		DISP OF AXIAL AQ		123*
METHYL	NCCoBIS(dmgH)	BENZYL-4-NITRO(-)	REARRANGEMENT OF BRIDGE-FLIPPED ISOMER (≥33% OF PROD)		123*
METHYL	NCCoBIS(dmgH)	BENZYL-4-NITRO(-)	REARRANGEMENT OF MIX OF RESPECTIVE 'SYMMETRIC' BRIDGED SPECIES (≥33% OF PROD)		123*
METHYL	AQ	RI	IIIA; ALK DISPROP MeOH	A	123
METHYL	CN(-)		DISP OF AXIAL PY	A AsPh4 SALT	123
ETHYL	PY	RI	IIIA; BH4 MeOH	A	223
PROPYL	PY	RCl(I)	IIIA; BH4 MeOH	A	101*,373

R	B	REAGENT	METHOD	NOTES	REF
PROPYL	AQ	RCl	IIIA; BH4 MeOH		101*
PROPYL	TRI(Bu)P	RCl	IIIA; BH4 MeOH		101*
PROPYL	DI(Me)S	RCl	IIIA; BH4 MeOH		101*
PROPYL-2-METHYL	PY	RBr	IIIA; BH4 MeOH	A	223
OCTYL	PY	RBr	IIIA; BH4 MeOH	A	223
BENZYL	PY	RBr	IIA; ACETONE		99a*
BENZYL	PY-4-Me	RBr	IIA; ACETONE OR PhH		99a*
BENZYL	1-MeIMID	RBr	IIA; BENZENE		99a*
BENZYL	NICOTINAMIDE	RBr	IIA; ACETONE		99a*
BENZYL	TRI(Et)P	RBr	IIA; BENZENE		99a*
BENZYL	TRI(Bu)P	RBr	IIA; BENZENE		99a*
BENZYL	TRI(c-HEX)P	RBr	IIA; BENZENE		99a*
BENZYL	TRI(Ph)P	RBr	IIA; PhH OR ACETONE		99a*
BENZYL	DI(Ph)PH	RBr	IIA; BENZENE		99a*
BENZYL	TRI(MeO)P	RBr	IIA; BENZENE		99a*
BUT-2-ENYL (+ 33% REAG.)	PY	RCoBis(dmgH)PY	IIIA; BH4 MeOH		73
ALLENYL	PY	PROPARGYLCoBIS(dmgH)PY	IIIA; BH4 MeOH		73

(DIMETHYLGLYOXIMATO) (CYCLOHEXANE-1,2-DIONEDIOXIMATO)

R	B	REAGENT	METHOD	NOTES	REF
METHYL	PY	MeI	IIIA (dmgH:c-hgH = 1:1); BH4 MeOH (50% OF PROD)		373

BIS(IMINOBIACETYLMONOXIMINO)

R	B	REAGENT	METHOD	NOTES	REF
METHYL	PY	RI	IIIA (L=dmgHMe); BH4 MeOH	A	118

BIS(DIARS)

R	B	REAGENT	METHOD	NOTES	REF
PHENYL-PERFLUORO	Br(-)	DI(R)TlBr	IIE;	A Br SALT	26

ACACEN

R	B	REAGENT	METHOD	NOTES	REF
METHYL	PY		ADDITION TO 'NONE' OR DISP OF AXIAL AQ	A (X-RAY)	34 (179a)
METHYL	PY-4-Me		ADDITION TO NONE		139*
METHYL	PY-4-CN		ADDITION TO NONE		139*
METHYL	BENZIMID		ADDITION TO 'NONE' OR DISP OF AXIAL AQ	A	34
METHYL	PIPERIDINE		ADDITION TO NONE		139*
METHYL	en(Co)Me		ADDITION TO 'NONE' OR DISP OF AXIAL AQ	A	34

R	B	REAGENT	METHOD	NOTES	REF
METHYL	ANILINE-4-Cl		ADDITION TO NONE		289*
METHYL	ANILINE-4-Me		ADDITION TO NONE		289*
METHYL	AQ	RMgBr	IA; THF	A	182
METHYL	AQ	RI	IIIA; Na(Hg) THF		284,34
METHYL	AQ	RI	IIIA; BH4 EtOH		284,34
METHYL	AQ	RI	IIIA; BH4/Pd MeOH (pH>13)		67
METHYL	AQ	DI(Me)Co(dotnH)	IA; MeOH OR AQ./THF		237
METHYL	NONE		REMOVAL OF AXIAL AQ	A (X-RAY)	182 (155)
METHYL	TRI(MeO)P		ADDITION TO NONE?		136*
METHYL	TRI(Ph)P		ADDITION TO NONE		139*
METHYL	CN(-)		DISP OF AXIAL AQ		67*
METHYL-TRIFLUORO	AQ	RI	IIIA; Na OR Na(Hg) THF	A	396
METHYL-TRIFLUORO	NONE		REMOVAL OF AXIAL AQ		396
ETHYL	PY		ADDITION TO 'NONE'		34*,139*, 395*,289*
ETHYL	PY-4-Me		ADDITION TO 'NONE'		289*
ETHYL	ANILINE		ADDITION TO 'NONE'		289*
ETHYL	ANILINE-4-Cl		ADDITION TO 'NONE'		289*
ETHYL	ANILINE-4-Me		ADDITION TO 'NONE'		289*
ETHYL	AQ	EtMgBr	IA; THF	A	182
ETHYL	AQ	EtBr	IIIA; Na(Hg) THF		34
ETHYL	AQ	EtBr	IIIA; BH4/Pd MeOH(pH>13)		67
ETHYL	NONE		REMOVAL OF AXIAL AQ	A	182
ETHYL	DMF		DISP OF AXIAL AQ		521*
ETHYL	CN(-)		DISP OF AXIAL AQ		67*
ETHYL-2-CN	PY		ADDITION TO NONE	A	34

R	B	REAGENT	METHOD	NOTES	REF
ETHYL-2-CN	NONE	ACRYLONITRILE	IIIB; Na(Hg) THF/AQ	A	34
ETHYL-PERFLUORO	NONE	RI	IIIA; Na(Hg) THF	A	297,396
ETHYL-1-KETO	PY		ADDITION TO NONE	A	34
ETHYL-1-KETO	1-MeIMID		ADDITION TO NONE		16*
ETHYL-1-KETO	NONE	RCl(ROR)	IIIA; Na(Hg) THF	A	284,34
PROPYL	PY		ADDITION TO 'NONE'		34*
PROPYL	AQ	PrBr	IIIA; Na(Hg) THF	A	34
PROPYL	NONE		REMOVAL OF AXIAL AQ	A	34
PROPYL-PERFLUORO	AQ	RI	IIIA; Na OR Na(Hg) THF	A	396
PROPYL-PERFLUORO	NONE		REMOVAL OF AXIAL AQ		396
BUTYL-4-Br	AQ	RBr	IIIA; Na(Hg) THF	A	34
BUTYL-4-Br	NONE		REMOVAL OF AXIAL AQ	A	34
VINYL	PY		ADDITION TO 'NONE' OR DISP OF AXIAL AQ	A	34
VINYL	4-MePY		ADDITION TO NONE		289*
VINYL	ANILINE		ADDITION TO 'NONE'		289*
VINYL	ANILINE-4-Cl		ADDITION TO 'NONE'		289*
VINYL	ANILINE-4-Me		ADDITION TO 'NONE'		289*
VINYL	DMF		DISP OF AXIAL AQ		292*
VINYL	AQ	RCl	IIIA; Na(Hg) THF	A (X-RAY)	34 (177)
VINYL	AQ	ACETYLENE	IIIB; Na(Hg) THF/AQ	A	34
VINYL	NONE		REMOVAL OF AXIAL AQ	A	34
PHENYL	PY		ADDITION TO NONE	A	182
PHENYL	PY-PENTA-D		ADDITION TO 'NONE'		186*
PHENYL	PY-4-Me		ADDITION TO 'NONE'		289*
PHENYL	BENZIMID		ADDITION TO 'NONE' OR DISP OF AXIAL AQ	A	34

R	B	REAGENT	METHOD	NOTES	REF
PHENYL	ANILINE		ADDITION TO 'NONE'		289*
PHENYL	ANILINE-4-Cl		ADDITION TO 'NONE'		289*
PHENYL	ANILINE-4-Me		ADDITION TO 'NONE'		289*
PHENYL	BENZYLAMINE		ADDITION TO 'NONE' OR DISP OF AXIAL AQ	A	34
PHENYL	PIPERIDINE		ADDITION TO 'NONE'		186*
PHENYL	enCo(acacen)Ph		ADDITION TO 'NONE' OR DISP OF AXIAL AQ	A	34
PHENYL	PIPERAZINE--Co(acacen)Ph		ADDITION TO 'NONE'	A	34
PHENYL	DMF		DISP OF AXIAL AQ		521*
PHENYL	AQ	PhMgBr	IA; THF	A (X-RAY)	182 (174)
PHENYL	AQ	PhLi	IA; THF		182
PHENYL	AQ?	RBr	IIIA; Na(Hg)? THF?		61
PHENYL	NONE		REMOVAL OF AXIAL AQ	A	182
PHENYL-4-Br	NONE	?	?		186
PHENYL-4-Br	PY-PENTA-D		ADDITION TO 'NONE'		186*
PHENYL-4-Br	PIPERIDINE		ADDITION TO 'NONE'		186*
PHENYL-4-I	NONE	?	?		186
PHENYL-4-I	PY-PENTA-D		ADDITION TO 'NONE'		186*
PHENYL-4-I	PIPERIDINE		ADDITION TO 'NONE'		186*
PHENYL-4-NITRO	NONE	?	?		186
PHENYL-4-NITRO	PY-PENTA-D		ADDITION TO 'NONE'		186*
PHENYL-4-NITRO	PIPERIDINE		ADDITION TO 'NONE'		186*
PHENYL-4-OMe	NONE	?	?		186
PHENYL-4-OMe	PY-PENTA-D		ADDITION TO 'NONE'		186*
PHENYL-4-CN	NONE	?			186

ACACEN

R	B	REAGENT	METHOD	NOTES	REF
PHENYL-4-CN	PY-PENTA-D		ADDITION TO 'NONE'		186*
PHENYL-4-CN	PIPERIDINE		ADDITION TO 'NONE'		186*
PHENYL-4-Me	NONE	?	?		186
PHENYL-4-Me	PY-PENTA-D		ADDITION TO 'NONE'		186*
METHOXYCARBONYL	PY		DISP OF AXIAL AQ		16*
METHOXYCARBONYL	AQ	CO	IC; PHOTOL OF Me(Co) MeOH	A	18
METHOXYCARBONYL	AQ	CO	IC(MeO(Co) OR (Co),O2); MeOH		18
BUTANE-1,4-DI(Co)	NONE	4-Br-BuCo(acacen)	IIIA; Na(Hg) THF	A	34

P-ACACEN

R	B	REAGENT	METHOD	NOTES	REF
METHYL	PY		ADDITION TO 'NONE'?		397*
METHYL	PY-4-CN		ADDITION TO 'NONE'?		397*
METHYL	PIPERIDINE		ADDITION TO 'NONE'?		397*
METHYL	PIPERIDINE-4-Me		ADDITION TO 'NONE'?		397*
METHYL	AQ	RI	IIIA; Na(Hg) THF	A	297
METHYL	NONE		REMOVAL OF AXIAL AQ?		397
ETHYL	AQ	RI	IIIA; Na(Hg) THF	A	297
ETHYL-PERFLUORO	AQ	RI	IIIA; Na OR Na(Hg) THF	A	396
ETHYL-PERFLUORO	NONE		REMOVAL OF AXIAL AQ		396

ACACEN

R	B	REAGENT	METHOD	NOTES	REF
ETHYL-PERFLUORO	AQ	RI	IIIA; Na OR Na(Hg) THF	A	396
ETHYL-PERFLUORO	NONE		REMOVAL OF AXIAL AQ		396

SALEN

R	B	REAGENT	METHOD	NOTES	REF
METHYL	PY		DISP OF AXIAL AQ	A	183,85,148
METHYL	PY		ADDITION TO 'NONE' (GREEN)		148
METHYL	PY	RI	IIIA; RMgX THF OR ETHER	A	148
METHYL	PY	RI	IIIA;LiBH4 THF	A	148
METHYL	BENZIMID		DISP OF AXIAL AQ	A	183
METHYL	AMMONIA		DISP OF AXIAL AQ	A	183
METHYL	DMF		DISP OF AXIAL AQ		292*,521*
METHYL	DMF		ADDITION TO 'NONE'		575*
METHYL	AQ(ORANGE)	MeMgBr	IA; THF	A	183
METHYL	AQ(ORANGE)	RI	IIIA; Na THF	A	85,148
METHYL	AQ	RI	IIIA; Na(Hg) THF		284,86
METHYL	AQ(BLACK)	RI(Cl)	IIIA; BH4/Pd MeOH HIGH pH	A	67,101*
METHYL	AQ	RI	IIIA; CYCLOOCTATETRAENE--DIANION THF		398
METHYL	AQ	DI(Me)Co(dotnH)	IA; MeOH OR AQ THF		237
METHYL	AQ	MeCo(acacen)AQ	IA; AQ MeOH		261
METHYL	AQ	RI	IIIA; CO AQ THF(pH13)	A	399
METHYL	NONE(GREEN)		REMOVAL OF AXIAL AQ(SOLID)	A	399
METHYL	NONE(RED)		REMOVAL OF AXIAL AQ(SOLN)	A	183

P	B	REAGENT	METHOD	NOTES	REF
METHYL	NONE(RED)		GREEN ANALOGUE IN ETHER	A	148
METHYL	DMSO		DISP OF AXIAL AQ		139*
METHYL	CN(-)		DISP OF AXIAL AQ		67*
METHYL-CHLORO	AQ	DICHLOROMETHANE	IIIA; BH4/Pd MeOH(HIGH pH)	A	67
METHYL-CHLORO	AQ	DICHLOROMETHANE	IIIA; Na THF		400
METHYL-CHLORO	DMF?	DICHLOROMETHANE	IIIA; BH4 DMF		400*
METHYL-NITRO	AQ	NITROMETHANE	IB; HO(Co)AQ AQ/MeOH	A	16
METHYL-NITRO	NONE	NITROMETHANE	IB; (Co) O2 MeOH		401,402
METHYL-CN	NONE (POLYMERIC)	ACETONITRILE	IB; (Co) O2 MeOH	A (X-RAY)	401,402,15 (161)
METHYL-CN	PY	ACETONITRILE	IB; (Co) O2 MeOH	A	15
METHYL-DICHLORO	AQ	CHLOROFORM	IIIA; Na THF		400
METHYL-DICHLORO	DMF?	CHLOROFORM	IIIA; BH4 DMF		400*
METHYL-DICYANO	PY		ADDITION TO 'NONE'	A	14
METHYL-DICYANO	PY		DISP OF AXIAL AQ		14
METHYL-DICYANO	PY	DI(CN)METHANE	IB; HO(Co)PY MeOH		14
METHYL-DICYANO	AQ		ADDITION TO 'NONE'	A	14
METHYL-DICYANO	AQ	DI(CN)METHANE	IB; MeO(Co) AQ/MeOH		14
METHYL-DICYANO	NONE (POLYMERIC)	DI(CN)METHANE	IB; (Co) O2 EtOH	A	14
METHYL-CN-AMINOCARBONYL	AQ	CYANOACETAMIDE	IB; (Co) O2 AQ/MeOH	A	15
METHYL-CN-ETHOXYCARBONYL	AQ	ETHYL CYANOACETATE	IB; (Co) O2 AQ/MeOH	A	15
METHYL-TRIFLUORO	PY		DISP OF AXIAL AQ	A	396
METHYL-TRIFLURO	AQ	RI	IIIA; Na OR Na(Hg) THF	A	396
METHYL-TRIFLUORO	NONE		REMOVAL OF AXIAL AQ		396
ETHYL	PY	EtMgBr	IA; THF	A	148

R	B	REAGENT	METHOD	NOTES	REF
ETHYL	PY		ADDITION TO 'NONE'	A	183
ETHYL	AMMONIA		ADDITION TO 'NONE'	A	183
ETHYL	DMF		ADDITION TO 'NONE'		292*,521*
ETHYL	AQ	RHal	IIIA; BH4/Pd MeOH(HIGH pH)	A	67
ETHYL	NONE	EtMgBr	IA; THF	A (X-RAY)	183 (156)
ETHYL	NONE	EtBr	IIIA; Na(Hg) THF		86
ETHYL	DMSO		ADDITION TO 'NONE'		139*
ETHYL	CN(-)		DISP OF AXIAL AQ		67*
ETHYL-2-METHYL	PY	RCl	IIIA; Na THF	A	148
ETHYL-2-METHYL	PY	RMgHal	IA; THF	A	148
ETHYL-2-METHYL	AQ	RHal	IIIA; BH4/Pd MeOH(HIGH pH)	A	67
ETHYL-2-HYDROXY	AQ		ADDITION TO 'NONE'		104*
ETHYL-2-HYDROXY	NONE	ETHYLENE OXIDE	IIIA; BH4/Pd MeOH(HIGH pH)	A	104
ETHYL-2-CN	PY		DISP OF AXIAL AQ	A	86
ETHYL-2-CN	AQ	ACRYLONITRILE	IIIB; Na(Hg) THF/AQ	A	86
ETHYL-2-KETO	NONE?	ACETALDEHYDE	IB; (Co) O2 MeOH		401,402
ETHYL-1-KETO	PY	RHal	IIIA; Na THF	A	148
ETHYL-1-KETO	PY		ADDITION TO 'NONE'	A	86
ETHYL-1-KETO	1-MeIMID		ADDITION TO 'NONE'		16*
ETHYL-1-KETO	NONE	RCl ROR	IIIA; Na(Hg) THF	A	284,86
ETHYL-1,1-DICHLORO	DMF?	1,1,1-TRICHLOROETHANE	IIIA; BH4 DMF		400*
ETHYL-PERFLUORO	PY		ADDITION TO 'NONE'	A	396
ETHYL-1-KETO-2-PHENYL	AQ	RCl	IIIA; Na(Hg) THF	A	403
ETHYL-PERFLUORO	NONE	RI	IIIA; Na OR Na(Hg) THF	A	396
PROPYL	PY		DISP OF AXIAL AQ	A	183

R	B	REAGENT	METHOD	NOTES	REF
PROPYL	AMMONIA		DISP OF AXIAL AQ		183*
PROPYL	AQ	PrMgBr	IA; THF	A	183
PROPYL	AQ	PrBr	IIIA; Na(Hg) THF		86
PROPYL	AQ	PrHal	IIIA; BH4/Pd MeOH(HIGH pH)	A	67
PROPYL-2-KETO	MeOH	ACETONE	IB; HO(Co)AQ MeOH	A (X-RAY)	16 (161)
PROPYL-2-KETO	NONE?	ACETONE	IB; (Co) O2 MeOH		401,402
PROPYL-1-KETO	NONE	RCl	IIIA; Na(Hg) THF	A	403
PROPYL-2,2-DIMETHYL	AQ	RHal	IIIA; BH4/Pd MeOH(HIGH pH)	A	67
PROPYL-1-KETO-2-METHYL	AQ	RCl	IIIA; Na(Hg) THF	A	403
PROPYL-PERFLUORO	PY		ADDITION TO 'NONE'	A	396
PROPYL-PERFLUORO	PY-2-Me		ADDITION TO 'NONE'	A	396
PROPYL-PERFLUORO	PY-4-Me		ADDITION TO 'NONE'	A	396
PROPYL-PERFLUORO	NONE	RI	IIIA; Na OR Na(Hg) THF	A	396
PROPYL-PERFLUORO	NONE	RI	IIIA; BH4/Pd MeOH (HIGH pH)	(LOW YIELD)	396
PROPYL-PERFLUORO	NONE	RI	IIIA?; Me(Co)AQ IN DIMETHOXYETHANE		297,396
BUTYL	PY		DISP OF AXIAL AQ	A	183
BUTYL	PY	RHal	IIIA; Na THF	A	148
BUTYL	AMMONIA		DISP OF AXIAL AQ		183*
BUTYL	DMF		ADDITION TO 'NONE'		575*
BUTYL	AQ	RMgBr	IA; THF	A	183
BUTYL	AQ	RBr	IIIA; Na THF	A	575
BUTYL	NONE		REMOVAL OF AXIAL AQ		575
BUTYL-4-BROMO	NONE	BUTANE-1,4-DIBROMO	IIIA; Na(Hg) THF	A	86
BUTYL-3-METHYL	DMF?	RCl	IIIA; BH4 DMF		400*
BENZYL	PY	RHal	IIIA; Na THF	A	148

R	B	REAGENT	METHOD	NOTES	REF
BENZYL	DMF		DISP OF AXIAL AQ		289*,521*
BENZYL	DMF	TRI(Me)NR(+) ClO4(-)	IIIA; CPR DMF		529*
BENZYL	AQ	RHal?	IIIA?; Na(Hg)? THF?		521
BENZYL-4-NITRO	1-MeIMID	RBr RCl	IIB; DICHLOROMETHANE/MeIMID	A	23
BENZYL-4-CN	1-MeIMID	RHal	IIB; DICHLOROMETHANE/MeIMID		23*
BENZYL-4-CN	DI(Me)PPh	RI	IIA; DICHLOROMETHANE		100*
BENZYL-a-CN-2-Br	NONE (POLYMERIC?)	RH	IB; (Co) O2 AQ/MeOH	A	15
VINYL	PY		DISP OF AXIAL AQ	A	86
VINYL	PY	?	IIIA; OR IIIB; BH4/Pd IN MeOH (HIGH pH)	A	67
VINYL	AQ	RCl	IIIA; Na(Hg) THF	A	86
VINYL	AQ	ACETYLENE	IIIB; Na(Hg) THF/AQ		86
VINYL	DMF		DISP OF AXIAL AQ		292*
PHENYL	PY		DISP OF AXIAL AQ	A	183
PHENYL	PY	RMgHal	IA; THF	A	148
PHENYL	AMMONIA		DISP OF AXIAL AQ	A	183
PHENYL	AQ	RMgBr	IA; THF	A	183
PHENYL	NONE		REMOVAL OF AXIAL AQ, NH3 OR PY	A	183
PHENYL	DMSO		DISP OF AXIAL AQ		139*
PHENYL	DMF		DISP OF AXIAL AQ		292*,521*
PHENYL	DMF	TRI(Me)NR(+) ClO4(-)	IIIA; CPR DMF		529*
PHENYL-PERFLUORO	PY	RMgBr	IA; THF	A	13
PHENYL-PERFLUORO	-SO2-**		DISP OF AXIAL PY	A **BRIDGED	13
METHOXYCARBONYL	PY		DISP OF AXIAL AQ	A	86
METHOXYCARBONYL	AQ	RCl	IIIA; Na(Hg) THF	A	284,86

