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Cobalt carbonyls : A versatile reagent and catalyst in organic synthesis

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Abstract

Cobalt carbonyls are versatile reagents for the insertion of carbon monoxide between carbon–cobalt bond. This methodology has been utilized for the synthesis of some naturally occurring compounds. In this review, cobalt carbonyl-mediated novel reactions (2+2+1 and 2+2+2 cycloaddition reactions, Nicholas reaction, carbonylation reactions, etc) have been discussed. Mechanisms of these reactions have also been presented.

Key words : Dicobalt octacarbonyl, cycloaddition, propargylic cobalt complex, carbonylation.

Introduction

One of the outstanding features in the growth of contemporary organic chemistry has been the emergence of transition metal-mediated organic reactions at the frontiers of organic synthesis. Its instant acceptance by synthetic chemists is primarily due to the fact that transition metal-mediated organic transformations are extremely versatile and experimentally convenient. Recent development in the catalysis of organic reaction by transition metals has paved the way for achieving a remarkable level of chemo- and stereoselectivity, and for certain reactions this achievement has reached an extent where near enzyme-like selectivity has been witnessed. This development has clearly expanded the arsenal of synthetic chemist which has eventually facilitated the intensity of assault on some of the most challenging problems of synthesis.

Transition metal carbonyls[1-2], particularly from Fe, Co, Rh, Ni, Pd, play an important role in industrial chemistry[3], since they allow for high selectivity and economic efficiency in such processes as hydrogenation, hydroformylation[4], oxidation[5], epoxidation[6], etc. In addition to this, metal carbonyls[7–12] derived from Mo, Cr, W have also been successfully applied to a wide range of unique organic transformations. The introduction of one carbon in organic substrates under the aegis of metal carbonyls constitutes a very important transformation in contemporary organic synthesis[13]. Among the various transition metal carbonyls, the carbonyls derived from Co have made outstanding contribution towards achieving a wide range of organic transformations, like hydroformylation, carbonylation, oxysilylation,

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cycloaddition reaction of alkynes, Nicholas reaction, etc. Impressive advances have been made in the domain of cobalt carbonyl-mediated organic synthesis over the last one decade as clearly evident from the remarkable level of efficiency and selectivity achieved during the synthesis of complex natural products.

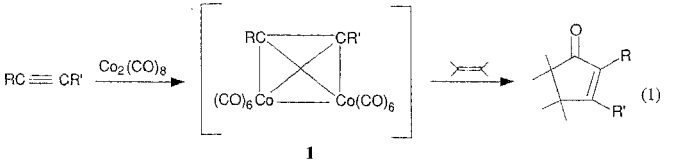
In view of the importance of these reactions this review covers literature on cobalt carbonyl-catalysed or mediated reactions in organic synthesis. The review has been divided into the following sections.

1. Cycloaddition reactions
   1.1 [2+2+1] Cycloaddition reactions
   1.2 [2+2+2] Cycloaddition reactions
2. Nicholas reaction
3. Carbonylation reaction
4. Miscellaneous reactions

1. Cycloaddition reactions

1.1. [2+2+1] Cycloaddition reactions

[2+2+1] Cycloaddition reactions (Pauson–Khand reaction) is a novel and useful method for the synthesis of cyclopentenone derivatives. This reaction, first reported by Pauson and Khand[14] in 1973, involves the cocyclization of alkynes with alkene and carbon monoxide under the aegis of dicobaltoctacarbonyl. This transformation is a [2+2+1] cycloaddition which involves thermally stable hexacarbonyldicobalt complex **1**[15], obtained by co-ordination of $Co_2(CO)_8$ with alkynes in hydrocarbon solvents of ether. Subsequent reaction of complex **1** with alkene followed by insertion of carbon monoxide leads to the formation of cyclopentenone (eqn 1).



(1)

1

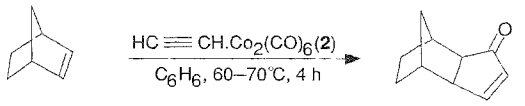
This reaction is compatible with a wide range of functionalities like ether, alcohols, tertamines, thioethers, ketones, ketals, esters, *tert*-amides[16] and aromatic rings including benzene, furan and thiophene[17].

This reaction can be divided into two categories: (a) Intermolecular reaction, and (b) Intramolecular reaction.

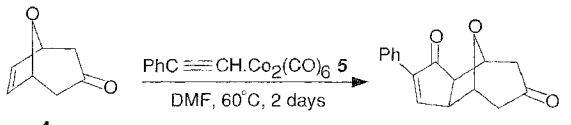
1.1.1. Intermolecular [2+2+1] cycloaddition reactions

Intermolecular reaction of strained alkenes[18] with acetylene and $Co_2(CO)_8$ reacts with norbornene and its derivatives to generate cyclopentenone derivatives **3** (eqn 2). Similarly,

unsymmetrical alkynes react with **4** *via* its Co-complex **5** to provide 8-oxabicyclo [3.2.1] oct-6-ene-3-one **6** in quantitative yields (eqn 3).

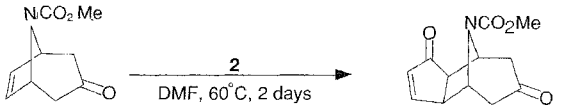


(2)



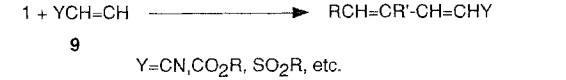
(3)

Nitrogen-bridged bicyclic[19] systems have also been shown to undergo Pauson–Khand cycloaddition. Thus, **7** undergoes addition to acetylenic Co-complex **2** to provide **8** in good yields (eqn 4). High regioselectivity in incorporation of the unsymmetrical alkyne in the product is a characteristic feature of this reaction. In addition, these reactions also occur with high stereoselectivity as exo-adduct is obtained as the predominant product.