SALEN

R	B	REAGENT	METHOD	NOTES	REF
METHOXYCARBONYL	AQ	CO	IC; PHOTOL OF R(Co) R = VARIOUS IN MeOH	A	17,18
METHOXYCARBONYL	AQ	CO	IC; MeO(Co), HO(Co) OR (Co) O2, MeOH		18
ETHOXYCARBONYL	PY		DISP OF AXIAL AQ	A	86
ETHOXYCARBONYL	AQ	RCl	IIIA; Na(Hg) THF	A	86
ETHOXYCARBONYL	AQ	CO	IC; PHOTOL OF R(Co) R = VARIOUS IN EtOH	A	17,18
ISOPROPOXYCARBONYL	AQ	CO	IC; PHOTOL OF R(Co) R = VARIOUS IN ISOPROPANOL	A	17,18

SALTN

R	B	REAGENT	METHOD	NOTES	REF
METHYL	AQ	RI	IIIA; BH4/Pd MeOH(HIGH pH)	A	67
METHYL	CN(-)		DISP OF AXIAL AQ		67*
METHYL	NONE		REMOVAL OF AXIAL AQ		67
ETHYL	AQ	RBr	IIIA; BH4/Pd MeOH(HIGH pH)	A	67
ETHYL	CN(-)		DISP OF AXIAL AQ		67*
ETHYL	NONE		REMOVAL OF AXIAL AQ		67

R	B	REAGENT	METHOD	NOTES	REF
METHYL-DICYANO	PY	DICYANOMETHANE	IB; HO(Co)PY? MeOH	A (X-RAY)	14 (14)
METHYL-DICYANO	AQ	DICYANOMETHANE	IB; (Co) O2 AQ/MeOH?	A	15
METHYL-DICYANO	ETHANOL	DICYANOMETHANE	IB; (Co) O2 EtOH?	A	15
METHYL-DICYANO	NONE (POLYMERIC)	DICYANOMETHANE	IB; (Co) O2 MeOH?	A	15

SALPR

R	B	REAGENT	METHOD	NOTES	REF
METHYL (B MAY BE A SALPR DONOR ATOM IN THESE COMPLEXES)	NONE	RI	IIIA; BH4/Pd MeOH(HIGH pH)	A	404
ETHYL	NONE	RI	IIIA; BH4/Pd MeOH(HIGH pH)	A	404
PROPYL	NONE	RBr(I)	IIIA; BH4/Pd MeOH(HIGH pH)	A	404
BUTYL	NONE	RBr(I)	IIIA; BH4/Pd MeOH(HIGH pH)	A	404
PENTYL	NONE	RBr(I)	IIIA; BH4/Pd MeOH(HIGH pH)	A	404
HEXYL	NONE	RBr(I)	IIIA; BH4/Pd MeOH(HIGH pH)	A	404
HEPTYL	NONE	RBr(I)	IIIA; BH4/Pd MeOH(HIGH pH)	A	404
OCTYL	NONE	RBr(I)	IIIA; BH4/Pd MeOH(HIGH pH)	A	404
DECYL	NONE	RBr(I)	IIIA; BH4/Pd MeOH(HIGH pH)	A	404
METHOXYCARBONYL	NONE	CO	IC; (Co) O2 MeOH	A	18

R	B	REAGENT	METHOD	NOTES	REF
METHYL	AQ	RI	IIIA; Na(Hg) THF, RAPID CRYST. FROM ACETONE/AQ	A	16
METHYL	AQ	DI(Me)Co(dotnH)	IA; MeOH OR AQ/THF		237
METHYL	AQ	MeCo(acacen)AQ	IA; AQ/MeOH		261
METHYL	THF	RI	IIIA; Na(Hg) THF, SLOW CRYST. FROM THF/AQ		16
METHYL	NONE	RI	IIIA; Na(Hg) THF, SLOW CRYST. FROM ACETONE/AQ	A	16
METHYL-NITRO	AQ	NITROMETHANE	IB; HO(Co)AQ AQ/MeOH	A	16
METHYL-DICYANO	MeOH	DICYANOMETHANE	IB; (Co),O2 MeOH	A	15
ETHYL	NONE	RHal	IIIA; Na(Hg)? THF?		395
ETHYL	AQ	RHal?	IIIA?; Na(Hg)? THF?		521
ETHYL	DMF		DISP OF AXIAL AQ		521*
ETHYL-1-KETO	PY		ADDITION TO 'NONE'		16*
ETHYL-1-KETO	1-MeIMID		ADDITION TO 'NONE'		16*
ETHYL-1-KETO	AQ	ROR	IIIA; Na(Hg) THF, CRYST. FROM ACETONE/AQ	A	16
ETHYL-1-KETO	AQ	RCl	IIIA; Na(Hg) THF, CRYST. FROM THF/AQ	A	403
ETHYL-1-KETO	NONE	ROR	IIIA; Na(Hg) THF, CRYST. FROM DICHLOROMETHANE/PhMe	A	16
BENZYL-2-NITRO	IMID	RCl	IIB; DICHLOROMETHANE/IMID		23*
BENZYL-4-NITRO	PY	RBr	IIA; DICHLOROMETHANE/PY		100*
BENZYL-4-NITRO	IMID	RCl(Br)	IIB; DICHLOROMETHANE/IMID		23*
BENZYL-4-NITRO	1-MeIMID	RCl(Br)	IIB; DICHLOROMETHANE/1-MeIMID		23*,100*
BENZYL-4-NITRO	BENZYLAMINE	RBr	IIB; DICHLOROMETHANE/BENZYLAMINE		23*
BENZYL-4-CYANO	PY	RI(Br)	IIA; CHLOROFORM(OR DI-CHLOROMETHANE)/PY	A	100
BENZYL-4-CYANO	PY-3-Cl	RI(Br)	IIA; DICHLOROMETHANE/PY-3-Cl		100*

R	B	REAGENT	METHOD	NOTES	REF
BENZYL-4-CYANO	PY-3,4--DI(Me)	RBr	IIA; DICHLOROMETHANE/3,4-DI(Me)PY		100*
BENZYL-4-CYANO	1-MeIMID	RI(Br)	IIA; CHLOROFORM(OR DI-CHLOROMETHANE)/1-MeIMID		100
BENZYL-4-CYANO	BENZYLAMINE	RBr	IIA; DICHLOROMETHANE/BENZYLAMINE		100*
BENZYL-4-CYANO	TRI(Me)P	RBr	IIA; DICHLOROMETHANE/TRI(Me)P		100*
BENZYL-4-CYANO	TRI(Et)P	RBr	IIA; DICHLOROMETHANE/TRI(Et)P		100*
BENZYL-4-CYANO	TRI(Bu)P	RBr	IIA; CHLOROFORM(OR DI-CHLOROMETHANE)/TRI(Bu)P		100
BENZYL-4-CYANO	DI(Me)PPh	RBr(Cl)	IIA; DICHLOROMETHANE/DI(Me)PPh		100*
BENZYL-4-CYANO	DI(Ph)PMe	RI(Br)	IIA; DICHLOROMETHANE/DI(Ph)PMe		100*
BENZYL-4-CYANO	TRI(Ph)P	RI(Br)	IIA; DICHLOROMETHANE/TRI(Ph)P		100*
PHENYL	AQ	RBr?	IIIA?; Na(Hg)? THF?	A	16
PHENYL	DMF		DISP OF AXIAL AQ		521*
UNSPEC ALKYL OR ARYL	UNSPEC	RMgHal	IA; THF		16
METHOXYCARBONYL	PY		DISP OF AXIAL AQ		16*
METHOXYCARBONYL	AQ	RCl	IIIA; Na(Hg) THF	A	16
METHOXYCARBONYL	AQ	CO	IC; HO(Co)AQ OR (Co),O2 MeOH	A	18,16

Cl-SALPHEN

R	B	REAGENT	METHOD	NOTES	REF
BENZYL-4-NITRO	IMID	RCl	IIB: DICHLOROMETHANE/IMID		23*

3,3'-MeO-SALEN

R	B	REAGENT	METHOD	NOTES	REF
METHYL-DICYANO	DMF	DICYANOMETHANE	IB; (Co) O2 AQ/DMF?	A	15

7,7'-Me-SALEN

R	B	REAGENT	METHOD	NOTES	REF
METHYL	METHANOL	RI	IIIA; CO AQ/THF (ALK)		399
METHYL	NONE	RI	IIIA; Na (Hg) THF	A	16
METHYL-NITRO	METHANOL	NITROMETHANE	IB; HO(Co) AQ AQ/MeOH	A	16
METHYL-DICYANO	AQ	DICYANOMETHANE	IB; (Co) O2 AQ/MeOH?	A	15
ETHYL	DMF		ADDITION TO 'NONE'		521*
ETHYL	NONE	RBr	IIIA; Na (Hg) THF	A	16
ETHYL-1-KETO	PY		ADDITION TO 'NONE'		16*
ETHYL-1-KETO	1-MeIMID		ADDITION TO 'NONE'		16*
ETHYL-1-KETO	NONE	ROR	IIIA; Na (Hg) THF	A	16
PROPYL-2-KETO	NONE	ACETONE	IB; HO(Co) AQ MeOH	A	16
BENZYL-4-NITRO	1-MeIMID	RBr	IIB; DI(Cl)-METHANE/1-MeIMID		23*
VINYL	DMF		ADDITION TO 'NONE'		292*
VINYL	NONE	ACETYLENE	IIIB; Na (Hg) THF/AQ	A	16
PHENYL	DMF		ADDITION TO 'NONE'		521*

R	B	REAGENT	METHOD	NOTES	REF
PHENYL	NONE	RBr	IIIA; Na(Hg) THF	A	16
UNSPEC ALKYL OR ARYL	UNSPEC	RMgHal	IA; THF		16
METHOXYCARBONYL	PY		DISP OF AXIAL AQ		16*
METHOXYCARBONYL	AQ	RCl	IIIA; Na(Hg) THF	A	16
METHOXYCARBONYL	AQ	CO	IC; HO(Co)AQ OR (Co),02 MeOH	A	18,16

NAPSALEN

R	B	REAGENT	METHOD	NOTES	REF
ETHYL-1-KETO	AQ	RCl	IIIA; Na(Hg) THF	A	403

NAPSALPHEN

ETHYL-1-KETO	NONE	RCl	IIIA; Na(Hg) THF	A	403

AETPOR

METHYL	AQ	RMgHal	IA; 1,2-DI(MeO)ETHANE		90,11
METHYL	AQ	RI	IIIA; Na(Hg) 1,2-DIMETHOXY-ETHANE	A	11
ETHYL	AQ	RMgBr	IA; DI(MeO)ETHANE	A	90,11
ETHYL	AQ	RI	IIIA; Na(Hg) 1,2-DIMETHOXY-ETHANE OR PY		91,11
ETHYL-2-HYDROXY	AQ	RBr	IIIA; Na(Hg) 1,2-DIMETHOXY-ETHANE	A	286,11

ARTPOR

METHYL	AQ	RMgHal	IA; 1,2-DI(MeO)ETHANE		90,11
ETHYL-2-CYANO	?	ACRYLONITRILE?	IIIB? MAY BE A DIFFERENT PORPHYRIN		202
ETHYL-1-KETO	AQ	ROR	IIIA; Na(Hg) 1,2-DIMETHOXY-ETHANE OR PY	A	91,11
PROPYL	AQ	RMgHal	IA; 1,2-DI(MeO)ETHANE	A	91,11
PROPYL-2-HYDROXY	AQ	RBr	IIIA; Na(Hg) 1,2-DIMETHOXY-ETHANE	A	286,11
PROPYL-2-HYDROXY	AQ	1-HO-2-Br-PROPANE (VIA PROPENE OXIDE?)	IIIA; Na(Hg) 1,2-DIMETHOXY-ETHANE		286,11
BUTYL	AQ	RMgHal	IA; 1,2-DI(MeO)ETHANE	A	91,11
CYCLOHEXYL	AQ	RMgHal	IA; 1,2-DI(MeO)ETHANE		90*
PROP-2-ENYL	AQ	RMgHal	IA; 1,2-DI(MeO)ETHANE		90*
PHENYL	AQ	RLi	IA; 1,2-DI(MeO)ETHANE	A	91,11
PHENYL-3-METHYL	AQ	RLi?	IA; 1,2-DI(MeO)ETHANE	A	91,11
PHENYL-4-METHYL	AQ	RLi?	IA; 1,2-DI(MeO)ETHANE	A	91,11

OCTETPOR

R	B	REAGENT	METHOD	NOTES	REF
SUBSTITUTED CARBENE?	?	DIAZO COMPOUNDS	(Co(III)) OR (Co(II))		49

ARTPOR

R	B	REAGENT	METHOD	NOTES	REF
METHYL	PY	RI	IIIA; BH4 PY		405*
METHYL	NONE	RI	IIIA; BH4 N,N-DI(Me) ACETAMIDE		405*

Me-DEUTPOR

R	B	REAGENT	METHOD	NOTES	REF
METHYL	PY	RI	IIIA; BH4 WITH ULTRAVIOLET IRRADIATION PY		405*
METHYL	NONE	RI	IIIA; BH4 WITH ULTRAVIOLET IRRADIATION N,N-DI(Me) ACETAMIDE		405*

PC

R	B	REAGENT	METHOD	NOTES	REF
METHYL	NONE?	RI	IIIA; HYDRAZINE N,N-DIMETHYLACETAMIDE/PY		63
METHYL	NONE?	RI?	IIIA?; BENZOPHENONE(2-)? THF		506
METHYL	CN(-)		ADDITION TO 'NONE'		63*
ETHYL	NONE?	RI	IIIA; HYDRAZINE? N,N-DIMETHYLACETAMIDE/PY?		63*
PROPYL	NONE?	RI	IIIA; BENZOPHENONE(2-) THF	A	406,407
BUTYL	NONE?	RBr	IIIA; HYDRAZINE? N,N-DIMETHYLACETAMIDE/PY?		63*
ETHYNYL-PHENYL	ETHYNYL-PHENYL	RLi	IA(Co(II)); THF	A Li SALT	408
PHENYL	NONE?	DI(R)(Co(II))(2-)	OXIDATION WITH IODINE THF	A	408

TSPC

R	B	REAGENT	METHOD	NOTES	REF
METHYL	AQ?	RI	IIIA; BH4 AQ(PHOSPHATE pH6.5)		63*

AMRPN

R	B	REAGENT	METHOD	NOTES	REF
METHYL-DICYANO	NONE (POLYMERIC)	DICYANOMETHANE	IB; (Co),O2? EtOH?	A	15

DORNH

R	B	REAGENT	METHOD	NOTES	REF
METHYL	AQ	RBr	IIIA; BH4 MeOH(pH10)	A BPh4 SALT	67
METHYL	AQ	RI?	IIIA?; BH4? MeOH?	ClO4 SALT	377
METHYL	CN(-)		DISP OF AXIAL AQ		67*
ETHYL	AQ	RBr	IIIA; BH4 MeOH(pH10)	A BPh4 SALT	67
ETHYL	CN(-)		DISP OF AXIAL AQ		67*
PROPYL	PY	RCl	IIIA; BH4 MeOH		101*
PROPYL	AQ	RCl	IIIA; BH4 MeOH		101*
PROPYL	TRI(Bu)P	RCl	IIIA; BH4 MeOH		101*
PROPYL	DI(Me)S	RCl	IIIA; BH4 MeOH		101*

R	B	REAGENT	METHOD	NOTES	REF
METHYL	I(-)		DISP OF AXIAL AQ	A	409,61
METHYL	PY		DISP OF AXIAL AQ		571*
METHYL	PY-4-Me		DISP OF AXIAL AQ		571*
METHYL	PY-4-CN		DISP OF AXIAL AQ		571*
METHYL	PY-4-AMINO		DISP OF AXIAL AQ		571*
METHYL	PY-3-Me		DISP OF AXIAL AQ		571*
METHYL	PY-3-CN		DISP OF AXIAL AQ		571*
METHYL	PY-3-AMINO		DISP OF AXIAL AQ		571*
METHYL	IMID	RHal	IIIA; BH4 MeOH	A BPh4 SALT	61
METHYL	IMID		DISP OF AXIAL AQ	BPh4 SALT	61
METHYL	IMID	RHal	IIIA; BH4 MeOH	A PF6 SALT	61
METHYL	IMID		DISP OF AXIAL AQ	PF6 SALT	61
METHYL	IMID	RHal?	IIIA?; BH4? MeOH?	ClO4 SALT	580
METHYL	1-MeIMID	RHal	IIIA; BH4 MeOH	A ClO4 SALT	61
METHYL	1-MeIMID		DISP OF AXIAL AQ	ClO4 SALT	61
METHYL	BENZIMID		DISP OF AXIAL AQ	A ClO4 SALT	61
METHYL	AMMONIA		DISP OF AXIAL AQ	A BPh4 SALT	61
METHYL	NCS(-)		DISP OF AXIAL AQ	A	61
METHYL	AQ	RMgBr(Cl)	IA; THF	A ClO4 SALT (X-RAY)	409,61,571 (178)
METHYL	AQ	RHal	IIIA; BH4 MeOH	ClO4 SALT	409,61
METHYL	AQ	DI(Me)(Co)	IA; MeOH OR AQ/THF		237
METHYL	AQ	RMgBr	IA; THF	A BPh4 SALT	61
METHYL	AQ		EXCHANGE OF ClO4 SALT	BPh4 SALT	409,61
METHYL	AQ		DISP OF AXIAL IODIDE	BPh4 SALT	409
METHYL	AQ	MeCo(acacen)AQ	IA; AQ/MeOH	ClO4 SALT?	261

R	B	REAGENT	METHOD	NOTES	REF
METHYL	AQ	MeCo(salen)AQ	IA; AQ/MeOH	ClO4 SALT?	261
METHYL	AQ	MeCo(salphen)AQ	IA; AQ/MeOH	ClO4 SALT?	261
METHYL	AQ	MeCobalamin	IA; AQ/MeOH	ClO4 SALT?	261,290
METHYL	AQ	RI	IIIA; (Co(I))CO CRYST, PhH	ClO4 SALT	399
METHYL	AQ	RI	IIIA; (Co(I))CO CRYST, AQ/THF(NEUT)	ClO4 SALT	399
METHYL	DMF		DISP OF AXIAL AQ	ClO4 SALT	292*,521*
METHYL	CN(-)		DISP OF AXIAL AQ		67*
METHYL	METHYL(-)	RMgHal	IA; THF	A	410,399
METHYL	METHYL(-)	RHal	IIIA; BH4 MeOH		410
METHYL	METHYL(-)	RHal	IIIA(Me(Co(I)); CO AQ/THF(ALK)		410
METHYL	METHYL(-)	RI	IIIA; CO AQ/THF(pH13)	A	411,399
METHYL	METHYL(-)	RI	IIIA(Me(Co(I))); CO AQ/THF(ALK)		411,399
METHYL	METHYL(-)	Me(Co)	IIIA(Me(Co(I))); CPR DMF		237,292
METHYL	METHYL(-)	RI	IIIA; (Co(I))CO CRYST AQ/THF(pH13)		399
METHYL	METHYL(-)	Me(Co)AQ	IIIA(Me(Co(I))); CO(NOT EXCESS) AQ/THF(ALKALINE)		399
METHYL	METHYL(-)	RI	IIIA; BH4(EXCESS) AQ/EtOH		399
METHYL	PHENYL(-)	RI	IIIA(Ph(Co(I))); CO AQ/THF(ALK)	A	410,399
METHYL	PHENYL(-)	RI(Br)	IIIA(Ph(Co(I)); Na(Hg) THF		410,399
METHYL	PHENYL(-)	RI	IIIA(Ph(Co(I))); BH4 AQ/EtOH		399
METHYL	Ph-3-F(-)	MeI?	IIIA(3-F-Ph(Co(I)))?	A	149
METHYL	Ph-4-F(-)	MeI?	IIIA(4-F-Ph(Co(I)))?	A	149
ETHYL	IMID	RHal	IIIA; BH4 MeOH	A BPh4 SALT	61
ETHYL	IMID		DISP OF AXIAL AQ	BPh4 SALT	61
ETHYL	IMID	RHal	IIIA; BH4 MeOH	A PF6 SALT	61

R	B	REAGENT	METHOD	NOTES	REF
ETHYL	IMID	RHal	DISP OF AXIAL AQ	PF6 SALT	61
ETHYL	1-MeIMID	RHal	IIIA; BH4 MeOH	A ClO4 SALT	61
ETHYL	1-MeIMID		DISP OF AXIAL AQ	ClO4 SALT	61
ETHYL	AQ	RMgBr	IA; THF	A ClO4 SALT	409,61
ETHYL	AQ	RHal	IIIA; BH4 MeOH	ClO4 SALT	409,61
ETHYL	AQ	RMgBr	IA; THF	A BPh4 SALT	61
ETHYL	AQ		EXCHANGE OF ClO4 SALT	BPh4 SALT	61
ETHYL	DMF		DISP OF AXIAL AQ	ClO4 SALT	292*,521*
ETHYL	CN(-)		DISP OF AXIAL AQ		67*
ETHYL	ETHYL(-)	Et(Co)	IIIA(Et(Co(I))); CPR DMF		292
ETHYL-2-HYDROXY	AQ	ETHYLENE OXIDE	IIIA; H2? MeOH?(NEUTRAL?)	A ClO4 SALT	104
ETHYL-1-KETO	1-MeIMID	ROR	IIIA; BH4 MeOH	A ClO4 SALT	16
PROPYL	IMID	RHal	IIIA; BH4 MeOH	A BPh4 SALT	61
PROPYL	IMID		DISP OF AXIAL AQ	ClO4 SALT?	197*
PROPYL	AQ	RHal	IIIA; BH4 MeOH	ClO4 SALT?	197,101*
PROPYL	TRI(Bu) P	RCl	IIIA; BH4 MeOH		101*
BENZYL	IMID	RHal	IIIA; BH4 MeOH	A ClO4 SALT	61
BENZYL	IMID		DISP OF AXIAL AQ	ClO4 SALT	61
BENZYL	IMID	RCl	IIIA;(Co(I))CRYST PhH,THEN B	ClO4 SALT	61
BENZYL	1-MeIMID	RHal	IIIA; BH4 MeOH	A ClO4 SALT	61
BENZYL	1-MeIMID		DISP OF AXIAL AQ	ClO4 SALT	61
BENZYL	1-MeIMID	RCl	IIIA; ALK DISPROP MeOH	ClO4 SALT	61
BENZYL	AQ	RMgBr	IA; THF	A ClO4 SALT	61
BENZYL	AQ	RHal	IIIA: BH4 MeOH	ClO4 SALT	61
BENZYL	DMF		DISP OF AXIAL AQ	ClO4 SALT	289*,521*