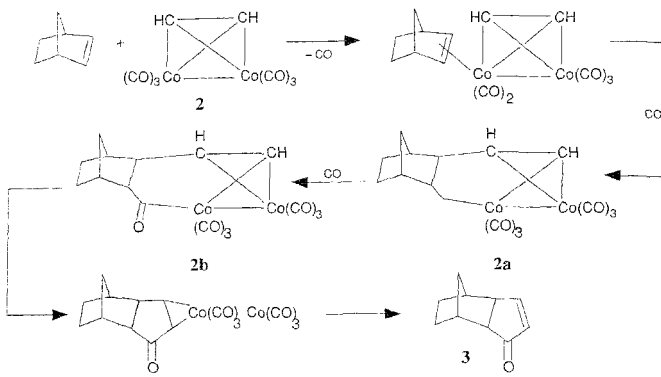
(4)

Simple unstrained alkenes[20] are unreactive under these reaction conditions; however, alkenes containing electron-withdrawing groups **9** react to yield conjugated dienes[21] (eqn 5). Alkenes containing one or more electron-withdrawing groups react with acetylenic cobalt complex[1] to give conjugated diene. However, due to the low yields, this reaction cannot be used as a general synthetic route to conjugated dienes.

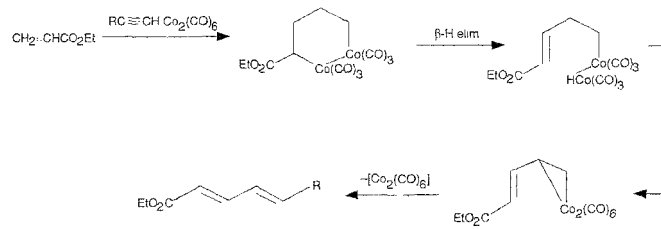


(5)

These reactions are believed to occur *via* the insertion of alkene into the cobalt–acetylene complex[22] to give **2a** which subsequently incorporates the carbon monoxide to afford **2b** which on reductive elimination of cobalt leads to cyclopentenone(Scheme 1). The formation of diene may be occurring *via* a similar pathway involving the hydrogen migration followed by a process of reductive elimination (Scheme 2).

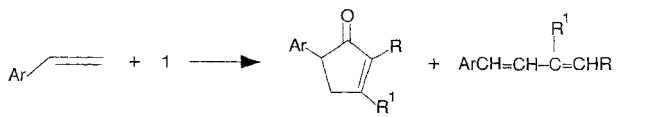


SCHEME 1.



SCHEME 2.

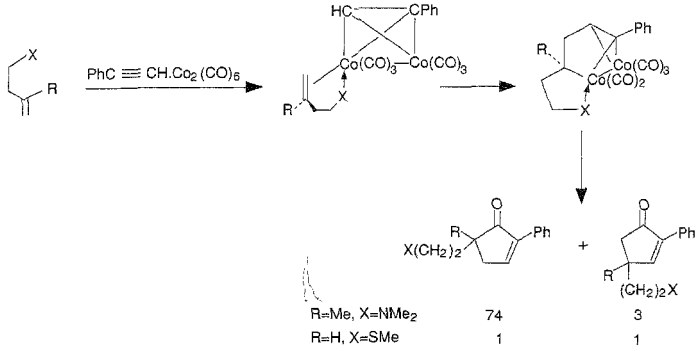
Styrene and substituted styrene[23] represent the borderline cases where both modes of reaction (*i.e.*, cyclopentenone and diene formation) are observed (eqn 6).



(6)

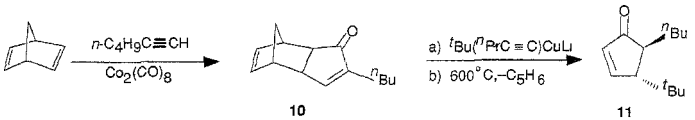
Usually terminal alkenes[24] give poor yields and regioselectivity. Krafft[25] has shown that alkenes containing groups capable of acting as soft ligands at a homoallylic position give both

enhanced yields and regioselectivity. This may be a result of coordination of heteroatom prior to insertion (Scheme 3).



SCHEME 3.

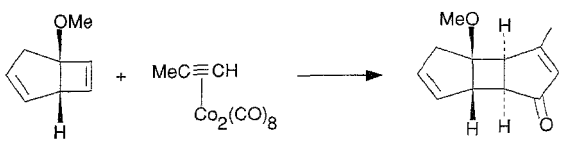
Schore[26] has synthesised 4,5-disubstituted 2-cyclopentenones **11** from the cycloaddition product **10** of norbornadiene using cuprate addition followed by retro Diels–Alder reaction (Scheme 4).



10 **11**

SCHEME 4

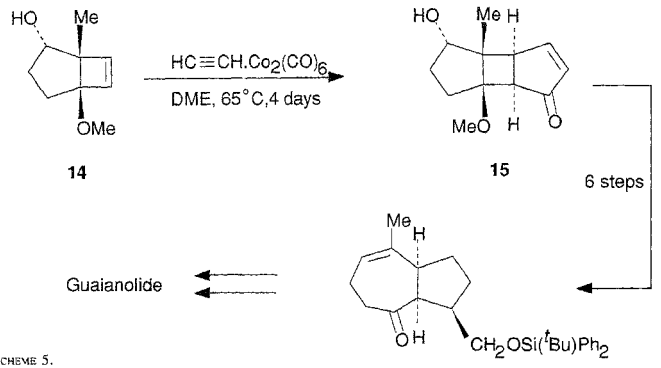
This reaction is regio- and stereoselective[27] as with bicyclic alkene **12**; the less-hindered face of the π-bond preferentially reacts to give exo-ring fusion product **13** exclusively (eqn 7).



12 **13**(60)
only isomer

(7)

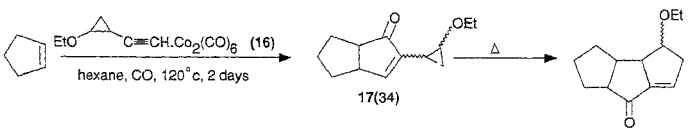
This high selectivity has been exploited by Schore and co-workers during the synthesis of guaianolide and pseudoguaianolide[28]. The stereochemistry of the ring fusion as present in the key intermediate **15** is remarkably achieved in the first step using the Pauson–Khand reaction on alkene **14** (Scheme 5).



14 **15**

SCHEME 5.

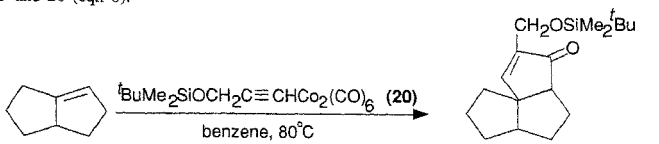
Interestingly, cyclopropane ring[29] is tolerated in the acetylenic partner during the cycloaddition on cyclic alkenes to give **17**. This methodology has been used during the synthesis of linearly fused triquinanes **18** from cyclopropyl acetylene **16** and cyclopentene (Scheme 6).



17(34) **18(39)**

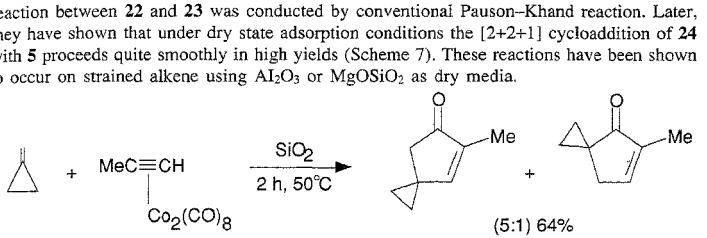
SCHEME 6.

Serratosa and co-workers[30] have synthesised angularly fused triquinanes **21** starting from **19** and **20** (eqn 8).



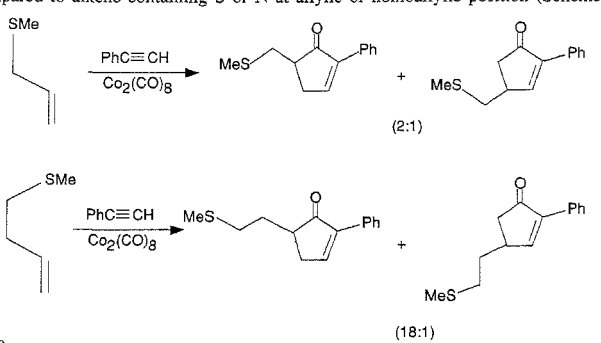
19 **21** (8)

Smit–Caple and co-workers[31] have shown that intramolecular Khand reaction could be carried out with an increased efficiency in a solvent-free system with the substrate adsorbed on the surface of chromatography adsorbent (dry state adsorption conditions). Intermolecular reaction between **22** and **23** was conducted by conventional Pauson–Khand reaction. Later, they have shown that under dry state adsorption conditions the [2+2+1] cycloaddition of **24** with **5** proceeds quite smoothly in high yields (Scheme 7). These reactions have been shown to occur on strained alkene using Al_2O_3 or $MgOSiO_2$ as dry media.



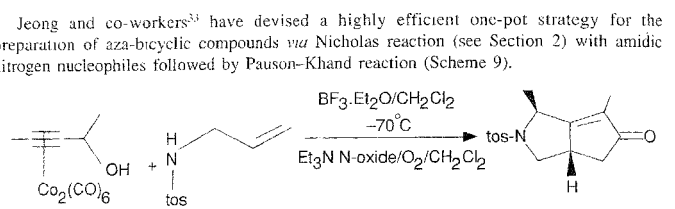
SCHEME 7.

Recently, Krafft and co-workers[32] have shown that the regioselectivity of co-cyclization is directed by the use of soft atom like sulfur or nitrogen. They observed that alkene containing S or N at homoallylic position is more effective in controlling the regioselectivity as compared to alkene containing S or N at allylic or homoallylic position (Scheme 8).



SCHEME 8.

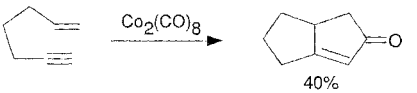
Jeong and co-workers[33] have devised a highly efficient one-pot strategy for the preparation of aza-bicyclic compounds *via* Nicholas reaction (see Section 2) with amidic nitrogen nucleophiles followed by Pauson–Khand reaction (Scheme 9).



SCHEME 9

1.1.2. Intramolecular 2+2+2 cycloaddition reactions

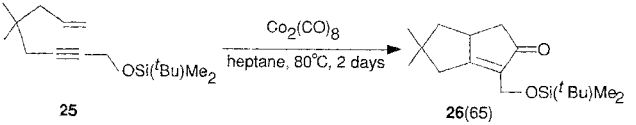
Intramolecular Pauson–Khand reaction was first reported by Schore and Croudace[34] in 1981. This methodology has been used during the synthesis of various natural products. Enynes cyclize, upon complexation to $Co_2(CO)_8$ and subsequent heating, to give bicyclic enones. The most extensively studied is the synthesis of bicyclo [3.3.0] oct-1-ene-3-one from hept-1-ene-6-yne (eqn 9). Hex-1-en-5-yne produces a mixture of products of trimerization of the alkyne functionality.



(9)

The presence of bicyclic [3.3.0] octane ring system in a variety of biologically active natural products has generated considerable interest in the synthesis of its functionalized derivatives. In these cycloadditions, substitution on both the alkyne as well as the chain linking the alkyne and the alkene is often readily tolerated.

Hua and co-workers[35] have prepared the key precursor **26** for the synthesis of optically active pentalene and racemic pentalenolactone E methyl ester from enyne **25** (eqn 10).

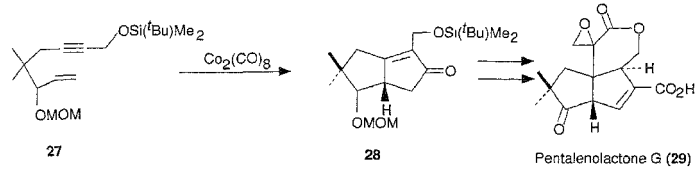


25 **26**(65)

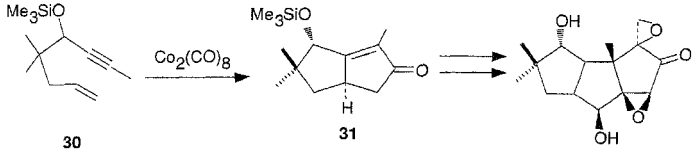
(10)

Later, Seto *et al*[36] have shown that $Co_2(CO)_8$-mediated cyclization of an acyclic-enyne **27** provides bicyclic pentenone **28**, which can be elaborated to antibiotic pentalenolactone G **29** (Scheme 10).