R	B	REAGENT	METHOD	NOTES	REF
BENZYL	BENZYL(-)	RMgHal	IA; THF	A	410,399
BENZYL	BENZYL(-)	RHal	IIIA; BH4 MeOH		410
BENZYL	BENZYL(-)	RHal	IIIA(R(Co(I))); CO AQ/THF(ALK)		410,399
BENZYL	BENZYL(-)	RHal	IIIA; CO AQ/THF(ALK)	A	399
BENZYL	BENZYL(-)	RCl	IIIA; BH4(EXCESS) AQ/EtOH		399
BENZYL	PHENYL(-)	RHal	IIIA(Ph(Co(I))); CO AQ/THF(ALK)	A	399
BENZYL-4-FLUORO	PY	RCl	IIIA; BH4 MeOH	A ClO4 SALT	47
BENZYL-4-FLUORO	NCCoBIS(dmgH)Me(-)		DISP OF AXIAL AQ		47*
BENZYL-4-FLUORO	AQ	RCl	IIIA; BH4 MeOH	A ClO4 SALT	47
BENZYL-4-FLUORO	TRIFLUOROACETATE(-)		DISP OF AXIAL AQ	A	47
BENZYL-4-FLUORO	TRI(Ph)P	RCl	IIIA; BH4 MeOH	ClO4 SALT	47
BENZYL-4-FLUORO	CN(-)		DISP OF AXIAL PY	A	47
PHENYL	BROMIDE(-)	RMgBr	IA; THF, THEN HBr AQ	A	61
PHENYL	I(-)		DISP OF AXIAL IODIDE	A	61
PHENYL	IMID		DISP OF AXIAL AQ	ClO4 SALT?	197*
PHENYL	BENZIMID		DISP OF AXIAL AQ	ClO4 SALT?	197*
PHENYL	AQ		DISP OF AXIAL BROMIDE	A ClO4 SALT	61
PHENYL	DMF		DISP OF AXIAL AQ	ClO4 SALT	292*,521*
PHENYL	TRI(Ph)P		DISP OF AXIAL AQ	ClO4 SALT?	197*
PHENYL	PHENYL(-)	Ph(Co)AQ	IIIA?(Ph(Co(I))); CO(NOT EXCESS) AQ/THF(ALKALINE)	A	399
PHENYL	PHENYL(-)	RMgHal	IA; THF		399
PHENYL-3-FLUORO	BROMIDE(-)	RMgBr?	IA?; THF?, THEN AQ HBr?	A	149
PHENYL-3-FLUORO	I(-)		DISP OF AXIAL BROMIDE?	A	149
PHENYL-3-FLUORO	NCO(-)		DISP OF AXIAL BROMIDE?	A	149

R	B	REAGENT	METHOD	NOTES	REF
PHENYL-3-FLUORO	SCN(-)		DISP OF AXIAL BROMIDE?	A	149
PHENYL-3-FLUORO	Ph-3-F(-)	R(Co)?	IIIA?(O-F-Ph(Co(I)))?	A	149
PHENYL-4-FLUORO	BROMIDE(-)	RMgBr?	IA?; THF?, THEN AQ HBr?	A	149
PHENYL-4-FLUORO	I(-)		DISP OF AXIAL BROMIDE?	A	149
PHENYL-4-FLUORO	NCO(-)		DISP OF AXIAL BROMIDE?	A	149
PHENYL-4-FLUORO	SCN(-)		DISP OF AXIAL BROMIDE?	A	149
PHENYL-4-FLUORO	Ph-4-F(-)	R(Co)?	IIIA?(4-F-Ph(Co(I)))?	A	149

5,7,7,12,14,14-Me6-[14]-ANE-1,4,8,11-N4

R	B	REAGENT	METHOD	NOTES	REF
METHYL	AQ	PENTAAMMINECoO.CO.Me	(Co(II)), IRRADIATE IN 0.1M HClO4 AQ.	A ClO4 SALT	574

5,7,7,12,14,14-Me6-[14]-4,11-DIENE-1,4,8,11-N4

R	B	REAGENT	METHOD	NOTES	REF
METHYL	AQ	PENTAAMMINECoO.CO.Me	(Co(II)-meso), IRRADIATE IN 0.1M HClO4 AQ.	A ClO4 SALT L = N-meso ISOMER	574
METHYL	AQ	R(Co-dl)CN(+) ClO4(-)	DISP OF AXIAL CN(-) IN ACID AQ.	ClO4 SALT L = N-dl ISOMER	574
METHYL	AQ	R(Co-dl)(2+) 2ClO4(-)	ADDITION TO 'NONE'	ClO4 SALT L = N-dl ISOMER	574
METHYL	NONE	R(Co-dl)AQ(2+) 2ClO4(-)	REMOVAL OF AXIAL AQ	ClO4 SALT L = N-dl ISOMER	574
METHYL	CN(-)	R(Co-meso)AQ(2+) 2ClO4(-)	DISP OF AXIAL AQ IN NaOH	ClO4 SALT L = N-dl ISOMER	574

CR

R	B	REAGENT	METHOD	NOTES	REF
METHYL	Br(-)	RI	IIIA; BH4 MeOH	A PF6 SALT	412,62
METHYL	Br(-)	RI?	IIIA?; BH4? MeOH?	BPh4 SALT	88
METHYL	PY		DISP OF AXIAL Br(-)		62*
METHYL	AQ		DISP OF AXIAL Br(-) IN AQ		62*
METHYL	TRI(Ph)P		DISP OF AXIAL Br(-)		62*
METHYL	NONE(?)		REMOVAL OF AXIAL Br(-) BY AGEING IN MeOH		62*
METHYL	METHYL(-)	RI	IIIA(Me(Co(I))); BH4 MeOH	BPh4 SALT	413,88
METHYL	METHYL(-)	RI	IIIA(Me(Co(I))); Na(Hg) MeCN	BPh4 SALT	413,88
METHYL	BENZYL(-)	BENZYL Hal	IIIA(Me(Co(I)));	BPh4? SALT	413,88
METHYL	BENZYL(-)	MeI	IIIA(BENZYL(Co(I)));	BPh4? SALT	413,88
METHYL-CHLORO	Br(-)	RCl	IIIA; BH4 MeOH	A PF6 SALT	412,62
ETHYL	Br(-)	RBr(I)	IIIA; BH4 MeOH	A PF6 SALT	412,62
ETHYL	AQ		DISP OF AXIAL Br(-) IN AQ		62*
ETHYL	NONE(?)		REMOVAL OF AXIAL Br(-) BY AGEING IN MeOH		62*
ETHYL-2(1?)-CYANO	Br(-)	ACRYLONITRILE	IIIB(C?); BH4 MeOH	A PF6 SALT	412,62
BUTYL	Br(-)	RBr	IIIA; BH4 MeOH	PF6 SALT	62
BUTYL	AQ		DISP OF AXIAL Br(-) IN AQ		62*
BENZYL	Br(-)	RCl	IIIA; BH4 MeOH	A PF6 SALT	412,62
BENZYL	AQ		DISP OF AXIAL Br(-) IN AQ		62*
BENZYL	BENZYL(-)	RHal	IIIA(R(Co(I)));	BPh4? SALT	413,88
PROP-2-ENYL	Br(-)	RHal	IIIA; BH4 MeOH	UNSTABLE?	412*,62*
VINYL	Br(-)	RBr	IIIA; BH4 MeOH	A PF6 SALT	412,62
UNSPECIFIED	MeCN	RHal	IIIA; Na(Hg) MeCN		89,88

R	B	REAGENT	METHOD	NOTES	REF
METHYL	Cl(-)	RI	IIIA; BH4 ACETONE/MeOH	A BPh4 SALT	522,587
METHYL	Cl(-)	RI	IIIA; BH4 ACETONE/MeOH	A PF6 SALT	522,587
METHYL	Br(-)	RI	IIIA; BH4 ACETONE/MeOH	A BPh4 SALT	88,522,587
METHYL	Br(-)	RI	IIIA; BH4 ACETONE/MeOH	A PF6 SALT	522,587
METHYL	I(-)	RI	IIIA; BH4 ACETONE/MeOH	A BPh4 SALT	413,522,587
METHYL	I(-)	RI	IIIA; BH4 ACETONE/MeOH	A PF6 SALT	522,587
METHYL	MeCN	RI	IIIA; BH4 MeCN/MeOH	A BPh4 SALT	522,587
METHYL	MeCN	RI	IIIA; BH4 MeCN/MeOH	A PF6 SALT	522,587
METHYL	MeCN	RI	IIIA; Na(Hg) MeCN	BPh4 SALT	522,587
METHYL	MeCN	RI	IIA; MeCN	BPh4 SALT	522,587
METHYL	MeCN		DISP OF AXIAL HALIDE(-)		587*
METHYL	MeOH		DISP OF AXIAL MeCN		587*
METHYL	ACETONE		DISP OF AXIAL MeCN		587*
METHYL	METHYL(-)	RI	IIIA(Me(Co(I))); BH4 MeOH	BPh4 SALT	413,88
METHYL	METHYL(-)	RI	IIIA(Me(Co(I))); Na(Hg) MeCN	BPh4 SALT	413,88
METHYL	BENZYL(-)	BENZYL Hal	IIIA(Me(Co(I)));	BPh4 SALT	413,88
METHYL	BENZYL(-)	MeI	IIIA(BENZYL(Co(I)));	BPh4 SALT	413,88
BENZYL	Cl(-)	RCl	IIIA; BH4 ACETONE/MeOH	A BPh4 SALT	522,587
BENZYL	Cl(-)	RCl	IIIA; BH4 ACETONE/MeOH	A PF6 SALT	522,587
BENZYL	Cl(-)	RBr	IIA; ACETONE	BPh4 SALT	522,587
BENZYL	Br(-)	RBr	IIIA; BH4 ACETONE/MeOH	A BPh4 SALT	413,522,587
BENZYL	Br(-)	RBr	IIIA; BH4 ACETONE/MeOH	A PF6 SALT	522,587
BENZYL	Br(-)	RBr	IIA; ACETONE	BPh4 SALT	522,587
BENZYL	I(-)	RBr	IIIA; BH4 ACETONE/MeOH	A BPh4 SALT	522,587
BENZYL	I(-)	RBr	IIIA; BH4 ACETONE/MeOH	A PF6 SALT	522,587

TIM (2,3,9,10-Me4-[14]-1,3,8,10-TETRAENE-1,4,8,11-N4)

R	B	REAGENT	METHOD	NOTES	REF
BENZYL	I(-)	RBr	IIA; ACETONE	BPh4 SALT	522,587
BENZYL	MeCN	RBr	IIIA; BH4 MeCN/MeOH	A PF6 SALT	522,587
BENZYL	MeCN	RBr	IIIA; Na(Hg) MeCN	PF6 SALT	522,587
BENZYL	MeCN	RBr	IIA; ACETONE/MeCN	BPh4 SALT	522,587
BENZYL	MeCN		DISP OF AXIAL HALIDE(-)		587*
BENZYL	MeOH		DISP OF AXIAL MeCN		587*
BENZYL	ACETONE		DISP OF AXIAL MeCN		587*
BENZYL	BENZYL(-)	BENZYL Hal	IIIA(BENZYL(Co(I)));	BPh4 SALT	413,88

BIS(DIMETHYLGLYOXIMATO-O-BORON DIFLUORIDE)

R	B	REAGENT	METHOD	NOTES	REF
METHYL	PY	MeCoBIS(dmgH)PY	BF3 ETHER, THEN PY	A	118
METHYL	AQ	MeCoBIS(dmgH)AQ	BF3 ETHER	A	118
METHYL	AQ	RCl	IIIA; BH4 MeOH		101*
METHYL	CN(-)		DISP OF AXIAL PY		67*
ETHYL	PY	EtCoBIS(dmgH)PY	BF3 ETHER, THEN PY		67
ETHYL	AQ	RBr	IIIA; BH4 MeOH		101*
ETHYL	CN(-)		DISP OF AXIAL PY		67*
ETHYL-2-OH	PY	ETHYLENE OXIDE	IIIA; H2? MeOH(NEUTRAL)?		104
ETHYL-2-CN	PY	ACRYLONITRILE?	IIIA?; BH4? MeOH?		110

R	REAGENT	METHOD	REF
METHYL	RI	IIIA; BH4 MeOH	31,27,414
METHYL	RI	IIIA; BH4 AQ	67
METHYL	DI(Me) SULPHATE	IIIA; BH4 MeOH	31,27
METHYL	MeTOSYLATE	IIIA; BH4 MeOH	27
METHYL	DI(Me) OXALATE	IIIA; BH4? MeOH? (SLOW)	416
METHYL	RHal	IIIA; BH4/Cu AQ/MeOH	65
METHYL	RI	IIIA; BH4/Co(2+) AQ	54
METHYL	RCl(Br,I)	IIIA; BH4/Pd OR Pt,MeOH OR AQ	101
METHYL	DIAZOMETHANE	IIIC; BH4 AQ	27
METHYL	DI(Me) SULPHATE	IIIA; Zn 5%HOAc AQ.	31,27
METHYL	DI(Me) SULPHATE	IIIA; Zn 10%NH4Cl AQ.	415,28
METHYL	RI	IIIA; Zn 10%NH4Cl AQ.	415,28
METHYL	MeTOSYLATE	IIIA; Zn 10%NH4Cl AQ.	415,28
METHYL	S-METHYLMETHIONINE(+) Br(-)	IIIA; Zn 10%NH4Cl AQ.	418
METHYL	S-ADENOSYLMETHIONINE(+) I(-)	IIIA; Zn 10%NH4Cl AQ.	93,418
METHYL	RI(DI(R)SULPHATE)	IIIA; Zn/Mg 10%NH4Cl AQ	545
METHYL	DIAZOMETHANE	IIIC; Zn 10%NH4Cl AQ.	28
METHYL	DIAZOMETHANE	IIIC; Zn 0.1N NaOH AQ.	28
METHYL	DI(Me) SULPHATE	IIIA; Cr(II) ACETATE EDTA AQ. (pH9.5)	31,27
METHYL	RI	IIIA; Cr(II) CHLORIDE EDTA AQ. (pH9.6)	192
METHYL	RI	IIIA; HO(Co) + EXCESS Na2S AQ	78,77
METHYL	MeTOSYLATE	IIIA; HO(Co) + EXCESS Na2S AQ	78,77
METHYL	RI	IIIA; HO(Co) + EXCESS GLUTATHIONE AQ	81,78,77
METHYL	RI	IIIA; (Co(II)) + DIHYDROLIPOATE DIMETHYLGLUTARATE AQ. (pH7.3)	422

R	REAGENT	METHOD	REF
METHYL	RI	IIIA; HO(Co) + VARIOUS THIOLS AQ	78,77,447
METHYL	RI	IIIA; HYDRAZINE N,N-DIMETHYLACETAMIDE	405*
METHYL	RI	IIIA; (Co(II)) + ENZYMATICALLY REDUCED FERREDOXIN,TRIS AQ.(pH7.0)	83*
METHYL	RI	IIIA; (Co(II)) + CO AQ(pH4-8)	58
METHYL	RI	IIIA; CPR AQ(pH8-10)	122a,417
METHYL	RI	IIIA; 2-NC-ETHYL(Co) + OH(-) AQ	211
METHYL	RI	IIIA; ACETYL(Co) + NH3 AQ	97
METHYL	RI	IIIA; (Co(II)) + H2/Pt AQ(pH7)	66
METHYL	RI	IIIA; H2 ALKALINE AQ.	419
METHYL	RI	IIIA; H2 1M NaCl AQ.	419
METHYL	RI	IIIA; ALK DISPROP AQ	419
METHYL	RI(DI(R)SULPHATE)	IIIA; NEUT DISPROP IN 1M NaCl AQ.	419
METHYL	RI	IIIA; NEUT DISPROP(CONC. SOLN.) AQ	419
METHYL	RI	IIIA; SELF REDUCTION OF AQ(Co) AQ(pH7) (SLOW)	57
METHYL	RI	IIIA?; PHOTOLYSIS OF PENTYL(Co) AQ	278
METHYL	DI(Me)Co(dotnH)	IA(AQ(Co)); MeOH OR AQ/THF	237
METHYL	MeCo(acacen)AQ	IA(AQ(Co)); AQ/MeOH	261
METHYL	MeCo(salen)AQ	IA(AQ(Co)); AQ/MeOH	261
METHYL	MeCo(salphen)AQ	IA(AQ(Co)); AQ/MeOH	261
METHYL	MeHgI	IA?(AQ(Co) OR I(Co)); AQ	586
METHYL	(NH4)3SiMeF6	IA?(AQ(Co) OR I(Co)); AQ	586
METHYL	MeCoBIS(dmgH)PY	PHOTOLYSIS OF MIXTURE WITH (Co(II)) AQ. (pH6.5)	67
METHYL	AQ(Co)Me	ISOMERISATION AQ 90-95° (c.85% YIELD)	420,421,189
METHYL	Me(cobyric acid)AQ	Et(Co) + CO AQ,90° OR PHOTOL AT 20°	188

R	REAGENT	METHOD	REF
METHYL	Me(cobyric acid)AQ	AQ(Co) + CO AQ,90° OR PHOTOL AT 20°	188
METHYL	Me(cobyric acid)AQ	NC(Co) + CO AQ,90°	188
METHYL	AQ(cobyric acid)Me	AQ(Co) + CO AQ,80°	188
METHYL	AQ(Co)Me	ISOMERISATION CO AQ,80° OR PHOTOL AT 20° (>80% CONVERSION)	189
METHYL	AQ(cobinamide phosphoribose)Me	AQ(Co) + CO AQ,80° OR PHOTOL AT 20°	189
METHYL	Me(Co)-10-Br	REDUCTION BH4 OR Zn/HOAc OR SULPHITE	84
METHYL-[^{57}Co]	MeI	IIIA(FROM [^{57}Co]-AQ(Co)); BH4 MeOH	516
METHYL-[^{60}Co]	DI(Me)SULPHATE	IIIA(FROM [^{60}Co]-NC(Co)); Zn/Mg 10%NH4Cl AQ./EtOH	549
METHYL-[^{14}C]	RI	IIIA; BH4 MeOH	31,27
METHYL-[^{14}C]	RI	IIIA; BH4 AQ	423
METHYL-[^{14}C]	S-ADENOSYLMETHIONINE-[Me-^{14}C](+) T(-)	IIIA; BH4 PHOSPHATE AQ.(pH7.4)	424
METHYL-[^{14}C]	RBr	IIIA; Cr(II)CHLORIDE? EDTA AQ.(pH9.6)?	277
METHYL-[^{14}C]	RI	IIIA; (Co(II)) + ENZYMATICALLY REDUCED FERREDOXIN,TRIS AQ.(pH7.0)	83
METHYL-[^{14}C]	RI	IIIA; Zn 10%NH4Cl AQ.	367,421
METHYL-[^{14}C]	RI	IIIA; (Co(II)) + EXCESS S(2-) AQ?	531
METHYL-TRIDEUTERIO	RI	IIIA; BH4 AQ	67
METHYL-TRIDEUTERIO	RI	IIIA; BH4 MeOH	563
METHYL-TRIDEUTERIO	RI	IIIA; Zn 10%NH4Cl AQ.	564
METHYL-[T]	DI(Me)SULPHATE	IIIA; Zn 3%HOAc TOH	425,81
METHYL-[T]	RI	IIIA; Zn 10%NH4Cl AQ.	564
METHYL-[T]	RI	IIIA; BH4 MeOH?	426
METHYL-CHLORO	RCl	IIIA; Zn 10%NH4Cl AQ.	433
METHYL-SULPHITO	RI	IIIA; BH4 MeOH?	126

R	REAGENT	METHOD	REF
METHYL-HYDROXYCARBONYL	RCl	IIIA; Zn HOAc	31,27
METHYL-HYDROXYCARBONYL	RCl	IIIA; Zn 10%NH4Cl AQ.	28
METHYL-HYDROXYCARBONYL	RCl	IIIA; Zn 15%NH4Cl AQ	54
METHYL-HYDROXYCARBONYL	RCl	IIIA; HO(Co) + EXCESS Na2S AQ	78,77
METHYL-HYDROXYCARBONYL	RHal	IIIA; BH4 MeOH?	126
METHYL-HYDROXYCARBONYL	RCl	IIIA; Cr(II)CHLORIDE EDTA AQ. (pH9.6)	192
METHYL-HYDROXYCARBONYL	RI(Br) Na SALT	IIIA; NEUT DISPROP IN 1M NaCl AQ.	419
METHYL-HYDROXYCARBONYL-[1-^{14}C]	RBr	IIIA; Zn 10%NH4Cl AQ.	367
METHYL-HYDROXYCARBONYL-[2-^{14}C]	RCl	IIIA; Zn 10%NH4Cl AQ.	367
METHYL-METHOXYCARBONYL	RCl	IIIA; Cr(II)CHLORIDE EDTA AQ. (pH9.6)	192
METHYL-AMINOCARBONYL	RCl	IIIA; Zn 10%NH4Cl AQ.	422
METHYL-AMINOCARBONYL	RI	IIIA; (Co(II)) + DIHYDROLIPOATE DIMETHYLGLUTARATE AQ. (pH7.3)	422
METHYL-(2,2,6,6-TETRAMETHYLPIPERIDINE--N-OXYL-4-AMINOCARBONYL)	RBr	IIIA; CPR BORATE AQ. (pH8) (LOW YIELD)	207
METHYL-DIFLUORO	RCl	IIIA; Zn 10%NH4Cl AQ.	434
METHYL-DICHLORO	RCl	IIIA; Zn 10%NH4Cl AQ.	433
METHYL-DICHLORO-[^{14}C]	RCl	IIIA; Zn 10%NH4Cl AQ.	433
METHYL-DIBROMO	RBr	IIIA; Zn 10%NH4Cl AQ.	433
METHYL-DIIODO	RI	IIIA; Zn 10%NH4Cl AQ.	433
METHYL-TRIFLUORO	RBr	IIIA; Zn 10%NH4Cl AQ.	434
METHYL-CHLORODIFLUORO	RCl	IIIA; Zn 10%NH4Cl AQ.	433
METHYL-FLUORODICHLORO	RCl	IIIA; Zn 10%NH4Cl AQ.	434
METHYL-TRICHLORO	RCl	IIIA; Zn 10%NH4Cl AQ.	433
ETHYL	RI	IIIA; BH4 MeOH	31,27
ETHYL	TRI(Et)PHOSPHATE	IIIA; BH4? MeOH?	27