Magnus and co-workers[37] have exploited intramolecular Pauson–Khand reaction to the total synthesis of coriolin **32**, a linearly fused triquinane. The key intermediate **31** was prepared in one step from the readily available enyne **30** (Scheme 11).

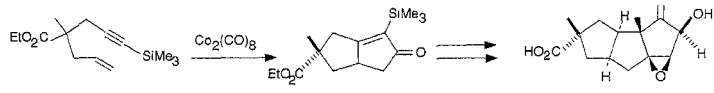


SCHEME 10.



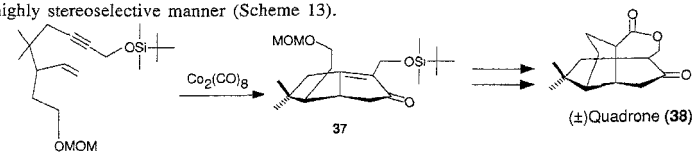
SCHEME 11.

Magnus has systematically examined the factors that contribute to the stereoselectivity shown in intramolecular Pauson–Khand reaction. This methodology has been used for the synthesis of hirsutic acid[38] **35** from enyne **33** *via* bicyclopentenone **34** (Scheme 12).



SCHEME 12.

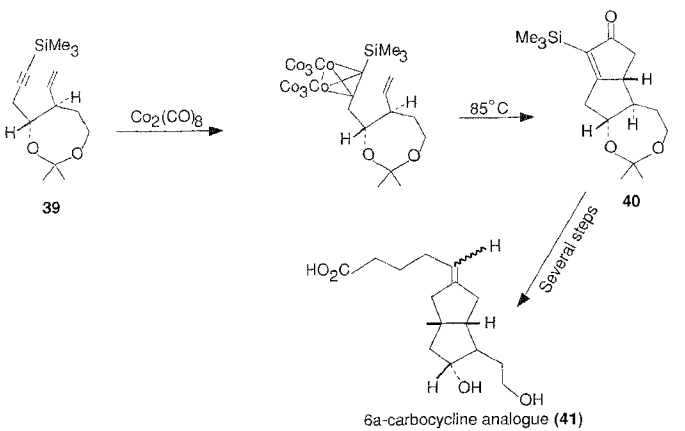
Magnus[39] has developed an elegant approach to the synthesis of quadrone **38** from the key precursor bicyclo [3.3.0] oct-1-ene-3-one **37** prepared in one step from the enyne **36** in a highly stereoselective manner (Scheme 13).



SCHEME 13.

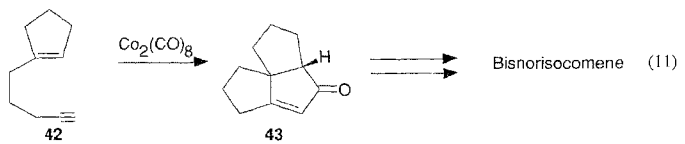
Magnus and co-workers have also achieved a stereoselective synthesis of a carbocycline analogue[40] **41** using the enyne **39** *via* the cyclopentenone **40** (Scheme 14).

The presence of alkene in a ring (*e.g.*, **42**) is compatible with intramolecular cyclization as angularly fused triquinanes like bisnorisocomene[41] can be synthesised from cyclopentenone

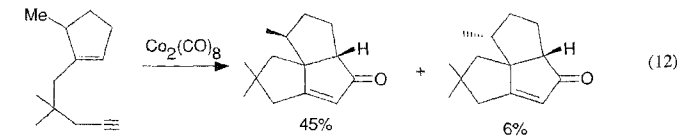


SCHEME 14

43 stereoselectively. This reaction has the limitation as only trisubstituted alkenes and simple terminal alkynes can be used for the cyclopentenone formation (eqn 11).

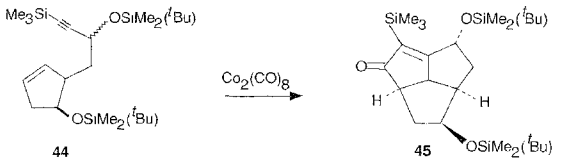


A stereocontrolled approach to pentalenes[42] has been shown by using the above methodology (eqn 12).



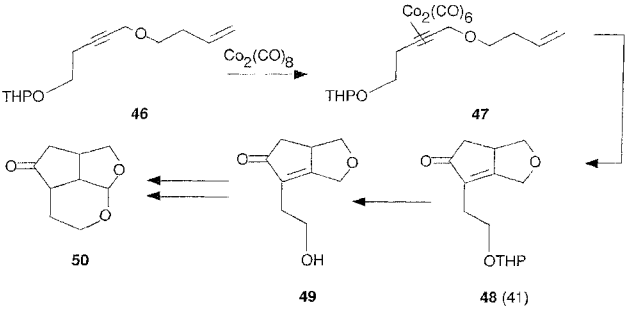
Serratosa and co-workers have developed an exceptionally efficient approach to triquinacenes[43] **45** making use of similar intramolecular cycloadditions of cyclic alkenes **44** containing alkynyl substitution (eqn 13).

Billington and co-workers[44] have cyclized substituted allyl-propargyl ethers **46** to give 3-oxa bicyclo [3.3.0] oct-5-en-7-ones **48** *via* hexacarbonyl dicobalt complexes **47**. Hydrogenation



44 45 (13)

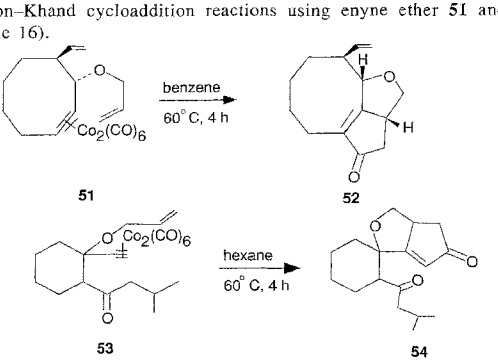
of **48** followed by deprotection afforded the key intermediate[49] for the synthesis of tetrahydro anhydroaucubigenone **50** (Scheme 15).



46 **47** **50** **49** **48** (41)

SCHEME 15.

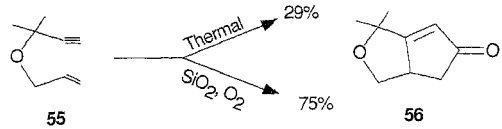
Schreiber[45] and Smit[46] have synthesised polyheterocycles **52** and **54** by combining Nicholas and Pauson–Khand cycloaddition reactions using enyne ether **51** and **53**, respectively (Scheme 16).



51 **52** **53** **54**

SCHEME 16.

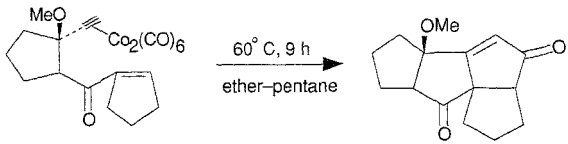
Later, Smit and co-workers[47] have shown unusual effect on the efficiency of Co-mediated conversion of an enyne–ether **55** into the corresponding bicyclo[3.3.0] octenone **56** by adsorption of Co-complexed enyne–ether on to silica gel under O_2 or air (Scheme 17).



55 **56**

SCHEME 17.

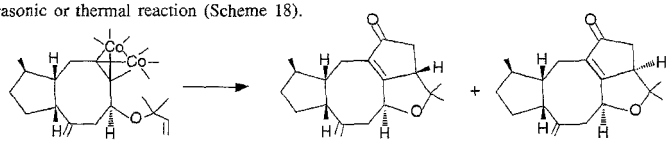
Veretenov and co-workers[48] have developed a simple route for the synthesis of polycyclic inearly and/or angularly fused compounds **58** from **57.** This cycloaddition occurs with participation of double bond, having an electron-withdrawing group (eqn 14).



(14)

57 **58**(73)

Schreiber and co-workers[49] have developed an efficient method which provides a milder and more stereoselective alternative to the corresponding thermal reactions. Tertiary amine oxide (*e.g.*, N-methylmorpholine-N-oxide, NMO) readily promotes intramolecular Pauson–Khand cyclization at room temperature on **59** under an inert atmosphere. Due to the milder condition required, this reaction tolerates various functional groups like alcohols, silyl ether ethers, acetals, remote olefins, etc., and leads to the formation of **60** and **61.** One of the outstanding features of this reaction is the high level of stereoselectivity as compared with ultrasonic or thermal reaction (Scheme 18).

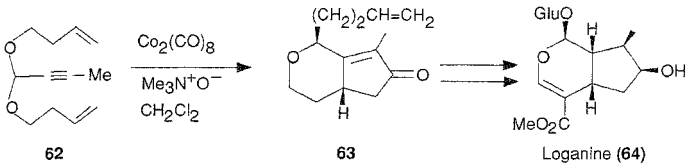


59 **60** **61**

NMO, CH_2Cl_2, r.t. (68) 11:1
CH_3CN, 82° C (75) 4:1
CH_3CN,))), 45° C (45) 3:1

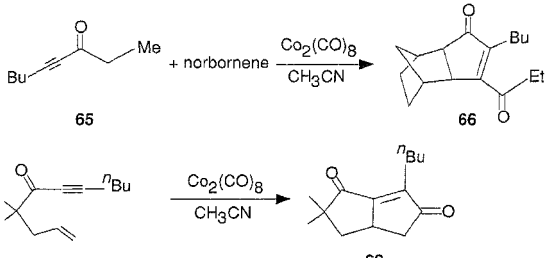
SCHEME 18.

A novel route to the precursor **63** of (±) Loganine **64** has been developed by Jeong and co-workers[50] from homoallyl-propargyl acetal **62** (Scheme 19).



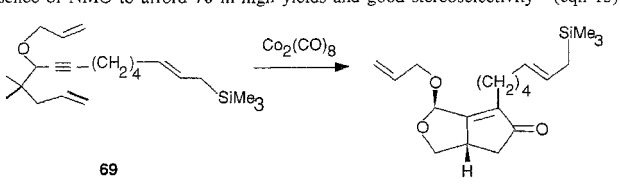
SCHEME 19

Recently, Hoye and Suriano[51] have shown that electron-deficient alkynones can be inter- or intramolecularly cyclized to give bicyclic enediones in good yields. They have observed that there is a remarkable effect on the reactivity by changing the solvent. The effect of solvent is evident from the reaction of **65** in acetonitrile with norbornene which gives **66** by intermolecular addition whereas the enyne **67** on intramolecular cyclization affords **68** in high yields. A similar transformation in methanol was quite sluggish (Scheme 20).



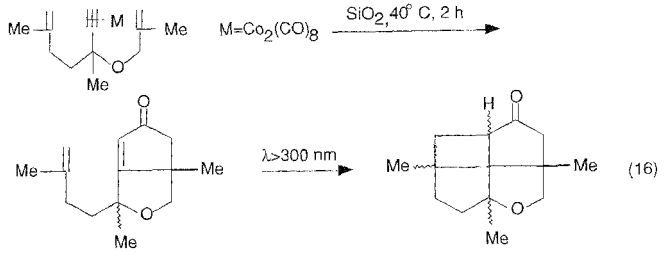
SCHEME 20.

Interestingly, the highly functionalized alkyne **69** undergoes intramolecular cyclization in the presence of NMO to afford **70** in high yields and good stereoselectivity[49] (eqn 15).