R	REAGENT	METHOD	REF
ETHYL	ETOSYLATE	IIIA; BH4? MeOH?	27
ETHYL	RI	IIIA; BH4 MeOH? (MILDLY ACIDIC,HOAc)	416
ETHYL	RBr?	IIIA; BH4 AQ	67
ETHYL	RCl(Br)	IIIA; BH4/Pd OR Pt MeOH	101*
ETHYL	RHal	IIIA; BH4/Cu AQ/MeOH	65
ETHYL	RHal	IIIA; Zn 10%NH4Cl AQ.	28
ETHYL	RI	IIIA; Zn/Mg 10%NH4Cl AQ.	545
ETHYL	ETHYLENE	IIIC; Zn ANHYD.HOAc OR MeOH/HOAc	41*
ETHYL	RI	IIIA; HO(Co) + EXCESS NaHS EtOH	78,77
ETHYL	RI	IIIA; Cr(II) CHLORIDE EDTA AQ. (pH9.6)	192
ETHYL	RBr	IIIA; CPR AQ(pH8)	417
ETHYL-[1-^{14}C]	RI	IIIA; BH4 AQ?	427
ETHYL-2-AMINO	RHal?	IIIA; Cr(II) CHLORIDE? EDTA AQ. (pH9.6)?	293,219
ETHYL-2-TRIMETHYLAMMONIUM	RHal?	IIIA?; Cr(II) CHLORIDE? EDTA AQ. (pH9.6)?	219
ETHYL-2-HYDROXY	RBr	IIIA; BH4 AQ	31,27,11
ETHYL-2-HYDROXY	ETHYLENE OXIDE	IIIA; BH4? AQ?	27
ETHYL-2-HYDROXY	ETHYLENE OXIDE	IIIA; Zn 10%NH4Cl AQ.	418
ETHYL-2-HYDROXY	ETHYLENE OXIDE	IIIA; CPR PHOSPHATE AQ(pH9)	54
ETHYL-2-HYDROXY	RCl	IIIA; Cr(II) CHLORIDE EDTA AQ. (pH9.6)	192
ETHYL-2-HYDROXY	RCl	IIIA; Zn 10%NH4Cl AQ.	418
ETHYL-2-HYDROXY-[1,2-^{14}C]	RBr	IIIA; BH4 MeOH?	432
ETHYL-2-HYDROXY-2-DEUTERIO	RCl	IIIA; Zn? 10%NH4Cl AQ?	104
ETHYL-2-METHOXY	ROTs	IIIA; Cr(II) CHLORIDE EDTA AQ. (pH9.6)	192
ETHYL-2-(2-TETRAHYDROPYRYLOXY)	RCl	IIIA; BH4 MeOH?	426
ETHYL-2-CYANO	RCl	IIIA; Cr(II) CHLORIDE EDTA AQ. (pH9.6)	192*

R	REAGENT	METHOD	REF
ETHYL-2-CYANO	RCl	IIIA; BH_4 AQ	211
ETHYL-2-CYANO	ACRYLONITRILE	IIIB; BH_4 AQ	211
ETHYL-2-CYANO-1-[^{14}C]	ACRYLONITRILE-1-[^{14}C]	IIIB; BH_4 AQ	211
ETHYL-2-HYDROXYCARBONYL	RBr	IIIA; Zn HOAc	27
ETHYL-2-HYDROXYCARBONYL	RCl	IIIA; HO(Co) + EXCESS Na_2S AQ	78
ETHYL-2-HYDROXYCARBONYL	RCl	IIIA; Cr(II) CHLORIDE $EDTA_4$ AQ. (pH9.6)	192
ETHYL-2-HYDROXYCARBONYL	ACRYLIC ACID	IIIB; Cr(II) ACETATE $EDTA_4$ AQ. (pH9.5)	27
ETHYL-2-METHOXYCARBONYL	RBr	IIIA; BH_4 MeOH?	216
ETHYL-2-METHOXYCARBONYL	Me ACRYLATE	IIIB; BH_4 MeOH?	216
ETHYL-2-METHOXYCARBONYL	RCl	IIIA; Cr(II) CHLORIDE $EDTA_4$ AQ. (pH9.6)	192
ETHYL-2-ETHOXYCARBONYL	Et ACRYLATE?	IIIB?; BH_4? MeOH?	204
MUSTARGEN-MONO(Co) DERIVATIVE?	MUSTARGEN	IIIA; BH_4 AQ	430
NITROMIN-MONO(Co) DERIVATIVE?	NITROMIN	IIIA; BH_4 AQ	430
CHLORAMBUCIL-MONO(Co) DERIVATIVE?	CHLORAMBUCIL	IIIA; BH_4 AQ/EtOH	430
DEGRANOL-MONO(Co) DERIVATIVE?	DEGRANOL	IIIA; BH_4 AQ/EtOH	430
ETHYL-1-METHYL	RI	IIIA; BH_4 MeOH? (UNSTABLE)	187
ETHYL-1-METHYL	PROPENE	IIIC; Zn ANHYD.HOAc OR $AcOH/HOAc$	41*
ETHYL-1-ETHOXYCARBONYL	ETHYL ACRYLATE	IIIC; Zn ANHYD.HOAc OR $AcOH/HOAc$	41*
ETHYL-1-KETO(RED)	ROR	IIIA; Zn 10%NH_4Cl AQ.	28
ETHYL-1-KETO(YELLOW)	RCl	IIIA; BH_4? MeOH?	27
ETHYL-1-KETO(YELLOW)	ROR	IIIA; BH_4? MeOH?	27
ETHYL-1-KETO	RCl	IIIA; HO(Co) + EXCESS Na_2S AQ	78
ETHYL-1-KETO	RCl(ROR)	IIIA; Zn 10%HOAc AQ	54
ETHYL-1-KETO(RED)	YELLOW ANALOGUE	PHOTOLYSIS UNDER OXYGEN	416
ETHYL-1-KETO-2-AMINO	RCl.HCl	IIIA; Zn 10%NH_4Cl AQ.	97

R	REAGENT	METHOD	REF
ETHYL-1-KETO-2-ACETYLAMINO	RCl	IIIA; Zn 10%NH4Cl AQ.	97
ETHYL-2,2,2-TRIFLUORO	RI	IIIA; BH4 MeOH?	126
ETHYL-1,1,2,2-TETRAFLUORO	TETRAFLUOROETHYLENE	IIIB; BH4? AQ	25
PROPYL	RHal	IIIA; Zn 10%NH4Cl AQ.	28
PROPYL	RCl(Br,I)	IIIA; HO(Co) + EXCESS N_2S AQ	78,77
PROPYL	RCl	IIIA; Cr(II)CHLORIDE EDTA AQ. (pH9.6)	192
PROPYL	RHal	IIIA; BH4 AQ	67
PROPYL	RBr(I)	IIIA; BH4 MeOH	419,428
PROPYL	RCl(Br)	IIIA; BH4/Pd OR Pt MeOH	101*
PROPYL-[1-^{14}C]	RBr	IIIA; BH4 MeOH?	428
3-(9-ADENYL)PROPYL	RCl	IIIA; BH4 50%MeOH AQ	431
PROPYL-3-CHLORO	RBr	IIIA; BH4 MeOH?	416
PROPYL-3-HYDROXYCARBONYL	RBr	IIIA; Zn? HOAc?	427
PROPYL-2-METHYL	RCl(Br)	IIIA; BH4/Pd OR Pt MeOH	101*
PROPYL-2-METHYL	RCl	IIIA; Zn/Mg 10%NH4Cl AQ.	545
PROPYL-2-HYDROXY	RBr	IIIA; Zn 10%NH4Cl Aq.	285a
PROPYL-1-METHYL	RI?	IIIA; BH4? MeOH?	202
PROPYL-2,3-DIHYDROXY	RCl	IIIA; Zn 10%NH4Cl Aq.	285a
PROPYL-2,2-DIMETHYL	RBr	IIIA; BH4/Pd OR Pt MeOH	101*
BUTYL	RHal	IIIA; Zn 10%NH4Cl Aq.	28
BUTYL	RI	IIIA; Zn/Mg 10%NH4Cl AQ.	545
BUTYL	RI(Br)	IIIA; BH4 MeOH	27,429
BUTYL	RCl	IIIA; BH4/Pd OR Pt MeOH	101*
BUTYL	RI	IIIA; HO(Co) + EXCESS Na_2S AQ	78
4-(9-ADENYL)BUTYL	RCl	IIIA; BH4 50%MeOH AQ	431

COBALAMINS

R	REAGENT	METHOD	REF
BUTYL-4-BROMO	RBr	IIIA; BH4 MeOH? (MINOR PROD)	416
BUTYL-4-HYDROXY	THF	IIIA; Zn 10%NH4Cl AQ	418
BUSULFAN-MONO(Co) DERIVATIVE?	BUSULFAN	IIIA; BH4 AQ/DMF	430
BUTYL-3-METHYL	RBr	IIIA; BH4/Pd OR Pt MeOH	101*
PENTYL	RHal	IIIA; Zn 10%NH4Cl AQ.	28
PENTYL	RHal	IIIA; BH4 AQ?	427
PENTYL	RCl	IIIA; BH4/Pd OR Pt MeOH	101*
HEXYL	RHal	IIIA; Zn 10%NH4Cl AQ.	28
HEXYL	RHal	IIIA; BH4 AQ?	427
HEXYL	RCl	IIIA; BH4/Pd OR Pt MeOH	101*
CYCLOHEXYL	RBr	IIIA; BH4/Cu AQ/MeOH (UNSTABLE)	65*
CYCLOHEXYL	CYCLOHEXENE	IIIC; Zn ANHYD.HOAc OR MeOH/HOAc	41*
HEPTYL	RHal	IIIA; Zn 10%NH4Cl AQ.	28
HEPTYL	RHal	IIIA; BH4 AQ?	427
OCTYL	RHal	IIIA; Zn 10%NH4Cl AQ.	28
NONYL	RHal	IIIA; Zn 10%NH4Cl AQ.	28
DECYL	RHal	IIIA; Zn 10%NH4Cl AQ.	28
BENZYL	RCl	IIIA; BH4? MeOH? (UNSTABLE TO OXYGEN)	31,416,54
1-NORBORNYL	NORBORNENE	IIIC; Zn ANHYD.HOAc OR MeOH/HOAc	41*
TETRAHYDROFURFURYL	2-METHYLENE-THF	IIIB; Zn? 10%NH4Cl AQ?	104
6-DEOXY-a-D-GLUCOPYRANOSYL	6-O-TOSYLGLUCOSE	IIIA; BH4 AQ/EtOH	199,576
6-DEOXY-a-D-GLUCOPYRANOSYL	6-Br-6-DEOXYGLUCOSE	IIIA; BH4 AQ/EtOH (MAJOR PROD)	199,576
6-DEOXY-b-D-GLUCOPYRANOSYL	6-Br-6-DEOXYGLUCOSE	IIIA; BH4 AQ/EtOH (MINOR PROD)	576
1-O-METHYL-5-DEOXYRIBOSYL	RI	IIIA; BH4 MeOH?	426
5'-DEOXYADENOSYL	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS	31,415,28,27, 546,64,431,436

R	REAGENT	METHOD	REF
5'-DEOXYADENOSYL	2',3'-O-p-ANISYLIDENE ANALOGUE	ACID HYDROLYSIS (MILD CONDITIONS)	439
5'-DEOXYADENOSYL	2',3'-DI-O-ACETYL ANALOGUE	ALKALINE HYDROLYSIS	27
5'-DEOXYADENOSYL	MIXTURE OF TOSYLATED ADENOSINES	IIIA; BH_4^-? 50%MeOH AQ? (LOW YIELD)	437,416
5'-DEOXYADENOSYL	ROTs	IIIA; BH_4^- AQ/EtOH/MeOH	438,243
5'-DEOXYADENOSYL	5'-O-TOSYLADENOSINE--2',3'-PHENYLBORONATE	IIIA; BH_4^- AQ/MeOH/EtOH?	243
5'-DEOXYADENOSYL	N^6-ACETYL-5'-Br-5'--DEOXYADENOSINE-2'(3')--ACETATE-3'(2')-(HYDROGENPHENYLBORONATE)	IIIA; BH_4^- AQ/MeOH?	243
5'-DEOXYADENOSYL	ROTs	IIIA; AQ(Co) + EXCESS THIOL MeOH/AQ (VARIOUS THIOLS USED)	550,551,552
5'-DEOXYADENOSYL	RI	IIIA; AQ(Co) + EXCESS THIOL MeOH/AQ (VARIOUS THIOLS USED)	550,551,552
5'-DEOXYADENOSYL	TOSYLATED ADENOSINE	IIIA; Zn/Mg 10%NH_4Cl AQ./EtOH	548
5'-DEOXYADENOSYL	e-CARBOXYL ANALOGUE	CONVERSION TO AMIDE WITH NH_3 DMF/TRI(Et)N/Et Cl-FORMATE	440
5'-DEOXYADENOSYL-[^{60}Co]	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS	441
5'-DEOXYADENOSYL-[8-^{14}C]	TOSYLATED ADENOSINE--[8-^{14}C]	IIIA; Zn/Mg 10%NH_4Cl AQ./EtOH	549
5'-DEOXYADENOSYL-[5'-T]	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS	442,335,443,444
2',3'-O-ISOPROPYLIDENE-5'-DEOXYADENOSYL	ROTs	IIIA; BH_4^- EtOH	31,27
2',3'-O-ISOPROPYLIDENE-5'-DEOXYADENOSYL	ROTs	IIIA; BH_4^- 50%MeOH AQ	27,64,431,436
2',3'-O-ISOPROPYLIDENE-5'-DEOXYADENOSYL	ROTs	IIIA; Zn 10%NH_4Cl AQ.	415*,28*
2',3'-O-ISOPROPYLIDENE-5'-DEOXYADENOSYL	ROTs	IIIA; Zn/Mg 10%NH_4Cl AQ./EtOH	546*
2',3'-O-ISOPROPYLIDENE-5'-DEOXYADENOSYL	ROTs	IIIA; AQ(Co) + EXCESS GLUTATHIONE AQ	294
2',3'-O-ISOPROPYLIDENE-5'-DEOXYADENOSYL	RI	IIIA; AQ(Co) + EXCESS THIOL MeOH/AQ (VARIOUS THIOLS USED)	550,552

R	REAGENT	METHOD	REF
2',3'-O-ISOPROPYLIDENE--5'-DEOXYADENOSYL-[^{60}Co]	ROTs	IIIA(^{60}Co); BH4 50%MeOH AQ.	441
2',3'-O-ISOPROPYLIDENE-5'-DEOXYADENOSYL-[5'-T]	ROTs	IIIA; BH4 50%MeOH AQ.	442*,335*,443*, 444*
2',3'-DI-O-ACETYL-5'-DEOXYADENOSYL	ROTs	IIIA; BH4 AQ (MILDLY ACID)	27
2',3'-O-p-ANISYLIDENE-5'-DEOXYADENOSYL	ROTs	IIIA; BH4 50%MeOH AQ.	439
L-5'-DEOXYADENOSYL	TOSYLATED L-ADENOSINE?	IIIA; Zn/Mg? 10%NH4Cl AQ./EtOH?	554
1-METHYL-5'-DEOXYADENOSYL	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS	547
2',3'-O-ISOPROPYLIDENE-1-METHYL--5'-DEOXYADENOSYL	ROTs	IIIA; Zn/Mg 10%NH4Cl AQ./EtOH	547*
N^6-METHYL-5'-DEOXYADENOSYL	N^6-METHYL-5'-O-TOSYL-ADENOSINE-2',3'--PHENYLBORONATE?	IIIA; BH4? AQ/EtOH?	445
N^6-METHYL-5'-DEOXYADENOSYL	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS	547
2',3'-O-ISOPROPYLIDENE-N^6-METHYL--5'-DEOXYADENOSYL	ROTs	IIIA; Zn/Mg 10%NH4Cl AQ./EtOH	547*
N^6-ACETYL-5'-DEOXYADENOSYL	N^6-ACETYL-5'-DE-5'--DEOXYADENOSINE-2'(3')--ACETATE-3'(2')-(HYDROGENPHENYLBORONATE)	IIIA; BH4 AQ/MeOH?	339
N^6-ACETYL-2',3'-O-ISOPROPYLIDENE--5'-DEOXYADENOSYL?	RI	IIIA; AQ(Co) + EXCESS THIOL NaOH/AQ (VARIOUS THIOLS USED)	550
N^6-BENZOYL-5'-DEOXYADENOSYL	N^6-BENZOYL-5'-O-TOSYL--ADENOSINE-2',3'--PHENYLBORONATE	IIIA; BH4 AQ/EtOH?	242
2',5'-DIDEOXYADENOSYL	TOSYLATED 2'-DEOXY-ADENOSINE?	IIIA; BH4? 50%MeOH AQ?	27,416
2',5'-DIDEOXYADENOSYL	3'-O-ACETYL ANALOGUE	ALKALINE HYDROLYSIS	446
2',5'-DIDEOXYADENOSYL	TOSYLATED 2'-DEOXY--ADENOSINE	IIIA; Zn/Mg 10%NH4Cl AQ./EtOH	548
3'-O-ACETYL-2',5'-DIDEOXYADENOSYL	3'-O-ACETYL-2'-DEOXY--5'-O-TOSYLADENOSINE	IIIA; Cr(II)CHLORIDE EDTA AQ. (pH9.6)	446

R	REAGENT	METHOD	REF
3',5'-DIDEOXYADENOSYL	TOSYLATED 3'-DEOXY--ADENOSINE	IIIA; Zn/Mg 10%NH4Cl AQ./EtOH	548
2'-AMINO-2',5'-DIDEOXYADENOSYL	TOSYLATED 2'-AMINO-2'--DEOXYADENOSINE?	IIIA; Zn/Mg? 10%NH4Cl AQ./EtOH?	554
5'-DEOXYADENOSYL LINKED (THROUGH N⁶?) TO POLY-D-GLUTAMIC ACID	5'-DEOXYADENOSYL(Co)	POLY-D-GLUTAMIC ACID, 3-DI(Et) N-Pr.N=C=N.Et AQ	579
5'-DEOXYADENOSYL LINKED (THROUGH N⁶?) TO SUCCINYLATED gammaG-GLOBULIN	5'-DEOXYADENOSYL(Co)	SUCCINYLATED gammaG-GLOBULIN, 3-DI(Et) N-Pr.N=C=N.Et AQ	579
7-DEAZA-5'-DEOXYADENOSYL	TOSYLATED 7-DEAZA-ADENOSINE?	IIIA; Zn/Mg? 10%NH4Cl AQ.EtOH?	554
5'-DEOXY-(3-b-ADENYL)-D-RIBOFURANOSYL	TOSYLATED 3-b-D-RIBO-FURANOSYLADENINE	IIIA; Zn/Mg 10%NH4Cl AQ./EtOH	548
2',3'-O-ISOPROPYLIDENE-5'-DEOXY--(3-b-ADENYL)-D-RIBOFURANOSYL	ROTs	IIIA; Zn/Mg 10%NH4Cl AQ./EtOH	548
5'-DEOXY-(9-b-ADENYL)-D-ARABINO-FURANOSYL	2',3'-DI-O-ACETYL ANALOGUE	ALKALINE HYDROLYSIS	431
2',3'-DI-O-ACETYL-5'-DEOXY-(9-b--ADENYL)-D-ARABINOFURANOSYL	ROTs	IIIA; BH4 50%MeOH AQ.	431
5'-DEOXYINOSYL	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS	31,27,28,431
5'-DEOXYINOSYL	5'-DEOXYADENOSYL(Co)	NITROSATION NITROUS ACID IN DILUTE ACIDIC AQ. LOW TEMPERATURE	222,27
5'-DEOXYINOSYL	5'-O-TOSYLINOSINE--2',3'-PHENYLBORONATE	IIIA; BH4 AQ/EtOH?	445,575
5'-DEOXYINOSYL-[8-¹⁴C]	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS	338
2',3'-O-ISOPROPYLIDENE-5'-DEOXYINOSYL	ROTs	IIIA; BH4 50%MeOH AQ	31,27,431
2',3'-O-ISOPROPYLIDENE-5'-DEOXYINOSYL	ROTs	IIIA; Zn 10%NH4Cl AQ	28*
2',3'-O-ISOPROPYLIDENE-5'-DEOXYINOSYL--[8-¹⁴C]	ROTs	IIIA; BH4 50%MeOH AQ.	338
5'-DEOXYURIDYL	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS	31,27,546,431
5'-DEOXYURIDYL	ROTs	IIIA; BH4 50%MeOH AQ	27

R	REAGENT	METHOD	REF
5'-DEOXYURIDYL	5'-O-TOSYLURIDINE--2',3'-PHENYLBORONATE	IIIA; BH4 AQ/EtOH	242
2',3'-O-ISOPROPYLIDENE-5'-DEOXYURIDYL	ROTs	IIIA; BH4 50%MeOH AQ	31,27,431
2',3'-O-ISOPROPYLIDENE-5'-DEOXYURIDYL	ROTs	IIIA; Zn/Mg 10%NH4Cl AQ./EtOH	546*
5'-DEOXY-5-BROMOURIDYL	ROTs?	IIIA; BH4? 50%MeOH AQ?	416
5'-DEOXYGUANOSYL	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS	418
2',3'-O-ISOPROPYLIDENE-5'-DEOXYGUANOSYL	MIX. OF TOSYLATED 2',3'-O-ISOPROPYLIDENE GUANOSINES	IIIA; Zn 10%NH4Cl AQ	418
5'-DEOXYCYTIDYL	5'-O-TOSYLCYTIDINE--2',3'-PHENYLBORONATE	IIIA; BH4 AQ/EtOH	242
5'-DEOXYCYTIDYL	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS	546
2',3'-O-ISOPROPYLIDENE-5'-DEOXYCYTIDYL	ROTs	IIIA; Zn/Mg 10%NH4Cl AQ./EtOH	546*
N4-TOSYL-5'-DEOXYCYTIDYL	N4,5'-DI-O-TOSYL-CYTIDINE-2',3'-PHENYLBORONATE	IIIA; BH4 AQ/EtOH?	242
N4-ACETYL-5'-DEOXYCYTIDYL	N4-ACETYL-5'-O-TOSYL-CYTIDINE-2',3'-PHENYL-BORONATE?	IIIA; BH4? AQ/EtOH?	445
5'-DEOXYTHYMIDYL	3'-O-ACETYL ANALOGUE	ALKALINE HYDROLYSIS	446
3'-O-ACETYL-5'-DEOXYTHYMIDYL	ROTs	IIIA; Cr(II)CHLORIDE EDTA AQ.(pH9.6)	446
CARBOCYCLIC 5'-DEOXYADENOSYL	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS	218
2',3'-O-ISOPROPYLIDENE-CARBOCYCLIC 5'-DEOXYADENOSYL	ROTs	IIIA; BH4 50%MeOH AQ.	218*
VINYL	ACETYLENE	IIIB; BH4 AQ	27
VINYL	RBr	IIIA; BH4 AQ	27
VINYL	ACETYLENE	IIIB; BH4/Co(2+) MeOH	54
VINYL	ACETYLENE?	IIIB?; Cr(II)CHLORIDE? EDTA AQ.(pH9.6)?	293

R	REAGENT	METHOD	REF
VINYL-2-BROMO	BROMOACETYLENE	IIIB; Cr(II) ACETATE EDTA AQ. (pH9.5) (MINOR PROD)	27
VINYL-2-BROMO	RBr	IIIA; Cr(II) ACETATE? EDTA AQ. (pH9.5)?	27
VINYL-2-HYDROXYCARBONYL	PROPIOLIC ACID	IIIB; Cr(II) ACETATE EDTA AQ. (pH9.5)	27
ETHINYL	RBr	IIIA; Cr(II) ACETATE EDTA AQ. (pH9.5)	27,54
METHOXYCARBONYL	CO	IC; MeOH	283,435
METHOXYCARBONYL	RCl	IIIA; Zn 10%NH4Cl AQ.	283
ETHOXYCARBONYL	RCl	IIIA; Zn 10%NH4Cl AQ.	418,283,435
ETHOXYCARBONYL	CO	IC; EtOH	283
ISOPROPOXYCARBONYL	RCl	IIIA; Zn 10%NH4Cl AQ.	435
BUTOXYCARBONYL	RCl	IIIA; Zn 10%NH4Cl AQ.	283
BUTOXYCARBONYL	CO	IC; BUTANOL	283
ISOBUTOXYCARBONYL	RCl	IIIA; Zn 10%NH4Cl AQ.	435
PHENOXYCARBONYL	R	IIIA; Zn 10%NH4Cl AQ.	435
BENZOYL	RCl?	IIIA; BH4? MeOH?	416
BUTANE-1,4-DI(Co)	BrRBr	IIIA; BH4 MeOH?	416
BUTANE-1,4-DI(Co)	4-Br-BUTYL(Co)	IIIA; BH4 MeOH?	416