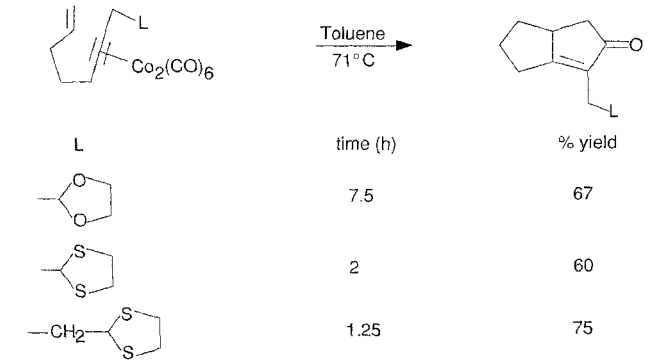
(15)

Smit and co-workers[52] have synthesised several fenestrane derivatives **72** based on intramolecular Pauson–Khand reaction followed by [2+2] photocycloaddition on intermediate **71** (eqn 16).



(16)

Krafft and co-workers[53] have shown the rate of the thermal intramolecular Pauson–Khand cycloaddition can be enhanced by 1,6-enyne-bearing co-ordinating ligands (sulfur or oxygen atom) in the homo and bishomopropargylic position. They have shown that sulfur provides more acceleration than oxygen (Scheme 21).



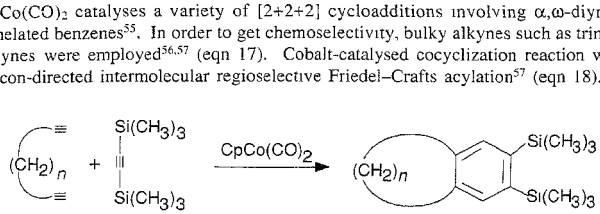
L	time (h)	% yield
	7.5	67
	2	60
	1.25	75

SCHEME 21.

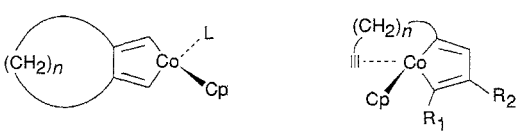
1.2. [2+2+2] Cycloaddition reactions

The discovery of new synthetic methods has already made possible to construct the most complex natural products and the most 'unnatural' assemblies. Despite these advancements

there remains much room for improvement of synthetic strategies to get the chemo-, regio- and stereoselectivity of the compounds. A simple analysis showed that a more powerful strategy would be based upon the [2+2+2] cycloadditions of the unsaturated moieties. $CpCo(CO)_2$ as a catalyst was found to promote the successful execution of [2+2+2] cycloadditions[54]. The many previously unattainable molecules generated in this way have been used as a starting material for the preparation of several unnatural and natural products of theoretical, medicinal and synthetic interest. Two decades earlier, it was found that $CpCo(CO)_2$ catalyses a variety of [2+2+2] cycloadditions involving α,ω-diynes to give annelated benzenes[55]. In order to get chemoselectivity, bulky alkynes such as trimethylsilyl-alkynes were employed[56,57] (eqn 17). Cobalt-catalysed cocyclization reaction was used in silicon-directed intermolecular regioselective Friedel–Crafts acylation[57] (eqn 18).

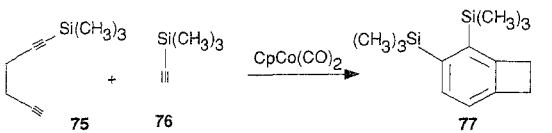


To understand the mechanism of these reactions[58-60] many studies have been carried out which resulted in the isolation of two intermediates **73** and **74.** Cyclobutadiene complexes derived from both **73** and **74** are obtained as byproducts in catalytic reactions employing α,ω-diynes[57] and are responsible for some of the catalyst depletion since they appear to be unsuitable as precursors for any catalytic intermediates[61].



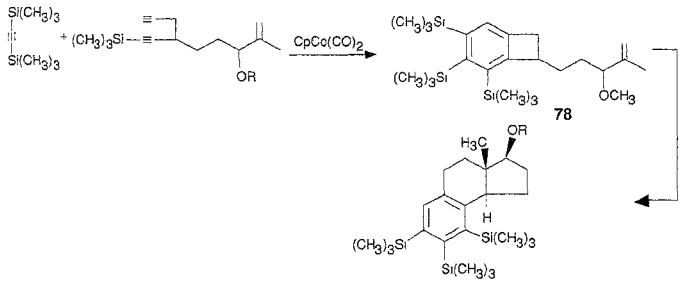
73 **74**

The trimethylsilyl group which is used extensively for controlling the chemo- and regioselectivity has a pronounced tendency to promote α-selectivity in the metallacycle. This effect was synthetically demonstrated in the formation of **77** as the sole isomer on cocyclization of 1-trimethylsily 1-1, 5-hexadiyne **75** and trimethylsilylacetylene[55] **76** (Scheme 22). On the other hand, if more Me_3Si groups are present, *i.e.*, **78** then the reaction proceeds



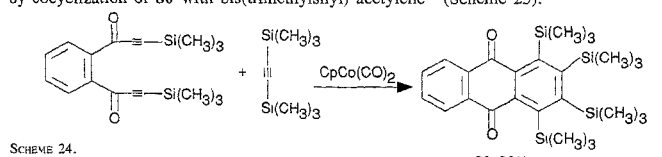
SCHEME 22

via *o*-xylylene formation and intramolecular ring closure to give benzhydrindane nucleus[62] **79** (Scheme 23).

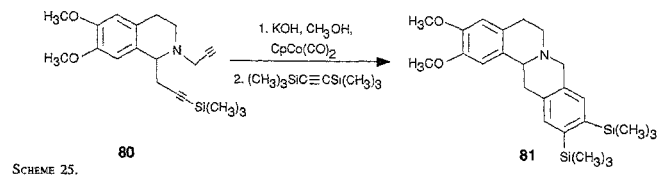


SCHEME 23

The $CpCo(CO)_2$- catalysed [2+2+2] cycloaddition of three alkyne units was applied to total synthesis of a variety of natural products such as antitumor anthracyclene aglycones[63] (Scheme 24) and the protoberberine alkaloids[64]. The protoberberine **81** is readily prepared by cocyclization of **80** with bis(trimethylsilyl) acetylene[65] (Scheme 25).