COBALAMINS WITH ALPHA-LINKED 5,6-DIMETHYLBENZIMIDAZOLE DISPLACED

R	B	REAGENT	METHOD	REF
METHYL	CN(-)		DISP OF AXIAL BENZIMID DMSO	143*,126*
METHYL	CN(-)		DISP OF AXIAL BENZIMID AQ	193*,201*
(SEVERAL OTHER COBALAMINS ARE RESISTANT TO C-Co CLEAVAGE BY CN(-) AQ, AND FORMATION OF ANALOGOUS COMPOUNDS IS PROBABLE				192*,430*,434*)
METHYL	CN(-)		DISP OF AXIAL BENZIMID SOLID STATE	190,126
CN(-)	METHYL		DISP OF AXIAL AQ	421
AQ	METHYL	MeI	IIIA; Zn 10%NH4Cl AQ. (c.8% OF PROD)	420,421
AQ	METHYL	DI(Me)SULPHATE	IIIA; Zn 10%NH4Cl AQ. (c.5% OF PROD)	420,421
AQ	METHYL	Me(Co)AQ	ISOMERISATION CO AQ 95° (c.2.5% CONVERSION)	420,421
AQ	METHYL	MeI?	IIIA; BH4 AQ (c.?% YIELD)	188
AQ	METHYL	MeI?	IIIA; Zn gly/HCl AQ.(pH2.2) (c.4% YIELD)	188
METHYL-SULPHITO	CN(-)		DISP OF AXIAL BENZIMID AQ	126*
METHYL-SULPHITO	CN(-)		DISP OF AXIAL BENZIMID SOLID STATE	126
METHYL-CARBOXY	CN(-)		DISP OF AXIAL BENZIMID DMSO	125*
METHYL-CARBOXY	CN(-)		DISP OF AXIAL BENZIMID SOLID STATE	126
ETHYL	CN(-)		DISP OF AXIAL BENZIMID DMSO	126*
ETHYL	CN(-)		DISP OF AXIAL BENZIMID SOLID STATE	190,126
AQ	ETHYL	EtI?	IIIA; Zn? 10%NH4Cl AQ.? (LOW YIELD)	448
ETHYL-2-HYDROXY	CN(-)		DISP OF AXIAL BENZIMID DMSO	126*
ETHYL-2-HYDROXY	CN(-)		DISP OF AXIAL BENZIMID SOLID STATE	126
ETHYL-2,2,2-TRIFLUORO	CN(-)		DISP OF AXIAL BENZIMID DMSO	126*
ETHYL-2,2,2-TRIFLUORO	CN(-)		DISP OF AXIAL BENZIMID SOLID STATE	126
PROPYL	CN(-)		DISP OF AXIAL BENZIMID DMSO	126*
PROPYL	CN(-)		DISP OF AXIAL BENZIMID SOLID STATE	126
6-DEOXYGLUCOSYL	CN(-)		DISP OF AXIAL BENZIMID AQ	445*

COBALAMINS WITH ALPHA-LINKED 5,6-DIMETHYLBENZIMIDAZOLE DISPLACED

R	B	REAGENT	METHOD		REF
5'-DEOXYADENOSYL	TRI(Ph)P		DISP OF AXIAL BENZIMID	EtOH	243*
5'-DEOXYADENOSYL	CN(-)		DISP OF AXIAL BENZIMID	DMSO	190*,126*
CARBOCYCLIC 5'-DEOXYADENOSYL	CN(-)		DISP OF AXIAL BENZIMID	AQ	218*
VINYL	CN(-)		DISP OF AXIAL BENZIMID	DMSO	126*
VINYL	CN(-)		DISP OF AXIAL BENZIMID	AQ	416?,193*,201*
VINYL	CN(-)		DISP OF AXIAL BENZIMID	SOLID STATE	190,126
ETHYNYL	CN(-)		DISP OF AXIAL BENZIMID	DMSO	126*
ETHYNYL	CN(-)		DISP OF AXIAL BENZIMID	AQ	416?,193*,201*, 67*
ETHYNYL	CN(-)		DISP OF AXIAL BENZIMID	SOLID STATE	190,126

COBINAMIDES

R	B	REAGENT	METHOD	REF
METHYL	PY		DISP OF AXIAL AQ	187*,191*,105*, 65*
METHYL	IMID		DISP OF AXIAL AQ	191*,65*
METHYL	1-MeIMID		DISP OF AXIAL AQ	191*
METHYL	AMMONIA		DISP OF AXIAL AQ	191*,105*,65*
METHYL	METHYLAMINE		DISP OF AXIAL AQ	105*
METHYL	ETHYLAMINE		DISP OF AXIAL AQ	105*
METHYL	ETHANOLAMINE		DISP OF AXIAL AQ	191*
METHYL	PIPERIDINE		DISP OF AXIAL AQ	191*
METHYL	AQ	DI(Me)SULPHATE	IIIA; Zn 10%NH4Cl AQ.	28
METHYL	AQ	DI(Me)SULPHATE	IIIA; BH4 MeOH?	416,450

R	B	REAGENT	METHOD	REF
METHYL	AQ	RHal	IIIA; BH_4/Cu AQ/MeOH	65
METHYL	AQ		DISP OF AXIAL CN(-) IN ACID SOLUTION (& ALSO FOR R = OTHER ALKYLS)	545,105
METHYL	AQ	RI	IIIA; NBUT DISPROP IN 1M NaCl AQ.	419
METHYL	AQ	RHal	IIIA; Cr(II) CHLORIDE EDTA AQ. (pH9.5)	191
METHYL	AQ	RI (DI(R) SULPHATE)	IIIA; Zn/Hg 10%NH_4Cl AQ.	545
METHYL	AQ	R(cobalamin)	ACID HYDROLYSIS 65% $HClO_4$ AQ.	545
METHYL	AQ	R(cobalamin)	ALKALINE HYDROLYSIS Co(III) HYDROXIDE AQ	545
METHYL-[^{14}C]	AQ	R(cobalamin)	Me(Co) 0.05M NaOAc 95° (50% TRANSFER AFTER 30 h.)	420,421
METHYL	4-HO-2,2,6,6-TETRA(Me)-PIPERIDINE-N-OXYL		DISP OF AXIAL AQ (WITH THE AID OF ETHYL ORTHOFORMATE)	287a
METHYL	DMSO		DISP OF AXIAL AQ	187*
METHYL	CN(-)		DISP OF AXIAL AQ	28*,545*,193*, 201*,191*,105*
METHYL-(2,2,6,6-TETRAMETHYLPIPERIDINE-N-OXYL-4--AMINOCARBONYL)	AQ	RBr	IIIA; CPR BORATE AQ. (pH8)	287
METHYL-(2,2,6,6-TETRAMETHYLPIPERIDINE-N-OXYL-4--AMINOCARBONYL)	AQ	R(cobalamin)	ALKALINE HYDROLYSIS Co(III) HYDROXIDE AQ	287
ETHYL	PY		DISP OF AXIAL AQ	187*,65*
ETHYL	IMID		DISP OF AXIAL AQ	65*
ETHYL	AMMONIA		DISP OF AXIAL AQ	65*
ETHYL	AQ	RI	IIIA; Zn/Hg 10%NH_4Cl AQ.	545
ETHYL	AQ	RHal	IIIA; BH_4 MeOH?	190,451
ETHYL	AQ	RHal	IIIA; BH_4/Cu AQ/MeOH	65
ETHYL	CN(-)		DISP OF AXIAL AQ	545*,190*,453*, 126*
ETHYL-2-HYDROXY	AQ	ETHYLENE OXIDE?	IIIA; Zn 10%NH_4Cl AQ.	104

R	B	REAGENT	METHOD	REF
ETHYL-1-METHYL	AQ	RI	IIIA; BH4 MeOH?	452,187
PROPYL	PY	RCl	IIIA; BH4 MeOH	101*
PROPYL	IMID		DISP OF AXIAL AQ	191*
PROPYL	AQ	RI	IIIA; Zn/Mg 10%NH4Cl AQ.	545
PROPYL	AQ	RHal	IIIA; BH4 MeOH?	451
PROPYL	AQ	RBr(Cl)	IIIA; BH4 MeOH	419,101*
PROPYL	AQ	RHal	IIIA; Cr(II) CHLORIDE EDTA AQ. (pH9.5)	191
PROPYL	c-HexNC	RCl	IIIA; BH4 MeOH	101*
PROPYL	CN(-)		DISP OF AXIAL AQ	545*,293*
PROPYL-2-METHYL	AQ	RCl	IIIA; Zn/Mg 10%NH4Cl AQ.	545
PROPYL-2-METHYL	CN(-)		DISP OF AXIAL AQ	545*
PROPYL-1-METHYL	AQ	RBr(I)	IIIA; BH4 MeOH	105
BUTYL	AQ	RI	IIIA; Zn/Mg 10%NH4Cl AQ.	545
BUTYL	AQ	RI	IIIA; Zn 10%NH4Cl AQ.	418
BUTYL	CN(-)		DISP OF AXIAL AQ	545*
PENTYL	AQ	RCl	IIIA; Zn/Mg 10%NH4Cl AQ./MeOH	545
CYCLOHEXYL	AQ	RBr(I)	IIIA; BH4 MeOH	105,131
OCTYL	AQ	RBr	IIIA; Zn/Mg 10%NH4Cl AQ./MeOH	545
DECYL	AQ	RBr	IIIA; Zn/Mg 10%NH4Cl AQ./MeOH	545
2,3-O-ISOPROPYLIDENE--5-DEOXY-b-D-RIBOSYL	AQ	ROTs?	IIIA?	530
5'-DEOXYADENOSYL	AQ	R(cobalamin)	ALKALINE HYDROLYSIS Ce(III)HYDROXIDE AQ	94
5'-DEOXYADENOSYL	AQ	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS	418,546,558
5'-DEOXYADENOSYL	AQ	ROTs	IIIA; BH4 AQ	287a
5'-DEOXYADENOSYL	4-HO-2,2,6,6-TETRA(Me)-PIPERIDINE-N-OXYL		DISP OF AXIAL AQ (WITH THE AID OF ETHYL ORTHOFORMATE)	287a

B	B	REAGENT	METHOD	REF
2',3'-O-ISOPROPYLIDENE--5'-DEOXYADENOSYL	AQ	ROTs	IIIA; Zn 10%NH4Cl AQ.	418
2',3'-O-ISOPROPYLIDENE--5'-DEOXYADENOSYL	AQ	ROTs	IIIA; Zn/Mg 10%NH4Cl AQ./EtOH	546*
2',3'-O-ISOPROPYLIDENE--5'-DEOXYADENOSYL	AQ	ROTs	IIIA; Cr(II)CHLORIDE EDTA AQ.(pH9.5)	558
5'-DEOXYINOSYL	AQ	5'-DEOXYADENOSYL(Co)	NITROSATION NITROUS ACID IN DILUTE ACIDIC AQ. LOW TEMPERATURE	418
5'-DEOXYURIDYL	AQ	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS	546
2',3'-O-ISOPROPYLIDENE--5'-DEOXYURIDYL	AQ	ROTs	IIIA; Zn/Mg 10%NH4Cl AQ./EtOH	546*
5'-DEOXYCYTIDYL	AQ	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS	546
2',3'-O-ISOPROPYLIDENE--5'-DEOXYCYTIDYL	AQ	ROTs	IIIA; Zn/Mg 10%NH4Cl AQ./EtOH	546*
VINYL	I(-)		DISP OF AXIAL AQ	190a*
VINYL	PY		DISP OF AXIAL AQ	187*
VINYL	AZIDE(-)		DISP OF AXIAL AQ	190a*
VINYL	AQ	ACETYLENE?	IIIB; BH4 MeOH?	190,451
VINYL	MeNC		DISP OF AXIAL AQ	190a*
VINYL	CN(-)		DISP OF AXIAL AQ	190*,126*
ETHYNYL	AQ	RBr?	IIIA?; Cr(II)ACETATE? EDTA AQ.(pH9.5)?	202
METHOXYCARBONYL	AQ	RCl	IIIA; Zn 10%NH4Cl AQ.	435
METHOXYCARBONYL	AQ	CO	IC; METHANOL	435
ETHOXYCARBONYL	AQ	RCl	IIIA; Zn/Mg 10%NH4Cl AQ.	545

R	B	REAGENT	METHOD	REF
METHYL	AQ	MeI	IIIA; Zn gly/HCl AQ. (pH2.2)	448
METHYL	AQ	DI(Me) SULPHATE	IIIA; Zn gly/HCl AQ. (pH2.2)	448
METHYL	AQ	AQ(Co) Me	ISOMERISATION CO AQ 80-95° OR PHOTOL AT 20° (92-93% CONVERSION)	448,188
METHYL-[^{14}C]	AQ	RI	IIIA; Zn 10%NH4Cl AQ.	367
METHYL	CN(-)		DISP OF AXIAL AQ	367*,448*
AQ	METHYL	MeI	IIIA; Zn gly/HCl AQ. (pH2.2) (c.10% OF PROD)	448
AQ	METHYL	DI(Me) SULPHATE	IIIA; Zn gly/HCl AQ. (pH2.2) (c.10% OF PROD)	448
AQ	METHYL	Me(Co) AQ	ISOMERISATION CO AQ 80-95° OR PHOTOL AT 20° (c.7-8% CONVERSION)	448,188
CN(-)	METHYL		DISP OF AXIAL AQ	448*
ETHYL	AQ	EtI	IIIA; Zn gly/HCl AQ. (pH2.2)	448
AQ	ETHYL	EtI	IIIA; Zn gly/HCl AQ. (pH2.2) (c.1.3% OF PROD)	448
ETHYL	CN(-)		DISP OF AXIAL AQ	448*
CN(-)	ETHYL		DISP OF AXIAL AQ	448*
METHOXYCARBONYL	AQ	RCl	IIIA; Zn 10%NH4Cl AQ.	435

COBYRINIC ACIDS

R	B	REAGENT	METHOD	RRF
METHYL	AQ	?	?	429
5'-DEOXYADENOSYL	AQ	?	?	578

COBAMIDES WITH OTHER ALPHA-LINKED BASES IN PLACE OF 5,6-DIMETHYLBENZIMIDAZOLE

R	B	REAGENT	METHOD	RRF
METHYL-[^{14}C]	5-HYDROXY--BENZIMID	RI	IIIA; BH4 MeOH?	450
METHYL-[^{14}C]	5-METHOXY--BENZIMID	RI	IIIA; Zn 10%NH4Cl AQ.	367
PROPYL	5-HYDROXY--BENZIMID	RHal?	IIIA?; BH4? MeOH?	450
BUTYL	BENZIMID	RI	IIIA; Zn 10%NH4Cl AQ.	418
BUTYL	2-MeADENINE	RI	IIIA; Zn 10%NH4Cl AQ.	418
5'-DEOXYADENOSYL	5-HYDROXY--BENZIMID	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS	363
2',3'-O-ISOPROPYLIDENE--5'-DEOXYADENOSYL	5-HYDROXY--BENZIMID	ROTs	IIIA; Zn 10%NH4Cl AQ.	363*
5'-DEOXYINOSYL	BENZIMID	5'-DEOXYADENOSYL(Co)	NITROSATION NITROUS ACID IN DILUTE ACIDIC AQ. LOW TEMPERATURE	418

R	REAGENT	METHOD	VARIANT	REF
METHYL	R(cobalamin)	CHLORAMINE T (1m.)	10-Cl	454,216,204, 425,81
METHYL	RI	IIIA; SULPHITO(Co) + b-NAPHTHYLAMINE EtOH?	10-Cl	294
METHYL	R(cobalamin)	N-Br-SUCCINIMIDE(1.2m.) 0.5M HOAc AQ.(50% OF PROD)	10-Br	84
METHYL	R(cobalamin)	N-Br-SUCCINIMIDE(1.2m.) HOAc (88% OF PROD)	10-Br	84
METHYL	RI	IIIA; SULPHITO(Co) + b-NAPHTHYLAMINE EtOH	10-Br	294,84
METHYL	R(cobalamin)	BROMINE AQ (+ 1 PROD)	10-Br	458,294
METHYL	R(cobalamin)	NOCl(2m.) HOAc(60% YIELD)	10-NO	84
METHYL	10-NITRO(?) ANALOGUE	REDUCTION	10-AMINO	585
METHYL	DI(Me) SULPHATE	IIIA; Zn HOAc AQ.	LACTAM	81
METHYL	RI	IIIA; ALK DISPROP AQ	LACTAM	419
METHYL	RI	IIIA; BH4 MeOH	LACTAM	429,419
METHYL	RI	IIIA(MIX OF (Co)); BH4 AQ	LACTAM	455
METHYL	RI	IIIA(MIX OF (Co)); ALK DISPROP AQ	LACTAM	455,429
METHYL	DI(Me) SULPHATE?	IIIA; Zn? HOAc AQ.?	10-Cl-LACTAM	81
METHYL	R(cobalamin)	CHLORAMINE T (3m.)	10-Cl--LACTONE	454,216,204
METHYL	R(cobalamin)	N-Br-SUCCINIMIDE(1.2m.) 0.5M HOAc AQ.(50% OF PROD)	10-Br(OR H)-LACTONE	84
METHYL	R(cobalamin)	N-Br-SUCCINIMIDE(1.2m.) HOAc (12% OF PROD)	10-Br(OR H)-LACTONE	84
METHYL	R(cobalamin)	BROMINE AQ (+ 1 PROD)	10-Br(OR H)-LACTONE	458,294
METHYL	R(cobalamin)	NOCl(2m.) HOAc(5% YIELD)	10-NO(OR H)-LACTONE	84
METHYL	RI	IIIA; BH4? MeOH?	e-CO.OH	437,416

R	REAGENT	METHOD	VARIANT	REF
METHYL	RI	IIIA(MIX OF (Co)); BH4 AQ	e(?)-CO.OH	455
METHYL	RI	IIIA(MIX OF (Co)); ALK DISPROP AQ	e(?)-CO.OH	455,429
METHYL	RI	IIIA(MIX OF (Co)); BH4 AQ	DI-CO.OH	455
METHYL	RI	IIIA(MIX OF (Co)); ALK DISPROP AQ	DI-CO.OH	455,429
METHYL	RI	IIIA(MIX OF (Co)); BH4 AQ	TRI-CO.OH	455
METHYL	RI	IIIA(MIX OF (Co)); ALK DISPROP AQ	TRI-CO.OH	455,429
METHYL	RI	IIIA; BH4 AQ.	5'-PHOSPHATE	569
METHYL	DI(Me) SULPHATE	IIIA; Zn 10%NH4Cl AQ.	Y=NHCMe2CH2O -etc.	30
METHYL	S-ADENOSYLMETHIONINE(+)	IIIA; Zn 10%NH4Cl AQ.	Y=NHCMe2CH2O -etc.	93
METHYL	S-ADENOSYLMETHIONINE(+)	IIIA; Zn 10%NH4Cl AQ.	Y=NHCHBtCH2O -etc.	93
METHYL	R(cobalamin)	TOH 100°	[T]	422
METHYL	RI	IIIA; BH4 MeOH?	[T]	428
ETHYL	RI	IIIA; BH4 AQ.	5'-PHOSPHATE	569
ETHYL	DI(Et) SULPHATE	IIIA; Zn 10%NH4Cl AQ.	Y=NHCMe2CH2O -etc.	30
ETHYL-2-AMINO	ETHYLENE IMINE	IIIA; Zn 10%NH4Cl AQ.	Y=NHCMe2CH2O -etc.	30
PROPYL	RBr	IIIA; BH4 MeOH	LACTAM	419
PROPYL	RI	IIIA; Zn 10%NH4Cl AQ.	Y=NHCMe2CH2O -etc.	30
BUTYL	RBr	IIIA(MIX OF (Co)); ALK DISPROP AQ	LACTAM	429
BUTYL	RBr	IIIA; BH4 MeOH	LACTAM	429
BUTYL	RBr	IIIA(MIX OF (Co)); ALK DISPROP AQ	e(?)-CO.OH	429

COBALAMIN VARIANTS

R	REAGENT	METHOD	VARIANT	REF
BUTYL	RBr	IIIA (MIX OF (Co)); ALK DISPROP AQ	DT-CO.OH	429
BUTYL	RBr	IIIA (MIX OF (Co)); ALK DISPROP AQ	TRI-CO.OH	429
5'-DEOXYADENOSYL	R(cobalamin)	CHLORAMINE T (1m.)	10-Cl	425,81
5'-DEOXYADENOSYL	R(cobalamin)	CHLORAMINE T (3m.) (60-70% OF PROD)	10-Cl	81
5'-DEOXYADENOSYL	RI	IIIA; BH4 (OR EXCESS MIDL?) MeOH/AQ?	10-Cl	456,457,528
5'-DEOXYADENOSYL	RI	IIIA; BH4 MeOH/AQ?	10-Br	528
5'-DEOXYADENOSYL	2',3'-O-ISOPROPYLIDENE ANALOGUE?	ACID HYDROLYSIS?	LACTAM	81
5'-DEOXYADENOSYL	2',3'-O-ISOPROPYLIDENE ANALOGUE?	ACID HYDROLYSIS?	10-Cl-LACTAM	81
5'-DEOXYADENOSYL	R(cobalamin)	CHLORAMINE T (3m.) (30-40% OF PROD)	10-Cl--LACTONE	81
5'-DEOXYADENOSYL	RI	IIIA; BH4 MeOH/AQ?	b-CO.OH	527
5'-DEOXYADENOSYL	ROTs	IIIA; Cr(II) CHLORIDE EDTA AQ. (pH9.5)	b-CO.OH	583
5'-DEOXYADENOSYL	RI	IIIA; BH4 MeOH/AQ?	d-CO.OH	527
5'-DEOXYADENOSYL	ROTs	IIIA; Cr(II) CHLORIDE EDTA AQ. (pH9.5)	d-CO.OH	583
5'-DEOXYADENOSYL	R(cobalamin)	ACID HYDROLYSIS (24% YIELD)	e-CO.OH	440
5'-DEOXYADENOSYL	2',3'-O-ISOPROPYLIDENE--5'-DEOXYADENOSYL (cobalamin)	ACID HYDROLYSIS (LOWER YIELD)	e-CO.OH	436,440
5'-DEOXYADENOSYL	e-CO.NHR (VARIOUS R)	ACID HYDROLYSIS	e-CO.OH	440
5'-DEOXYADENOSYL	RI	IIIA; BH4 MeOH/AQ?	e-CO.OH	527
5'-DEOXYADENOSYL	ROTs	IIIA; Cr(II) CHLORIDE EDTA AQ. (pH9.5)	e-CO.OH	583
5'-DEOXYADENOSYL	e-CO.OH ANALOGUE	MeNH2 DMF/TRI(Et)N/ Et CHLOROFORMATE	e-CO.NHMe	440

R	REAGENT	METHOD	VARIANT	REF
5'-DEOXYADENOSYL	e-CO.OH ANALOGUE	EtNH2 DMF/TRI(Et)N/ Et CHLOROFORMATE	e-CO.NHEt	440
5'-DEOXYADENOSYL	MIX. OF TOSYLATED ADENOSINES?	IIIA; BH4? 50%MeOH AQ.?	e-CO.NHPh	416
5'-DEOXYADENOSYL	e-CO.OH ANALOGUE	PhNH2 DMF/TRI(Et)N/ Et CHLOROFORMATE	e-CO.NHPh	440
5'-DEOXYADENOSYL	e-CO.OH ANALOGUE	2,4-DINITRO-PhNH? DMF/ TRI(Et)N/Et CHLOROFORMATE	e-CO.NHPh--2,4-DINITRO	440
5'-DEOXYADENOSYL	ROTs	IIIA; Cr(II) CHLORIDE EDTA AQ. (pH9.5)	e-CO.NH--DODECYL	583
5'-DEOXYADENOSYL	e-CO.OH ANALOGUE	1,12-DIAMINODODECANE 3-DI(Et)N-Pr.N=C=N.Et AQ	e-CO.NH--(1,12-DODECANE)-NH2	583
5'-DEOXYADENOSYL	ROTs	IIIA; Cr(II) CHLORIDE EDTA AQ. (pH9.5)	e-CO.NH--(1,12-DODECANE)-NH--AGAROSE	583
5'-DEOXYADENOSYL	2',3'-O-ISOPROPYLIDENE--5'-DEOXYADENOSYL (cobalamin)	ACID HYDROLYSIS (<10% YIELD)	b(OR d),e--DI-CO.OH	440
5'-DEOXYADENOSYL	RI	IIIA; BH4 MeOH/AQ?	b(OR d),e--DI-CO.OH	527
5'-DEOXYADENOSYL	RI	IIIA; BH4 MeOH/AQ?	b,d,e-TRI--CO.OH	527
5'-DEOXYADENOSYL	RI	IIIA; BH4 AQ.	5'-PHOSPHATE	569
5'-DEOXYADENOSYL	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS	Y=NHCMe2CH2O --etc.	30
5'-DEOXYADENOSYL	R(cobalamin)	POLY-L-LYSINE, 3-DI(Et)N-Pr.N=C=N.Et AQ	LINKED TO POLYPEPTIDE THROUGH PHOSPHATE	579
2',3'-O-ISOPROPYLIDENE-5'-DEOXYADENOSYL?	ROTs?	IIIA?; Zn? 10%NH4Cl AQ.?	LACTAM	81
2',3'-O-ISOPROPYLIDENE-5'-DEOXYADENOSYL?	ROTs?	IIIA?; Zn? 10%NH4Cl AQ.?	10-Cl-LACTAM	81
2',3'-O-ISOPROPYLIDENE-5'-DEOXYADENOSYL	ROTs	IIIA; Zn 10%NH4Cl AQ.	Y=NHCMe2CH2O --etc.	30

COBALAMIN VARIANTS

R	REAGENT	METHOD	VARIANT	REF
5'-DEOXYURIDYL	ROTs?	IIIA; BH4? 50%MeOH AQ.?	e-CO.OH	437,416
5'-DEOXYURIDYL	ROTs?	IIIA; BH4? 50%MeOH AQ.?	e-CO.NHPh	416
PROP-2-ENYL	RBr	IIIA; Zn 10%NH4Cl AQ.	Y=NHCMe2CH2O -etc.	30
METHOXYCARBONYL	RCl	IIIA; Zn 10%NH4Cl AQ.	LACTAM	435
METHOXYCARBONYL	CO	IC; MeOH	LACTAM	435

COBALAMINS WITH ALPHA-LINKED 5,6-DIMETHYLBENZIMIDAZOLE DISPLACED - VARIANTS

R	B	REAGENT	METHOD	VARIANT	REF
METHYL	AQ	DI(Me)SULPHATE	IIIA(cobalamin); Zn 10%NH4Cl AQ. (c.9% OF PROD)	BENZIMID--N3-Me(+)	420,421
METHYL	AQ	DI(Me)SULPHATE	IIIA; Zn/Hg 10%NH4Cl AQ.	BENZIMID--N3-Me(+)	545
METHYL	CN(-)		DISP OF AXIAL AQ	BENZIMID--N3-Me(+)	421
CYCLOHEXYL	AQ	RBr(I)	IIIA; BH4 MeOH?	BENZIMID--N3-Me(+)	105
5'-DEOXYADENOSYL	AQ	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS	BENZIMID--N3-Me(+)	546
2',3'-O-ISOPROPYLIDENE--5'-DEOXYADENOSYL	AQ	ROTs	IIIA; Zn/Hg 10%NH4Cl AQ./EtOH	BENZIMID--N3-Me(+)	546*
5'-DEOXYURIDYL	AQ	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS	BENZIMID--N3-Me(+)	546
2',3'-O-ISOPROPYLIDENE--5'-DEOXYURIDYL	AQ	ROTs	IIIA; Zn/Hg 10%NH4Cl AQ./EtOH	BENZIMID--N3-Me(+)	546*
5'-DEOXYCYTIDYL	AQ	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS	BENZIMID--N3-Me(+)	546
2',3'-O-ISOPROPYLIDENE--5'-DEOXYCYTIDYL	AQ	ROTs	IIIA; Zn/Hg 10%NH4Cl AQ./EtOH	BENZIMID--N3-Me(+)	546*

R	R	REAGENT	METHOD	VARIANT	REF
METHYL	AQ	RI	IIIA; BH_4 MeOH	10-Cl	131
METHYL	AQ	DI(Me) SULPHATE	IIIA; Zn gly/HCl AQ. (pH2.2) (c.78% OF PROD)	d-CO.OH	188
METHYL	CN(-)		DISP OF AXIAL AQ	d-CO.OH	188*
METHYL (PARTLY AQ?)	AQ (PARTLY Me?)	RI	IIIA; Zn 10%NH_4Cl AQ.	PHOSPHATE	421
METHYL	AQ	RI	IIIA; Zn 10%NH_4Cl AQ/MeOH (c.50% OF PROD)	PHOSPHO-RIBOSE	189
METHYL	CN(-)		DISP OF AXIAL AQ	PHOSPHO-RIBOSE	189*
METHYL	AQ	AQ(Co)Me	CO AQ 100° OR PHOTOL AT 20° (89,70% CONVERSION)	PHOSPHO-RIBOSE	189
AQ	METHYL	DI(Me) SULPHATE	IIIA; Zn gly/HCl AQ. (pH2.2) (c.22% OF PROD)	d-CO.OH	188
CN(-)	METHYL		DISP OF AXIAL AQ	d-CO.OH	188*
AQ	METHYL	RI	IIIA; Zn 10%NH_4Cl AQ/MeOH (c.50% OF PROD)	PHOSPHO-RIBOSE	189
AQ	METHYL	Me(Co)AQ	CO AQ 100° OR PHOTOL AT 20° (11,30% CONVERSION)	PHOSPHO-RIBOSE	189
CN(-)	METHYL		DISP OF AXIAL AQ	PHOSPHO-RIBOSE	189*
5'-DEOXYADENOSYL?	AQ	a(ADENYL) COBAMIDE ANALOGUE	MILD ACID HYDROLYSIS	PHOSPHO-RIBOSE?	268
5'-DEOXYADENOSYL	AQ	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS	PHOSPHATE	558
5'-DEOXYADENOSYL	AQ	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS	GUANOSINE DIPHOSPHATE	558
5'-DEOXYADENOSYL	AQ	2',3'-O-ISOPROPYLIDENE ANALOGUE	ACID HYDROLYSIS	GUANOSINE DIPHOSPHATE-$-[^{32}P]$	558
2',3'-O-ISOPROPYLIDENE--5'-DEOXYADENOSYL	AQ	BOTs	IIIA; Cr(II) CHLORIDE EDTA AQ. (pH9.5)	PHOSPHATE	558
2',3'-O-ISOPROPYLIDENE--5'-DEOXYADENOSYL	AQ	BOTs	IIIA; Cr(II) CHLORIDE EDTA AQ. (pH9.5)	PHOSPHATE-$-[^{32}P]$	558

COBINAMIDE VARIANTS

R	B	REAGENT	METHOD	VARIANT	REF
2',3'-O-ISOPROPYLIDENE--5'-DEOXYADENOSYL	AQ	ROT:	IIIA; Cr(II) CHLORIDE EDTA AQ. (pH9.5)	GUANOSINE DIPHOSPHATE	558
2',3'-O-ISOPROPYLIDENE--5'-DEOXYADENOSYL	AQ	ROTs	IIIA; Cr(II) CHLORIDE EDTA AQ. (pH9.5)	GUANOSINE DIPHOSPHATE--[^{32}P]	558
METHOXYCARBONYL	AQ	RCl	IIIA; Zn 10%NH4Cl AQ.	LACTAM	435
METHOXYCARBONYL	AQ	CO	IC; METHANOL	LACTAM	435
METHOXYCARBONYL	AQ	RCl	IIIA; Zn 10%NH4Cl AQ.	13-EPI	435
METHOXYCARBONYL	AQ	CO	IC; METHANOL	13-EPI	435

COBYRIC ACID VARIANTS

R	B	REAGENT	METHOD	VARIANT	REF
METHYL	AQ	DI(Me) SULPHATE	IIIA(cobyric acid); Zn gly/HCl AQ. (pH2.2)/MeOH (LOW YIELD)	METHYL ESTER	448

COBYRINIC ACID VARIANTS

R	B	REAGENT	METHOD	VARIANT	REF
METHYL	AQ	RI	IIIA; (Co(III)) AT 120° 30%NaOH AQ.	LACTAM	455,429
METHYL	AQ	RI	IIIA; NC(cobalamin) AT 120° 30%NaOH AQ.	LACTAM	455,429
METHYL	AQ	RI	IIIA; BH4 AQ	LACTAM NH4 SALT	455,429
METHYL	AQ	RI	IIIA; Zn 10%NH4Cl AQ.	a,c,g--TRIAMIDE	421
METHYL	AQ	RI	IIIA; Zn HOAc/AQ	HEPTA-Et ESTER	81

COBYRINIC ACID VARIANTS

R	B	REAGENT	METHOD	VARIANT	REF
METHYL	AQ	HEPTA-Et ESTER ANALOGUE	MeMgI THF/ETHER	HEPTA-CMe2OH	81
METHYL	AQ	MeMgI	IA(DI(NC)(Cn-HEPTA-Et ESTER)); THF/ETHER	HEPTA-CMe2OH	81
METHYL	AQ	DI(Me)SULPHATE	IIIA(a,c,g-TRIAMIDE); Zn 10%NH4Cl AQ.	a,c,g-TRI-AMIDE-b,d,e,f--TETRA(Me ESTER)?	421
BUTYL	AQ	RLi	IA; THF/ETHER?	HEPTA-CMe2OH	294
BUTYL	AQ	RMgI	IA; THF/ETHER?	HEPTA-CMe2OH	294

NATURAL SOURCES

COMPLEX	SOURCE	REF
METHYLCOBALAMIN	P.SHERMANII-1 CORRIN-POLYPEPTIDE COMPLEX (1.5-2%)	518
METHYLCOBALAMIN	P.FREUDENREICHII-3 CORRIN-POLYPEPTIDE COMPLEX (1.5-2%)	518
METHYLCOBALAMIN	P.ARABINOSUM-563 CORRIN-POLYPEPTIDE COMPLEX (1.5-2%)	518
METHYLCOBALAMIN	E.COLI	310
METHYLCOBALAMIN	E.COLI, AQ(Co), S-ADENOSYLMETHIONINE, REDUCING SYSTEM	511
METHYLCOBALAMIN	E.COLI ALK PHOSPHATASE, METHYLCOBALAMIN--5'-PHOSPHATE	569
METHYLCOBALAMIN	STREPTOMYCES RIMOSUS	310
METHYLCOBALAMIN	M.KUZNECEOVII	485
METHYLCOBALAMIN	MICROORGANISM (PATENTED,UNSPECIFIED) (c.2.5% OF PROD R(Co))	310,519
METHYLCOBALAMIN	HUMAN BLOOD PLASMA OR SERUM (MAJOR PROD)	523,310,524,515
METHYLCOBALAMIN	HUMAN URINE (MAJOR PROD)	515

COMPLEX	SOURCE	REF
METHYLCOBALAMIN	CALF LIVER (c.6% OF PROD R(Co))	523,310,520
METHYLCOBALAMIN	RAT LIVER & KIDNEY (MINOR PROD)	516
[^{14}C]-METHYLCOBALAMIN	METHANOSARCINA BARKERII, (Co(I)) (BY CPR OR RH4) [^{14}C]-METHANOL ATP	491,233,508
[^{14}C]-METHYLCOBALAMIN	M.OMELIANSKII, (Co(II)) [^{14}C]-MeCoBIS(dmgH)AQ H2	377
[^{14}C]-METHYLCOBALAMIN	E.COLI B ENZYME, D,L-N^5-[^{14}C]-METHYL--TETRAHYDROFOLATE, S-ADENOSYLMETHIONINE, REDUCING SYSTEM	532,492,424
[^{14}C]-METHYLCOBALAMIN	E.COLI B ENZYME, [^{14}C-Me]-S-ADENOSYL-METHIONINE(+) I(-), REDUCING SYSTEM	532,492,424
[^{14}C]-METHYLCOBALAMIN	E.COLI B ENZYME, [^{14}C]-MeT, REDUCING SYSTEM	424
[^{14}C]-METHYLCOBALAMIN	HOG KIDNEYS ENZYME, D,L-N^5-[^{14}C]-METHYL--TETRAHYDROFOLATE, S-ADENOSYLMETHIONINE, EXCESS METHIONINE, REDUCED FLAVIN	493
[T]-METHYLCOBALAMIN	METHANOSARCINA BARKERII, (Co(I)) (CPR) [T-Me]-METHANOL ATP	233,508
[T]-METHYLCOBALAMIN	E.COLI ENZYME, [Y-Me]-S-ADENOSYL-METHIONINE, REDUCING SYSTEM	532
[T]-METHYLCOBALAMIN	HOG KIDNEYS ENZYME, [T-Me]-S-ADENOSYL-METHIONINE, EXCESS METHIONINE, REDUCED FLAVIN	493
[^{14}C],[T]-METHYLCOBALAMIN	METHANOSARCINA BARKERII, [^{14}C],[T]-MeOH, CPR, ATP	508
[^{57}Co]-METHYLCOBALAMIN	HUMAN SKIN FIBROBLASTS IN TISSUE CULTURE, [^{57}Co]-AQ(Co) (MULTIPLYING CELLS) (c.60% OF PROD R(Co))	537
[^{60}Co]-METHYLCOBALAMIN	STREPTOMYCES OLIVACEUS 605, [^{60}Co]-CoCl2, GLYCEROL (FAVOURED IN EARLY STAGE OF GROWTH)	534
[^{14}C]-HYDROXYCARBONYLMETHYLCOBALAMIN?	C.THERMOACETICUM, [^{14}C]-HCO3 (TRACE)	367
ETHYLCOBALAMIN	P.SHERMANII, ETHYLCOBINAMIDE 5,6-DIMETHYLBENZIMID	458

COMPLEX	SOURCE	REF
ETHYLCOBALAMIN	E.COLI ALK PHOSPHATASE, ETHYLCOBALAMIN-5'-PHOSPHATE	569
ETHYLCOBALAMIN	M.OMELIANSKII, (Co(II)) EtI ATP H2	377
PROPYLCOBALAMIN	M.OMELIANSKII, (Co(II)) PrI ATP H2	377
PROPYLCOBALAMIN	E.COLI B ENZYME, PrI, REDUCING SYSTEM	424
BUTYLCOBALAMIN	P.SHERMANII, BUTYLCOBINAMIDE 5,6-DIMETHYLBENZIMID (SHORT INCUBATION)	418
BUTYLCOBALAMIN	P.SHERMANII, a(2-MeADENYL)-BuCOBAMIDE 5,6-DIMETHYLBENZIMID	418
BUTYLCOBALAMIN	P.SHERMANII, a(BENZIMID)-BuCOBAMIDE 5,6-DIMETHYLBENZIMID	418
CARBOCYCLIC [5'-T]-5'-DEOXYADENOSYLCOBALAMIN	AEROBACTER AEROGENES ENZYME, UNTRITIATED ANALOGUE, D,L-1,2-PROPANEDIOL-[1-T]	218
5'-DEOXYADENOSYLCOBALAMIN	P.SHERMANII (X-RAY)	468,469,470, 541,544,471 (106)
5'-DEOXYADENOSYLCOBALAMIN	P.SHERMANII-1	518
5'-DEOXYADENOSYLCOBALAMIN	P.SHERMANII, AQ(Co) OR NC(Co)	514,541,542, 553,510
5'-DEOXYADENOSYLCOBALAMIN	P.SHERMANII, 5,6-DIMETHYLBENZIMID	514,544
5'-DEOXYADENOSYLCOBALAMIN	P.SHERMANII, NC(cobinamide)CN, 5,6-DIMETHYLBENZIMID	514,513
5'-DEOXYADENOSYLCOBALAMIN	P.SHERMANII, 5'-DEOXYINOSYL(Co)	418
5'-DEOXYADENOSYLCOBALAMIN	P.SHERMANII, 5'-DEOXYINOSYLCOBINAMIDE 5,6-DIMETHYLBENZIMID	418
5'-DEOXYADENOSYLCOBALAMIN	P.SHERMANII, B(Co) R=Me,Et,Pr,Bu,Pe	418
5'-DEOXYADENOSYLCOBALAMIN	P.SHERMANII, a(BENZIMID)-BuCOBAMIDE	418
5'-DEOXYADENOSYLCOBALAMIN	P.SHERMANII, a(2-MeADENYL)-BuCOBAMIDE	418
5'-DEOXYADENOSYLCOBALAMIN	P.SHERMANII, BuCOBINAMIDE	418
5'-DEOXYADENOSYLCOBALAMIN	P.SHERMANII, a(BENZIMID)-5'-DEOXY-INOSYLCOBAMIDE	418

COMPLEX	SOURCE	REF
5'-DEOXYADENOSYLCOBALAMIN	P.SHERMANII, a(2-MeADENYL)-BuCOBAMIDE 5,6-DIMETHYLBENZIMID	418
5'-DEOXYADENOSYLCOBALAMIN	P.SHERMANII, a(BENZIMID)-BuCOBAMIDE 5,6-DIMETHYLBENZIMID	418
5'-DEOXYADENOSYLCOBALAMIN	P.SHERMANII, a(BENZIMID)-5'-DEOXY-INOSYLCOBAMIDE 5,6-DIMETHYLBENZIMID	418
5'-DEOXYADENOSYLCOBALAMIN	P.SHERMANII, BUTYLCOBINAMIDE 5,6-DIMETHYLBENZIMID (LONG INCUBATION)	418
5'-DEOXYADENOSYLCOBALAMIN	P.SHERMANII, 5'-DEOXYADENOSYL-COBALAMIN-5'-PHOSPHATE	569
5'-DEOXYADENOSYLCOBALAMIN	P.SHERMANII, 5'-DEOXYADENOSYL-COBALAMIN-MONO, DI & TRI-CO.OH	526,578,581
5'-DEOXYADENOSYLCOBALAMIN	P.SHERMANII ENZYME, AQ(Co), ATP, GLUTATHIONE, REDUCED FLAVIN	474
5'-DEOXYADENOSYLCOBALAMIN	P.FREUDENREICHII	468,469,470, 544,471
5'-DEOXYADENOSYLCOBALAMIN	P.FREUDENREICHII, 5,6-DIMETHYLBENZIMID	544
5'-DEOXYADENOSYLCOBALAMIN	P.TECHNICUM	469,470,471
5'-DEOXYADENOSYLCOBALAMIN	P.ARABINOSUM, 5,6-DIMETHYLBENZIMID OR 2,3-DIMETHYL-5,6-DIAMINOBENZENE	469
5'-DEOXYADENOSYLCOBALAMIN	P.PETERSONII	544
5'-DEOXYADENOSYLCOBALAMIN	P.PETERSONII, 5,6-DIMETHYLBENZIMID OR 2,3-DIMETHYL-5,6-DIAMINOBENZENE	469,544
5'-DEOXYADENOSYLCOBALAMIN	P.JENSENII, 5,6-DIMETHYLBENZIMID OR 2,3-DIMETHYL-5,6-DIAMINOBENZENE	469
5'-DEOXYADENOSYLCOBALAMIN	P.PENTOSACEUM, 5,6-DIMETHYLBENZIMID OR 2,3-DIMETHYL-5,6-DIAMINOBENZENE	469
5'-DEOXYADENOSYLCOBALAMIN	DRIED CELLS OF A SPECIES OF PROPIONIBACTERIUM	303
5'-DEOXYADENOSYLCOBALAMIN	C.TETANOMORPHUM, 5,6-DIMETHYLBENZIMID	303,468
5'-DEOXYADENOSYLCOBALAMIN	C.TETANOMORPHUM ENZYME, MC(Co), ATP OR ADP, GLUTATHIONE OR MERCAPTOETHANOL, YEAST EXTRACT OR REDUCED FLAVIN	472,307

COMPLEX	SOURCE	REF
5'-DEOXYADENOSYLCOBALAMIN	C.TETANOMORPHUM ENZYME, AQ(Co), ATP, MERCAPTOETHANOL, REDUCED LIPOIC ACID	480
5'-DEOXYADENOSYLCOBALAMIN	C.TETANOMORPHUM ENZYME, AQ(Co), ATP, DH4	480,306
5'-DEOXYADENOSYLCOBALAMIN	C.TETANOMORPHUM ENZYME, AQ(Co), ATP, NADH-DEPENDANT FLAVOPROTEINS(EX C.TET.), FAD	481,538
5'-DEOXYADENOSYLCOBALAMIN?	E.COLI B, NC(Co)	476
5'-DEOXYADENOSYLCOBALAMIN	E.COLI 113-3, NC(Co)	476
5'-DEOXYADENOSYLCOBALAMIN	E.COLI ALK PHOSPHATASE, 5'-DEOXYADENOSYL-COBALAMIN-5'-PHOSPHATE	569
5'-DEOXYADENOSYLCOBALAMIN	STREPTOMYCES OLIVACEUS 605, GLUCOSE/LACTOSE (MAJOR PROD)	533
5'-DEOXYADENOSYLCOBALAMIN	AZOTOBACTER VINELANDII OP	475
5'-DEOXYADENOSYLCOBALAMIN	NOCARDIA LUTEA, NC(Co)	542
5'-DEOXYADENOSYLCOBALAMIN	RHIZOBIUM MELILOTI	477,478,479
5'-DEOXYADENOSYLCOBALAMIN	SOYBEAN NODULES	482,483
5'-DEOXYADENOSYLCOBALAMIN	RHODOPSEUDOMONAS SPHEROIDES	484
5'-DEOXYADENOSYLCOBALAMIN	RHODOPSEUDOMONAS SPHEROIDES PM-8	517
5'-DEOXYADENOSYLCOBALAMIN	BACILLUS MEGATERIUM, NC(Co)	510
5'-DEOXYADENOSYLCOBALAMIN	M.KUZNECEOVII	485
5'-DEOXYADENOSYLCOBALAMIN	MICROORGANISM (PATENTED, UNSPECIFIED) (c.97.5% OF PROD R(Co))	310,519
5'-DEOXYADENOSYLCOBALAMIN	HUMAN BLOOD PLASMA (MINOR PROD)	310
5'-DEOXYADENOSYLCOBALAMIN	HUMAN SKIN FIBROBLASTS IN TISSUE CULTURE	536
5'-DEOXYADENOSYLCOBALAMIN	RABBIT LIVER	303,309
5'-DEOXYADENOSYLCOBALAMIN	HUMAN LIVER	309
5'-DEOXYADENOSYLCOBALAMIN	LAMB LIVER	309
5'-DEOXYADENOSYLCOBALAMIN	CHICKEN LIVER	309