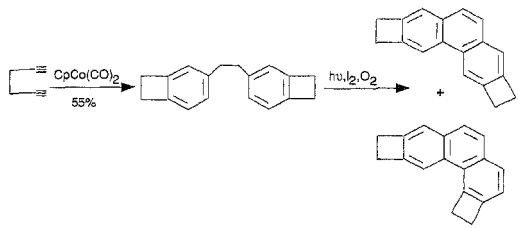


SCHEME 24.



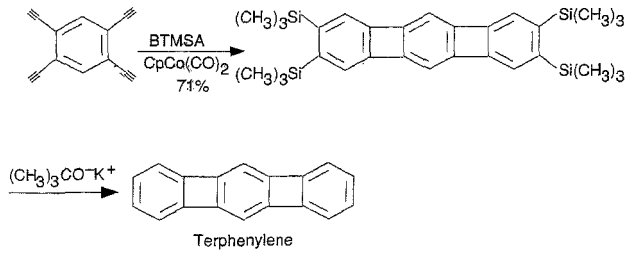
SCHEME 25.

1,2-Dihydrocyclobutabenzenes are used in the construction of a host of theoretically interesting benzenoid hydrocarbons[66-68]. Initially, 1,5-hexadiyne undergoes one-step trimerization which on oxidative photocyclization gives the two isomeric dicyclobutaphenanthrenes showing the tandem cyclization–cycloaddition reaction[69] (Scheme 26). A novel series of



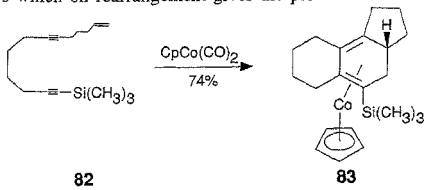
SCHEME 26

compounds called as multiphenylenes have been prepared using cobalt complexes as catalyst[70,71] (Scheme 27). Apart from their use in the synthesis of different strained ring systems, the ,2-dihydrocyclobutabenzenes have been used in producing polycyclic systems[72,73].



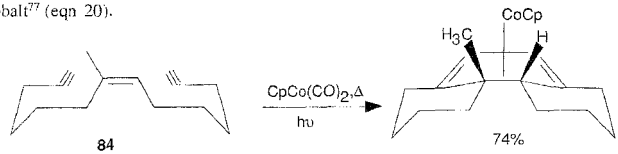
SCHEME 27.

Enediyne **82** undergoes intramolecular cyclization to yield stereospecific cyclohexadiene complex **83** in the presence of stoichiometric amount of $CpCo(CO)_2$[74,75] (eqn 19). A sequence of 2D NMR experiments in conjunction with labelling experiments has shown the presence of intermediates which on rearrangement gives the product.



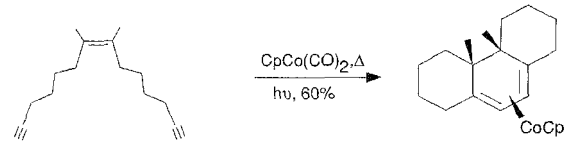
82 **83** (19)

In the same way, enediynes **84** with internal double bonds undergo intramolecular cyclization[76] to give **85**. This cyclization procedure proceeds efficiently and with remarkable stereoselectivity, both with respect to the stereochemistry of the original double bond and of cobalt[77] (eqn 20).



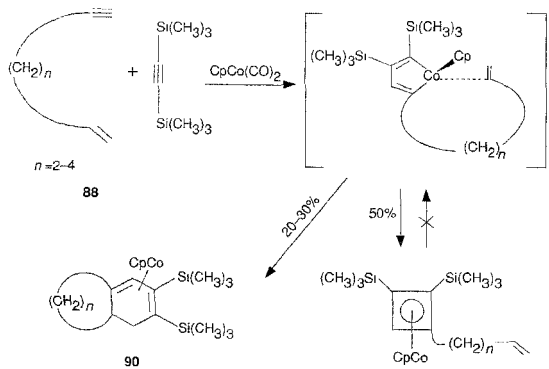
84 **85** (20)

This reaction showed that the steric encumberance of the double bond has little influence on the success of the reaction. This advantage was utilized in the preparation of tricyclic diene **87** from a substrate containing tetrasubstituted double bond[78] **86** (eqn 21).



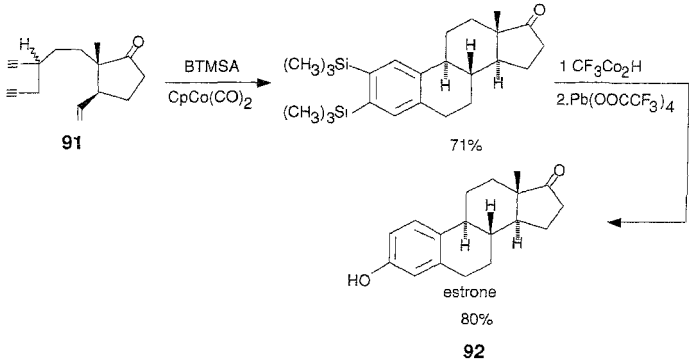
86 **87** (21)

Intermolecular [2+2+2] cycloadditions of enynes **88** on co-oligomerization with BTMSA gave mainly cyclobutadiene **89** rather than expected bicycle[60,79] **90** (Scheme 28).



SCHEME 28.

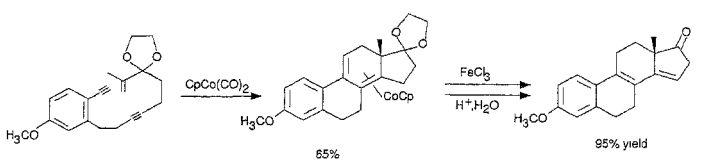
Based on the 'Tandem principle' described earlier, $CpCo(CO)_2$-catalysed synthesis of steroids was achieved starting from 1,5 hexadiyne. Alkylated 1,5-hexadiyne **91** underwent tandem co-catalysed cyclization followed by intramolecular ring closure *via* *o*-xylene formation to give key precursor **92** of (±) estrone[80] (Scheme 29).