COMPLEX	SOURCE	REF
5'-DEOXYADENOSYLCOBALAMIN	CALF LIVER (c.94% OF PROD R(Co))	310,520
5'-DEOXYADENOSYLCOBALAMIN	MITOCHONDRIA FROM LIVER OF TUMOUR-BEARING RATS (SARCOMA), NC(Co), BOVINE LIVER CATALASE	510
5'-DEOXYADENOSYLCOBALAMIN	GUINEA-PIG ILEUM	486
5'-DEOXYADENOSYLCOBALAMIN	GUINEA-PIG PLASMA	486
([^{14}C]-5'-DEOXYADENOSYL)COBALAMIN	C.TETANOMORPHUM ENZYME, NC(Co) OR (Co(II)), [^{14}C]-ATP, GLUTATHIONE OR MERCAPTO-ETHANOL, YEAST EXTRACT OR REDUCED FLAVIN OR REDUCED FERREDOXIN	473,512,83
([^{14}C]-5'-DEOXYADENOSYL)COBALAMIN	C.SP. ENZYME, NC(Co), [^{14}C]-ATP, REDUCING SYSTEM	337
[8-^{14}C]-5'-DEOXYADENOSYLCOBALAMIN	P.SHERMANII ENZYME, AQ(Co) OR NC(Co), [8-^{14}C]-ATP, MERCAPTOETHANOL, REDUCED FLAVIN	305
[8-^{14}C]-5'-DEOXYADENOSYLCOBALAMIN	C.TETANOMORPHUM ENZYME, AQ(Co) OR NC(Co), [8-^{14}C]-ATP, GLUTATHIONE, YEAST EXTRACT	472
[5'-T]-5'-DEOXYADENOSYLCOBALAMIN	AEROBACTER AEROGENES ENZYME, UNTRITIATED ANALOGUE, D,L-[1-T]-1,2-PROPANEDIOL	442,487,335, 334,340
[5'-T]-5'-DEOXYADENOSYLCOBALAMIN	LACTOBACILLUS LEICHMANNII ENZYME, UNTRITIATED ANALOGUE, TOH, DITHIOL, NUCLEOTIDE	488,443
[5'-T]-5'-DEOXYADENOSYLCOBALAMIN	C.TETANOMORPHUM ENZYME, UNTRITIATED ANALOGUE, SODIUM [T-Me]-3-METHYL-ASPARTATE	333
[5'-T]-5'-DEOXYADENOSYLCOBALAMIN	C.SP. ENZYME, UNTRITIATED ANALOGUE, [1-T]-ETHANOLAMINE	331,342
5'-DEOXYADENOSYLCOBALAMIN-[LABELLED]	P.SHERMANII, [LABELLED]-CHLOROPHYLLS	509
[^{57}Co]-5'-DEOXYADENOSYLCOBALAMIN	HUMAN SKIN FIBROBLASTS IN TISSUE CULTURE, [^{57}Co]-AQ(Co) (MULTIPLYING CELLS) (c.40% OF PROD R(Co))	537
[^{57}Co]-5'-DEOXYADENOSYLCOBALAMIN	GUINEA-PIG ILEUM (& LATER IN PORTAL PLASMA), FEED GUINEA-PIG WITH [^{57}Co]-NC(Co)	486
[^{58}Co]-5'-DEOXYADENOSYLCOBALAMIN	P.SHERMANII, [^{58}Co]-CoCl2	469,309

COMPLEX	SOURCE	REF
[^{58}Co]-5'-DEOXYADENOSYLCOBALAMIN	SHEEP LIVER, [^{58}Co]-NC(Co)	489
[^{60}Co]-5'-DEOXYADENOSYLCOBALAMIN	P.SHERMANII, [^{60}Co]-CoCl2, 5,6-DIMETHYLBENZIMID	549
[^{60}Co]-5'-DEOXYADENOSYLCOBALAMIN	STREPTOMYCES OLIVACEUS 605, [^{60}Co]-CoCl2, GLYCEROL (MAJOR PROD AT LATE STAGE OF GROWTH)	534
[^{60}Co]-5'-DEOXYADENOSYLCOBALAMIN	HUMAN LIVER & KIDNEY, [^{60}Co]-NC(Co)	540
[^{60}Co]-5'-DEOXYADENOSYLCOBALAMIN	WHITE RAT LIVER & KIDNEY, [^{60}Co]-NC(Co)	540
[^{60}Co]-5'-DEOXYADENOSYLCOBALAMIN	RABBIT LIVER & KIDNEY, INJECT RABBIT WITH [^{60}Co]-NC(Co)	539,540
[^{60}Co],[8-^{14}C]-5'-DEOXYADENOSYLCOBALAMIN	RAT LIVER, B12 DEFICIENT RATS INJECTED WITH [^{60}Co]-NC(Co) & [8-^{14}C]-ADENINE	490
5'-DEOXYINOSYLCOBALAMIN	P.SHERMANII, 5'-DEOXYINOSYLCOBINAMIDE 5,6-DIMETHYLBENZIMID	418
5'-DEOXYINOSYLCOBALAMIN	P.SHERMANII, a(BENZIMID)-5'-DEOXY-INOSYLCOBAMIDE 5,6-DIMETHYLBENZIMID	418
5'-DEOXYINOSYLCOBALAMIN?	C.TETANOMORPHUM ENZYME, AQ(Co), ITP, BH4	306
5'-DEOXYCYTIDYLCOBALAMIN	C.TETANOMORPHUM ENZYME, AQ(Co), CTP, BH4	306
5'-DEOXYURIDYLCOBALAMIN?	C.TETANOMORPHUM ENZYME, AQ(Co), UTP, BH4	306
5'-DEOXYGUANOSYLCOBALAMIN?	C.TETANOMORPHUM ENZYME, AQ(Co), GTP, BH4	306
[^{14}C]-METHYLCOBINAMIDE	C.THERMOACETICUM, [^{14}C]-HCO3 (TRACE)	364,559
5'-DEOXYADENOSYLCOBINAMIDE	P.SHERMANII (ANAEROBIC)	470,514,541,544
5'-DEOXYADENOSYLCOBINAMIDE	P.SHERMANII, NC(Co) OR AQ(Co)	514,541,542, 558,553
5'-DEOXYADENOSYLCOBINAMIDE	P.SHERMANII, LEVULINIC ACID (ANAEROBIC) (MINOR PROD)	525
5'-DEOXYADENOSYLCOBINAMIDE	P.SHERMANII, 5'-DEOXYINOSYL(Co)	418
5'-DEOXYADENOSYLCOBINAMIDE	P.SHERMANII ENZYME, (Co(II)) OR NC(Co), ATP, REDUCED FLAVIN (FRACTIONS FROM P.FREUDENREICHII, P.PETERSONII & P.ARABINOSUM ALSO UTILISED)	543

COMPLEX	SOURCE	REF
5'-DEOXYADENOSYLCOBINAMIDE	P.PREUDENREICHII (ANAEROBIC)	470,544
5'-DEOXYADENOSYLCOBINAMIDE	P.TECHNICUM (ANAEROBIC)	470
5'-DEOXYADENOSYLCOBINAMIDE	P.RUBRUM (MINOR PROD)	470
5'-DEOXYADENOSYLCOBINAMIDE	P.THOENII (MINOR PROD)	470
5'-DEOXYADENOSYLCOBINAMIDE	P.ZEAE (MINOR PROD)	470
5'-DEOXYADENOSYLCOBINAMIDE	P.PETERSONII (MINOR PROD)	470,544
5'-DEOXYADENOSYLCOBINAMIDE	P.JENSENII (MINOR PROD)	470
5'-DEOXYADENOSYLCOBINAMIDE	P.RAFFINOSACEUM (MINOR PROD)	470
5'-DEOXYADENOSYLCOBINAMIDE	P.PENTOSACEUM (MINOR PROD)	470
5'-DEOXYADENOSYLCOBINAMIDE	P.ARABINOSUM (MINOR PROD)	470,544
5'-DEOXYADENOSYLCOBINAMIDE	C.THERMOACETICUM (4%)	494,364
5'-DEOXYADENOSYLCOBINAMIDE	NOCARDIA LUTEA, NC(Co)	542
[^{60}Co]-5'-DEOXYADENOSYLCOBINAMIDE	STREPTOMYCES OLIVACEUS 605, [^{60}Co]-CoCl2, GLYCEROL (MAJOR PROD WITH OPTIMAL Co(2+))	534
[8-^{14}C]-5'-DEOXYADENOSYLCOBINAMIDE	P.SHERMANII ENZYME, AQ(Co), [8-^{14}C]-ATP, MERCAPTOETHANOL, REDUCED FLAVIN	305
[^{14}C]-METHYLCOBYRIC ACID	C.THERMOACETICUM, [^{14}C]-HCO3 (0.3%)	367,364
5'-DEOXYADENOSYLCOBYRIC ACID	P.SHERMANII, NC(Co)CN	513
5'-DEOXYADENOSYLCOBYRIC ACID	P.SHERMANII, LEVULINIC ACID (ANAEROBIC) (MINOR PROD)	525
5'-DEOXYADENOSYLCOBYRIC ACID	C.THERMOACETICUM (49.5%)	494,364
5'-DEOXYADENOSYLCOBYRIC ACID	NOCARDIA RUGOSA STRAIN 466	495
5'-DEOXYADENOSYLCOBYRIC ACID	M.KUZNECHOVII (MINOR PROD)	485
[8-^{14}C]-5'-DEOXYADENOSYLCOBYRIC ACID	P.SHERMANII ENZYME, AQ(Co), [8-^{14}C]-ATP, MERCAPTOETHANOL, REDUCED FLAVIN	305
a(BENZIMIDAZOLYL)-5'-DEOXYADENOSYLCOBAMIDE	P.SHERMANII ENZYME, NC(Co),AQ(Co) OR (Co(II)), ATP OR ADP, GLUTATHIONE OR MERCAPTOETANOL, REDUCED FLAVIN	474,305

COMPLEX	SOURCE	REF
a(BENZIMIDAZOLYL)-5'-DEOXYADENOSYLCOBAMIDE	C.TETANOMORPHUM, BENZIMID	303,468
a(BENZIMIDAZOLYL)-5'-DEOXYADENOSYLCOBAMIDE	E.COLI 113-3, DI(NC)COBINAMIDE, BENZIMID	476
a(BENZIMIDAZOLYL)-5'-DEOXYADENOSYLCOBAMIDE	BACILLUS MEGATERIUM, BENZIMID	476
a([2-^{14}C]-BENZIMIDAZOLYL)-5'-DEOXYADENOSYLCOBAMIDE	P.SHERMANII, BENZIMID-[2-^{14}C]	496
a(BENZIMIDAZOLYL)-([^{14}C]-5'-DEOXYADENOSYL)COBAMIDE	P.SHERMANII ENZYME, AQ(Co), [^{14}C]-ATP, MERCAPTOETHANOL, REDUCED FLAVIN	305
a(BENZIMIDAZOLYL)-[8-^{14}C]-5'-DEOXYADENOSYLCOBAMIDE	P.SHERMANII ENZYME, AQ(Co) OR NC(Co), [8-^{14}C]-ATP, MERCAPTOETHANOL, REDUCED FLAVIN	305
a(5(6)-METHYLBENZIMIDAZOLYL)-5'-DEOXYADENOSYLCOBAMIDE	P.SHERMANII, NC(Co)	541,542,553
a(5(6)-METHYLBENZIMIDAZOLYL)-5'-DEOXYADENOSYLCOBAMIDE	P.ARABINOSUM, 5-METHYLBENZIMID	497
a(5-HYDROXYBENZIMIDAZOLYL)-[1-^{14}C]-PROPYLCOBAMIDE	M.OMELIANSKII, [1-^{14}C]-PrI, H2	365
a(5-HYDROXYBENZIMIDAZOLYL)-5'-DEOXYADENOSYLCOBAMIDE	P.SHERMANII, NC(Co)	541,542,553
a(5-HYDROXYBENZIMIDAZOLYL)-5'-DEOXYADENOSYLCOBAMIDE	M.OMELIANSKII (MAJOR PROD)	363
a(5-HYDROXYBENZIMIDAZOLYL)-5'-DEOXYADENOSYLCOBAMIDE	METHANOSARCINA BARKERII (MAJOR PROD)	555
a(5-METHOXYBENZIMIDAZOLYL)-[^{14}C]-METHYLCOBAMIDE	C.THERMOACETICUM, [^{14}C]-HCO3 (0.3%)	367,364
a(5-METHOXYBENZIMIDAZOLYL)-5'-DEOXYADENOSYLCOBAMIDE	C.THERMOACETICUM (13.5%)	494,364
a(5-ETHOXYBENZIMIDAZOLYL)-5'-DEOXYADENOSYLCOBAMIDE	P.SHERMANII, NC(Co)	541,542,449
a(5(6)-NITROBENZIMIDAZOLYL)-5'-DEOXYADENOSYLCOBAMIDE	P.ARABINOSUM, 5-NITROBENZIMID	497
a(5(6)-NITROBENZIMIDAZOLYL)-5'-DEOXYADENOSYLCOBAMIDE	P.ARABINOSUM, 5-AMINOBENZIMID (MAJOR PROD)	497
a(5(6)-AMINOBENZIMIDAZOLYL)-5'-DEOXYADENOSYLCOBAMIDE	P.ARABINOSUM, 5-AMINOBENZIMID (MINOR PROD)	497
a(5(6)-TRIFLUOROMETHYLBENZIMIDAZOLYL)-5'-DEOXYADENOSYLCOBAMIDE	P.ARABINOSUM, 4-TRIFLUOROMETHYL--1,2-DIAMINOBENZENE	497
a(6',7'-DIMETHYLNAPHTHO-(2',3')-IMIDAZOLYL-4,5)-5'--DEOXYADENOSYLCOBAMIDE	P.SHERMANII (St33), 6',7'-DI(Me)NAPHTHO--(2',3')-IMID-4,5 (ANAEROBIC)	507
a(ADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.SHERMANII, NC(Co)	541,542,553
a(ADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.SHERMANII, DI(NC)COBINAMIDE, ADENINE?	321

COMPLEX	SOURCE	REF
a(ADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.SHERMANII (ANAEROBIC) (<1%, ONE STRAIN EXCEPTED)	470,544
a(ADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.ARABINOSUM	497
a(ADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.FREUDENREICHII (ANAEROBIC) (<1%)	470,544
a(ADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.TECHNICUM (ANAEROBIC) (<1%)	470
a(ADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.RUBRUM	470
a(ADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.THOENII	470
a(ADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.ZEAE	470
a(ADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.PETERSONII	470,544
a(ADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.JENSENII	470
a(ADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.RAFFINOSACEUM	470
a(ADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.PENTOSACEUM	470
a(ADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.ARABINOSUM (MAJOR PROD)	470,541,544
a(ADENYL)-5'-DEOXYADENOSYLCOBAMIDE	C.TETANOMORPHUM	302,304
a(ADENYL)-5'-DEOXYADENOSYLCOBAMIDE	C.PERFRINGENS	498,499
a(ADENYL)-5'-DEOXYADENOSYLCOBAMIDE	C.STICKLANDII	500
a(ADENYL)-[8-^{14}C]-5'-DEOXYADENOSYLCOBAMIDE	P.SHERMANII ENZYME, NC(Co), [8-^{14}C]-ATP, MERCAPTOETHANOL, REDUCED FLAVIN	305
a(2-METHYLADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.SHERMANII (MINOR PROD)	544
a(2-METHYLADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.SHERMANII, NC(Co)	541,542,553
a(2-METHYLADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.RUBRUM	470
a(2-METHYLADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.THOENII	470
a(2-METHYLADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.ZEAE	470
a(2-METHYLADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.PETERSONII	470,544
a(2-METHYLADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.JENSENII	470
a(2-METHYLADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.RAFFINOSACEUM	470

COMPLEX	SOURCE	REF
a(2-METHYLADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.PENTOSACEUM	470
a(2-METHYLADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.ARABINOSUM	470,544
a(2-METHYLADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.FREUDENREICHII (MINOR PROD)	544
a(2-METHYLADENYL)-5'-DEOXYADENOSYLCOBAMIDE	C.THERMOACETICUM (0.5%)	364,559
a(2-CHLOROADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.ARABINOSUM, 2-CHLOROADENINE	501
a(2-THIOADENYL)-5'-DEOXYADENOSYLCOBAMIDE	P.ARABINOSUM, (NC)COBINAMIDE(AQ) 2-THIOADENINE	502
a(PURINYL)-5'-DEOXYADENOSYLCOBAMIDE	P.ARABINOSUM, PURINE	503
a(PURINYL)-5'-DEOXYADENOSYLCOBAMIDE	P.SHERMANII, PURINE	503
a(PURINYL)-5'-DEOXYADENOSYLCOBAMIDE	P.PETERSONII, PURINE	503
a(2,6-DIAMINOPURINYL)-5'-DEOXYADENOSYLCOBAMIDE	P.RUBRUM, 2,6-DIAMINOPURINE	470
a(2,6-DIAMINOPURINYL)-5'-DEOXYADENOSYLCOBAMIDE	P.THOENII, 2,6-DIAMINOPURINE	470
a(2,6-DIAMINOPURINYL)-5'-DEOXYADENOSYLCOBAMIDE	P.ZEAE, 2,6-DIAMINOPURINE	470
a(2,6-DIAMINOPURINYL)-5'-DEOXYADENOSYLCOBAMIDE	P.PETERSONII, 2,6-DIAMINOPURINE	470
a(2,6-DIAMINOPURINYL)-5'-DEOXYADENOSYLCOBAMIDE	P.JENSENII, 2,6-DIAMINOPURINE	470
a(2,6-DIAMINOPURINYL)-5'-DEOXYADENOSYLCOBAMIDE	P.ARABINOSUM, 2,6-DIAMINOPURINE	470,497
a(2,6-DIAMINOPURINYL)-5'-DEOXYADENOSYLCOBAMIDE	P.PENTOSACEUM, 2,6-DIAMINOPURINE	470
a(2,6-DIAMINOPURINYL)-5'-DEOXYADENOSYLCOBAMIDE	P.FREUDENREICHII, 2,6-DIAMINOPURINE (ANAEROBIC)	470
a(2,6-DIAMINOPURINYL)-5'-DEOXYADENOSYLCOBAMIDE	P.SHERMANII, 2,6-DIAMINOPURINE (ANAEROBIC)	470
a(2,6-DIAMINOPURINYL)-5'-DEOXYADENOSYLCOBAMIDE	P.TECHNICUM, 2,6-DIAMINOPURINE (ANAEROBIC)	573
5'-DEOXYADENOSYLCOBALAMIN-10-CHLORO	P.SHERMANII, NC(Co) OR AQ(Co)	84,456,457,528
5'-DEOXYADENOSYLCOBALAMIN-10-BROMO	P.SHERMANII, NC(Co) OR AQ(Co)	84,528
5'-DEOXYADENOSYLCOBALAMIN LACTAM	P.SHERMANII, AQ(Co) OR NC(Co)	425,81,581
5'-DEOXYADENOSYLCOBALAMIN 10-CHLORO LACTAM	P.SHERMANII, AQ(Co)	425,81

COMPLEX	SOURCE	REF
5'-DEOXYADENOSYLCOBALAMIN LACTONE	P.SHERMANII, NC(Co)	581
5'-DEOXYADENOSYLCOBALAMIN-MONO-CO.OH	P.SHERMANII (MINOR PROD, FAVOURED IN YOUNG CULTURES)	544
5'-DEOXYADENOSYLCOBALAMIN-MONO-CO.OH	P.PETERSONII (MINOR PROD, FAVOURED IN YOUNG CULTURES)	544
5'-DEOXYADENOSYLCOBALAMIN-MONO-CO.OH	P.FREUDENREICHII (MINOR PROD, FAVOURED IN YOUNG CULTURES)	544
5'-DEOXYADENOSYLCOBALAMIN-b-CO.OH	P.SHERMANII, AQ(Co) OR NC(Co)	526,578,582
5'-DEOXYADENOSYLCOBALAMIN-b-CO.NHEt	P.SHERMANII, NC(Co) OR AQ(Co)	582
5'-DEOXYADENOSYLCOBALAMIN-b-CO.NEt2	P.SHERMANII, NC(Co) OR AQ(Co)	582
5'-DEOXYADENOSYLCOBALAMIN-b-CO.NHPh	P.SHERMANII, NC(Co) OR AQ(Co)	582
5'-DEOXYADENOSYLCOBALAMIN-c-CO.OH	P.SHERMANII, 5'-DEOXYADENOSYL-COBALAMIN LACTONE	581
5'-DEOXYADENOSYLCOBALAMIN-c-CO.OH	P.SHERMANII, NC(Co) OR AQ(Co) (LOW YIELD)	582
5'-DEOXYADENOSYLCOBALAMIN-c-CO.NHEt	P.SHERMANII, NC(Co) OR AQ(Co) (LOW YIELD)	582
5'-DEOXYADENOSYLCOBALAMIN-c-CO.NHEt2	P.SHERMANII, NC(Co) OR AQ(Co) (LOW YIELD)	582
5'-DEOXYADENOSYLCOBALAMIN-c-CO.NHPh	P.SHERMANII, NC(Co) OR AQ(Co) (LOW YIELD)	582
5'-DEOXYADENOSYLCOBALAMIN-d-CO.OH	P.SHERMANII, AQ(Co) OR NC(Co) (LOW YIELD)	526,578,582
5'-DEOXYADENOSYLCOBALAMIN-d-CO.NHEt	P.SHERMANII, NC(Co) OR AQ(Co) (LOW YIELD)	582
5'-DEOXYADENOSYLCOBALAMIN-d-CO.NEt2	P.SHERMANII, NC(Co) OR AQ(Co) (LOW YIELD)	582
5'-DEOXYADENOSYLCOBALAMIN-d-CO.NHPh	P.SHERMANII, NC(Co) OR AQ(Co)	582
5'-DEOXYADENOSYLCOBALAMIN-e-CO.OH	P.SHERMANII, AQ(Co) OR NC(Co)	526,578,582
5'-DEOXYADENOSYLCOBALAMIN-e-CO.NHEt	P.SHERMANII, NC(Co) OR AQ(Co)	582
5'-DEOXYADENOSYLCOBALAMIN-e-CO.NEt2	P.SHERMANII, NC(Co) OR AQ(Co)	582
5'-DEOXYADENOSYLCOBALAMIN-e-CO.NHPh	P.SHERMANII, NC(Co) OR AQ(Co)	582
[5'-T]-5'-DEOXYADENOSYLCOBALAMIN-e-CO.NHPh	LACTOBACILLUS LEICHMANNII ENZYME, UNTRITIATED ANALOGUE, TOH, DITHIOL, NUCLEOTIDE	440

COMPLEX	SOURCE	REF
5'-DEOXYADENOSYLCOBALAMIN-b(OR d),e-DI-CO.OH	P.SHERMANII, AQ(Co) OR NC(Co)	526
5'-DEOXYADENOSYLCOBALAMIN-b,d-DI-CO.OH	P.SHERMANII, NC(Co) OR AQ(Co)	578
5'-DEOXYADENOSYLCOBALAMIN-d,e-DI-CO.OH	P.SHERMANII, NC(Co) OR AQ(Co) (LOW YIELD)	578
5'-DEOXYADENOSYLCOBALAMIN-b,d,e-TRI-CO.OH	P.SHERMANII, AQ(Co) OR NC(Co) (LOW YIELD)	526,578
5'-DEOXYADENOSYLCOBINAMIDE-MONO-CO.OH	P.SHERMANII (MINOR PROD, FAVOURED IN YOUNG CULTURES)	544
5'-DEOXYADENOSYLCOBINAMIDE-MONO-CO.OH	P.PETERSONII (MINOR PROD, FAVOURED IN YOUNG CULTURES)	544
5'-DEOXYADENOSYLCOBINAMIDE-MONO-CO.OH	P.FREUDENREICHII (MINOR PROD, FAVOURED IN YOUNG CULTURES)	544
5'-DEOXYADENOSYLCOBINAMIDE-MONO-CO.OH	P.ARABINOSUM (MINOR PROD, FAVOURED IN YOUNG CULTURES)	544
5'-DEOXYADENOSYLCOBINAMIDE-b-CO.OH	P.SHERMANII, NC(Co) OR AQ(Co)	578,582
5'-DEOXYADENOSYLCOBINAMIDE-b-CO.NHEt	P.SHERMANII, NC(Co) OR AQ(Co)	582
5'-DEOXYADENOSYLCOBINAMIDE-b-CO.NHPh	P.SHERMANII, NC(Co) OR AQ(Co)	582
5'-DEOXYADENOSYLCOBINAMIDE-c-CO.OH	P.SHERMANII, NC(Co) OR AQ(Co) (LOW YIELD)	582
5'-DEOXYADENOSYLCOBINAMIDE-c-CO.NHEt	P.SHERMANII, NC(Co) OR AQ(Co) (LOW YIELD)	582
5'-DEOXYADENOSYLCOBINAMIDE-c-CO.NEt2	P.SHERMANII, NC(Co) OR AQ(Co) (LOW YIELD)	582
5'-DEOXYADENOSYLCOBINAMIDE-c-CO.NHPh	P.SHERMANII, NC(Co) OR AQ(Co) (LOW YIELD)	582
5'-DEOXYADENOSYLCOBINAMIDE-d-CO.OH	P.SHERMANII, NC(Co) OR AQ(Co)	578,582
5'-DEOXYADENOSYLCOBINAMIDE-d-CO.NHEt	P.SHERMANII, NC(Co) OR AQ(Co)	582
5'-DEOXYADENOSYLCOBINAMIDE-d-CO.NEt2	P.SHERMANII, NC(Co) OR AQ(Co) (LOW YIELD)	582
5'-DEOXYADENOSYLCOBINAMIDE-d-CO.NHPh	P.SHERMANII, NC(Co) OR AQ(Co)	582
5'-DEOXYADENOSYLCOBINAMIDE-e-CO.OH	P.SHERMANII, NC(Co) OR AQ(Co)	578,582
5'-DEOXYADENOSYLCOBINAMIDE-e-CO.NHEt	P.SHERMANII, NC(Co) OR AQ(Co)	582
5'-DEOXYADENOSYLCOBINAMIDE-e-CO.NEt2	P.SHERMANII, NC(Co) OR AQ(Co)	582
5'-DEOXYADENOSYLCOBINAMIDE-e-CO.NHPh	P.SHERMANII, NC(Co) OR AQ(Co)	582

COMPLEX	SOURCE	REF
5'-DEOXYADENOSYLCOBINAMIDE-b,d-DI-CO.OH	P.SHERMANII, NC(Co) OR AQ(Co)	578
5'-DEOXYADENOSYLCOBINAMIDE-b,e-DI-CO.OH	P.SHERMANII, NC(Co) OR AQ(Co)	578
5'-DEOXYADENOSYLCOBINAMIDE-d,e-DI-CO.OH	P.SHERMANII, NC(Co) OR AQ(Co)	578
5'-DEOXYADENOSYLCOBINAMIDE-b,d,e-TRI-CO.OH	P.SHERMANII, NC(Co) OR AQ(Co)	578
5'-DEOXYADENOSYLCOBINAMIDE-b,d,e,g-TETRA-CO.OH	P.SHERMANII, NC(Co) OR AQ(Co)	578
5'-DEOXYADENOSYLCOBINAMIDE - Y=NH.CMe2CH2OH	P.SHERMANII, NC(Co) CN	513
5'-DEOXYADENOSYLCOBINAMIDE - Y=NH.CH2.CO.Me	P.SHERMANII, NC(Co) CN	513
5'-DEOXYADENOSYLCOBINAMIDE PHOSPHATE	P.SHERMANII (MINOR PROD, FAVOURED IN YOUNG CULTURES)	544
5'-DEOXYADENOSYLCOBINAMIDE PHOSPHATE	P.SHERMANII, NC(Co)	558
5'-DEOXYADENOSYLCOBINAMIDE PHOSPHATE	P.PETERSONII (MINOR PROD, FAVOURED IN YOUNG CULTURES)	544
5'-DEOXYADENOSYLCOBINAMIDE PHOSPHATE	P.FREUDENREICHII (MINOR PROD, FAVOURED IN YOUNG CULTURES)	544
5'-DEOXYADENOSYLCOBINAMIDE PHOSPHATE	P.ARABINOSUM (MINOR PROD, FAVOURED IN YOUNG CULTURES)	541,544
5'-DEOXYADENOSYLCOBINAMIDE PHOSPHATE	C.THERMOACETICUM (4.5%)	494,364
5'-DEOXYADENOSYLCOBINAMIDE PHOSPHATE	POTATO PYROPHOSPHATE, 5'-DEOXYADENOSYLCOBINAMIDE GUANOSINE DIPHOSPHATE	558
5'-DEOXYADENOSYLCOBINAMIDE GUANOSINE DIPHOSPHATE	P.SHERMANII, NC(Co)	542
5'-DEOXYADENOSYLCOBINAMIDE GUANOSINE DIPHOSPHATE	C.THERMOACETICUM (1.5%)	364,559
2',3'-O-ISOPROPYLIDENE-5'-DEOXYADENOSYLCOBINAMIDE GUANOSINE-[8-^{14}C] DIPHOSPHATE	P.SHERMANII, 2',3'-O-ISOPROPYLIDENE-5'--DEOXYADENOSYLCOBINAMIDE PHOSPHATE, GTP-[8-^{14}C]	558
2',3'-O-ISOPROPYLIDENE-5'-DEOXYADENOSYLCOBINAMIDE GUANOSINE DIPHOSPHATE-[^{32}P]	P.SHERMANII, 2',3'-O-ISOPROPYLIDENE-5'--DEOXYADENOSYLCOBINAMIDE PHOSPHATE-[^{32}P], GTP	558
5'-DEOXYADENOSYLCOBYRINIC ACID MONOAMIDE	P.SHERMANII, NC(Co) OR AQ(Co) (LOW YIELD)	578
5'-DEOXYADENOSYLCOBYRINIC ACID DIAMIDE	C.THERMOACETICUM (1%)	494,364
5'-DEOXYADENOSYLCOBYRINIC ACID DIAMIDE	M.KUZNECOVII (MINOR PROD)	485

COMPLEX	SOURCE	REF
5'-DEOXYADENOSYLCOBYRINIC ACID DIAMIDE	P.SHERMANII, LEVULINIC ACID (ANAEROBIC) (MAJOR PROD)	525
5'-DEOXYADENOSYLCOBYRINIC ACID-a,c-DIAMIDE	P.SHERMANII, NC(Co) OR AQ(Co)	578
5'-DEOXYADENOSYLCOBYRINIC ACID-c,g-DIAMIDE	P.SHERMANII, NC(Co) OR AQ(Co) (LOW YIELD)	578
[^{14}C]-METHYLCOBYRINIC ACID TRIAMIDE	C.THERMOACETICUM, [^{14}C]-HCO3 (TRACE)	364,559
5'-DEOXYADENOSYLCOBYRINIC ACID TRIAMIDE	C.THERMOACETICUM (3%)	494,364
5'-DEOXYADENOSYLCOBYRINIC ACID TRIAMIDE	M.KUZNECEOVII (MINOR PROD)	485
5'-DEOXYADENOSYLCOBYRINIC ACID TRIAMIDE	P.SHERMANII, LEVULINIC ACID (ANAEROBIC) (MAJOR PROD)	525
5'-DEOXYADENOSYLCOBYRINIC ACID-a,c,g-TRIAMIDE	P.SHERMANII, NC(Co) OR AQ(Co)	578
[^{14}C]-METHYLCOBYRINIC ACID TETRAMIDE	C.THERMOACETICUM, [^{14}C]-HCO3 (TRACE)	364,559
5'-DEOXYADENOSYLCOBYRINIC ACID TETRAMIDE	C.THERMOACETICUM (5%)	494,364
5'-DEOXYADENOSYLCOBYRINIC ACID TETRAMIDE	M.KUZNECEOVII (MINOR PROD)	485
5'-DEOXYADENOSYLCOBYRINIC ACID TETRAMIDE	P.SHERMANII, LEVULINIC ACID (ANAEROBIC) (MINOR PROD)	525
5'-DEOXYADENOSYLCOBYRINIC ACID-a,c,e,g-TETRAMIDE	P.SHERMANII, NC(Co) OR AQ(Co)	578
5'-DEOXYADENOSYLCOBYRINIC ACID-a,c,d,g-TETRAMIDE	P.SHERMANII, NC(Co) OR AQ(Co)	578
5'-DEOXYADENOSYLCOBYRINIC ACID-a,b,c,g-TETRAMIDE	P.SHERMANII, NC(Co) OR AQ(Co)	578
[^{14}C]-METHYLCOBYRINIC ACID PENTAMIDE	C.THERMOACETICUM, [^{14}C]-HCO3 (TRACE)	364,559
5'-DEOXYADENOSYLCOBYRINIC ACID PENTAMIDE	C.THERMOACETICUM (10%)	494,364
5'-DEOXYADENOSYLCOBYRINIC ACID PENTAMIDE	M.KUZNECEOVII (MINOR PROD)	485
5'-DEOXYADENOSYLCOBYRINIC ACID PENTAMIDE	P.SHERMANII, LEVULINIC ACID (ANAEROBIC) (MINOR PROD)	525
5'-DEOXYADENOSYLCOBYRINIC ACID-a,c,d,e,g-PENTAMIDE	P.SHERMANII, NC(Co) OR AQ(Co)	578
5'-DEOXYADENOSYLCOBYRINIC ACID-a,b,c,e,g-PENTAMIDE	P.SHERMANII, NC(Co) OR AQ(Co)	578
5'-DEOXYADENOSYLCOBYRINIC ACID-a,b,c,d,g-PENTAMIDE	P.SHERMANII, NC(Co) OR AQ(Co)	578

R	B¹	B²	REAGENT	METHOD	NOTES	REF
METHYL	IODO(-)	TRI(Ph)P	MeMgI	IA; (C5H5)Co(PPh3)I2 BENZENE/ETHER	A	462,8
METHYL	IODO(-)	DI(Ph)PMe	MeMgI	IA; (C5H5)Co(MePPh2)I2 BPNZENE/ETHER	A	8
METHYL	METHYL(-)	TRI(Ph)P	MeMgI	IA; (C5H5)Co(PPh3)I2 BENZENE/ETHER	A	462,8
METHYL	METHYL(-)	TRI(Ph)P	MeMgBr	IA; (C5H5)Co(PPh3)I2 ETHER	A	465
METHYL	METHYL(-)	DI(Ph)PMe	MeMgI	IA; (C5H5)Co(MePPh2)I2 BENZENE/ETHER	A	8
METHYL	METHYL(-)	TRI(Ph)As	MeMgI	IA; (C5H5)Co(AsPh3)I2 BENZENE/ETHER	A	8
METHYL	BENZYL(-)	TRI(Ph)P	BENZYLMgCl	IA; MeCo(C5H5)(PPh3)I BENZENE/ETHER	A	462,8
BENZYL	BENZYL(-)	TRI(Ph)P	BENZYLMgCl	IA; (C5H5)Co(PPh3)I2 BENZENE/ETHER	A	462,8
METHYL-TRI(P)	IODO(-)	CO	RI	IIIA; (C5H5)Co(CO)2 PhH 45°	A	9,461
ETHYL-PER(P)	IODO(-)	CO	RI	IIIA; (C5H5)Co(CO)2 PhH 45°	A	9,461
ETHYL-PER(P)	IODO(-)	TRI(Ph)P	RCo(C5H5)(CO)I	TRI(Ph)P BENZENE	A	557
ETHYL-PER(P)	PY	PY	RCo(C5H5)(CO)(PPh3)(+) ClO4(-)	PYRIDINE	A ClO4 SALT	557
ETHYL-PER(F)	PY	PY	RCo(C5H5)bis(PPh3)(+) ClO4(-)	PYRIDINE	ClO4 SALT	557
ETHYL-PER(F)	TRI(Ph)P	MeCN	RCo(C5H5)(CO)(PPh3)(+) ClO4(-)	MeCN	A ClO4 SALT	557
ETHYL-PER(F)	CO	CO	RCo(C5H5)(CO)I	CO AgClO4 BENZENE	ClO4 SALT	557
ETHYL-PER(F)	CO	TRI(Ph)P	RCo(C5H5)(CO)I	TRI(Ph)P AgClO4 BENZENE	ClO4 SALT	557
ETHYL-PER(F)	CO	TRI(Ph)P	RCo(C5H5)(CO)I	CO AgClO4 BENZENE	ClO4 SALT	557
ETHYL-PER(F)	CO	TRI(Ph)P	RCo(C5H5)bis(CO)(+) ClO4(-)	TRI(Ph)P ACETONE	ClO4 SALT	557
ETHYL-PER(F)	CO	TRI(Ph)P		EXCHANGE OF ClO4 SALT	A PF6 SALT	557

$RCo(h^5-C5H5)B^1B^2(+)$

R	B^1	B^2	REAGENT	METHOD	NOTES	REF
ETHYL-PER(F)	TRI(Ph)P	TRI(Ph)P	RCo(C5H5)(PPh3)I	TRI(Ph)P AgClO4 BENZENE	A ClO4 SALT	557
ETHYL-PER(F)	PROP-1-ENYL--1-Me-PER(F)(-)	CO	RCo(C5H5)(CO)I	B^1Ag DICHLOROMETHANE	A	562
PROPYL-PER(F)	IODO(-)	CO	RI	IIIA; (C5H5)Co(CO)2 PhH 45°	A	460,9,461
PROPYL-PER(F)	IODO(-)	TRI(Ph)P	RI	IIIA; (C5H5)Co(PPh3)(CO) BENZENE 80°	A	465
PROPYL-PER(F)	PY	PY	RCo(C5H5)(CO)I	PY AgClO4 BENZENE	ClO4 SALT	557
PROPYL-PER(F)	PY	PY	RCo(C5H5)(CO)(PPh3)(+) ClO4(-)	PYRIDINE	ClO4 SALT	557
PROPYL-PER(F)	PY	PY		EXCHANGE OF ClO4 SALT	A PF6 SALT	557
PROPYL-PER(F)	----BIPY-----		RCo(C5H5)(CO)I	BIPY AgClO4 BENZENE	ClO4 SALT	557
PROPYL-PER(F)	----BIPY-----			EXCHANGE OF ClO4 SALT	A PF6 SALT	557
PROPYL-PER(F)	MeCN	MeCN	RCo(C5H5)(CO)I	MeCN AgClO4 BENZENE	A ClO4 SALT	557
PROPYL-PER(F)	CO	CO	RCo(C5H5)(CO)I	CO AgClO4 BENZENE	ClO4 SALT	557
PROPYL-PER(F)	CO	TRI(Ph)P	RCo(C5H5)(CO)I	TRI(Ph)P AgClO4 BENZENE	A ClO4 SALT	557
PROPYL-PER(F)	PROP-1-ENYL--1-Me-PER(F)(-)	CO	RCo(C5H5)(CO)I	B^1Ag DICHLOROMETHANE	A	562
-1,4-BUTANE-PERFLUORO-(-)		CO	PERFLUOROETHYLENE	IIIB?; (C5H5)Co(CO)2 CYCLOHEXANE 160°	A	459
-CPh=CPh-(-) (APPEARS INTERMED BETWEEN THIS & A Co(I) pi-COMPLEX)		TRI(Ph)P	DIPHENYLACETYLENE	IIIB?; (C5H5)Co(PPh3)I2 + i-PrMgBr THF/ETHER	A	463,8
-CPh=CPh-(-) (APPEARS INTERMED BETWEEN THIS & A Co(I) pi-COMPLEX)		TRI(Ph)P	DIPHENYLACETYLENE	IIIB?; (C5H5)Co(PPh3)I2 + PhMgHal THF/ETHER		8
-CPh=CPh-CPh=CPh-(-)		TRI(Ph)P	DI(Ph)ACETYLENE(EXCESS)	IIIB?; (C5H5)Co(PPh3)I2 + i-PrMgBr THF/ETHER	A	463,8
-CPh=CPh-CPh=CPh-(-)		TRI(Ph)P	DIPHENYLACETYLENE	(PhCCPh)Co(C5H5)(PPh3) BENZENE 80°		463,8
-CPh=CPh-CPh=CPh-(-)		TRI(Ph)P	DIPHENYLACETYLENE	(C5H5)(PPh3)Co(Me)2 PhH 80°		463,8
-CPh=CPh-CPh=CPh-(-)		TRI(Ph)P	DIPHENYLACETYLENE	(C5H5)(PPh3)Co(BENZYL)2 BENZENE 80°		8

$RCo(h^5\text{-}C5H5)B^1B^2(+)$

R	B^1	B^2	REAGENT	METHOD	NOTES	REF
-CPh=CPh-CPh=CPh- (-)		TRI(Ph) P	DI(Ph) ACETYLENE(EXCESS)	IIIB?; (C5H5)Co(PPh3)2 BENZENE 60°		464
-CPh=CPh-CPh=CPh- (-)		TRI(Ph) P	DI(Ph) ACETYLENE(EXCESS)	IIIB?; (C5H5)Co(PPh3)I2 + PhMgHal THF/ETHER		8
-CH=CPh-CPh=CPh- (-)?		TRI(Ph) P	PHENYLACETYLENE	(PhCCPh)Co(C5H5)(PPh3) BENZENE 60°	A	8
-CPh=CPh-C(CO.OMe)=C(CO.OMe)- (-)?		TRI(Ph) P	DIMETHOXYCARBONYL-ACETYLENE	(PhCCPh)Co(C5H5)(PPh3) BENZENE 60°	A	8
C(=S)---------S(-)		TRI(Ph) P	CS2	IIIA?; (C5H5)Co(PPh3)2 PhH	A	464

CIS-R^1R^2Co3IS(BIDENTATE B)

R^1	R^2	B	REAGENT	METHOD	NOTES	REF
METHYL	METHYL	BIPY	MeI	IIIA; BH4 MeOH	A ClO4 SALT	7
ETHYL	ETHYL	BIPY	EtHal	IIIA; BH4 MeOH	A ClO4 SALT	7
BENZYL	BENZYL	BIPY	BENZYL CHLORIDE	IIIA; BH4 MeOH	A I SALT	7
BENZYL	BENZYL	BIPY	BENZYL CHLORIDE	IIIA; BH4 MeOH	A ClO4 SALT	7
BENZYL	BENZYL	BIPY	BENZYL CHLORIDE	IIIA; BH4 MeOH	A PF6 SALT	7
BENZYL	BENZYL	PHEN	BENZYL CHLORIDE	IIIA; BH4 MeOH	A I SALT	7
METHYL--TRI(Me)Si	METHYL--TRI(Me)Si	BIPY	TRIMETHYLSILYLMETHYL IODIDE	IIIA; BH4 MeOH	A ClO4 SALT	466

OTHER COMPLEXES

COMPLEX	REAGENT	METHOD	NOTES	REF
Mobis(TRI(Et)P)Co(PHEN)I(+) PF6(-)	RI	bis(TRI(Et)P)bis(H)Co(PHEN)(+) MeOH	A	561
Etbis(TRI(Bu)P)Co(BIPY)I(+) PF6(-)	RI	bis(TRI(Bu)P)bis(H)Co(BIPY)(+) MeOH	A	561
CIS-DIETHYLCo(H)([P(Ph)2-CH2]3CCH2PPh2)	DI(Et)A10Et	IA;TRIS(acac)Co C(CH2PPh2)4 BENZENE (VERY AIR SENS.)	A	467
TRIETHYNYLCo.6NH3	ETHYNYL ALKALI METAL	IA; Co(NH3)6(3+) 3NO3(-)	UNSTABLE	3
TRI(Me-ETHYNYL)Co.6NH3	Me-ETHYNYL ALKALI METAL	IA; Co(NH3)6(3+) 3NO3(-)	UNSTABLE	3
TRI(Ph-ETHYNYL)Co.6NH3	Ph-ETHYNYL ALKALI METAL	IA; Co(NH3)6(3+) 3NO3(-)	UNSTABLE	3
HEXAETHYNYLCo(3-) 3K(+)	Co(II) ANALOGUE 4K(+)	OXIDATION BY O2 LIQ.NH3	A	3
HEXA(Me-ETHYNYL)Co(3-) 3Na(+)	Co(II) ANALOGUE 4Na(+)	OXIDATION BY O2 LIQ.NH3	A	3
CIS-TRIS(2-Me2NCH2-Ph)Co	RLi	CoCl2 ETHER/HEXANE	(A)	593
CIS-TRIS(5-tBu-2-Me2NCH2-Ph)Co	RLi	CoCl2 ETHER/HEXANE	A	593
BIS[(B10C2H10)2]Co(-) NEt4(+)	Co(II) ANALOGUE	OXIDATION WITH Cu(II)	A (X-RAY)	535 (572)