91 **92**

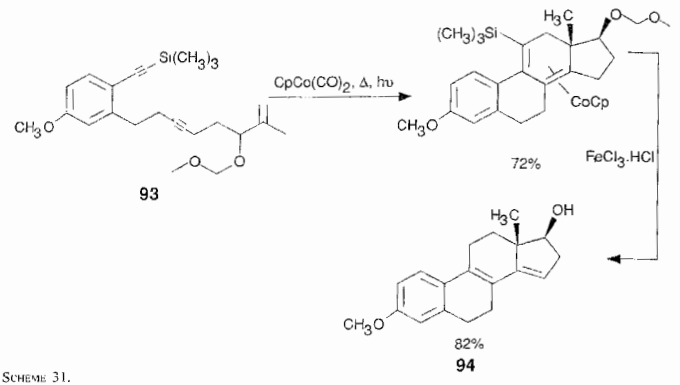
SCHEME 29.

Another way[81] of synthesising steroids is using $CpCo(CO)_2$ in which the –BCD portion of their framework would be fused to a pre-existing aromatic A-ring[82,83] (Scheme 30). A

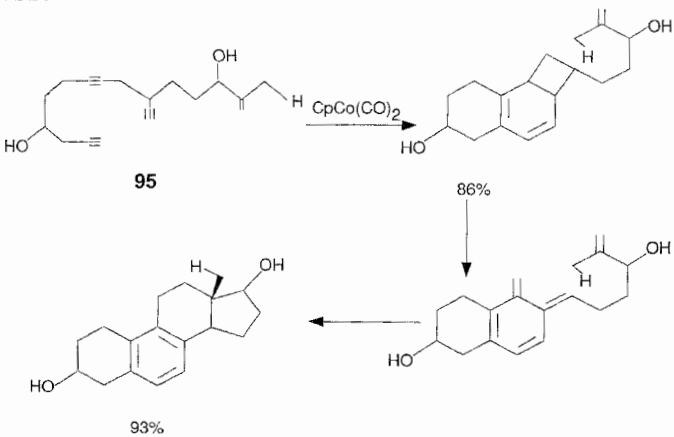


SCHEME 30.

diastereoselective synthesis of steriod[84] has been achieved using the enediyne **93**. Cyclization followed by demetallation under acidic conditions gave the known estrapentaneol[85] **94** (Scheme 31). Another approach to the steroid synthesis employing $CpCo(CO)_2$ as a matrix is O->ABCD, *i.e.*, all four rings are assembled in one step from enetriyne **95** to give B-ring aromatic derivatives with the complete control of the crucial stereochemistry of the C,D-ring juncture[86] (Scheme 32).

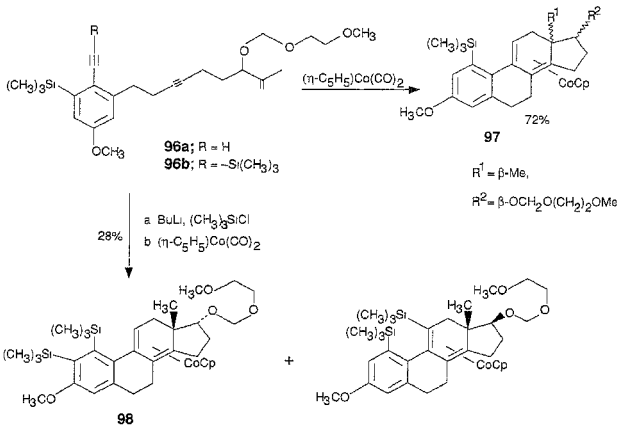


SCHEME 31.



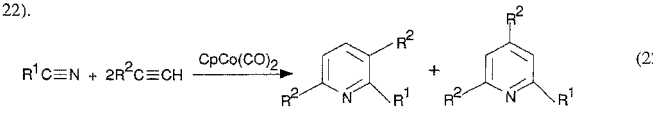
SCHEME 32.

Highly crowded steroids[87] were prepared using the enediyne **96a** to give **97** whereas the corresponding silylated derivative **96b** afforded a highly stereoselective formation of **98** (Scheme 33). The outcome of this reaction demonstrates once again the unique ability of the catalyst to make highly hindered compounds.



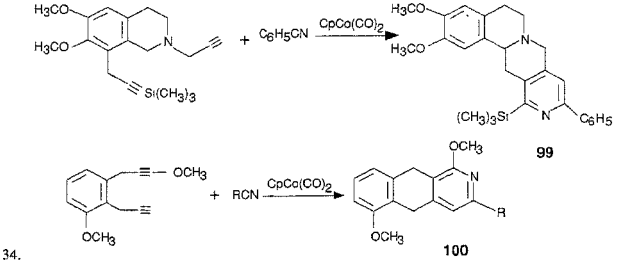
SCHEME 33.

In the early 1970s, several groups independently discovered that cobalt complexes could cocyclize alkynes with nitriles to furnish pyridine in stoichiometric and catalytic reactions[88,89] (eqn 22).



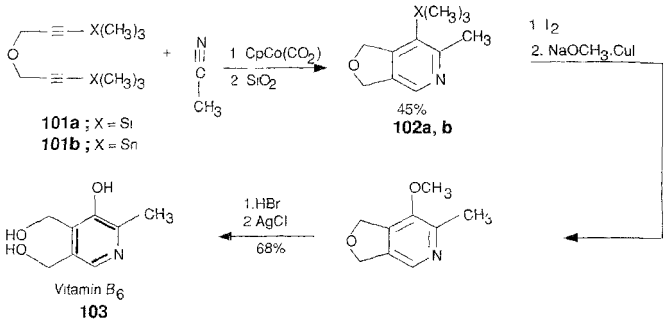
(22)

This reaction can be used in producing some very rare isoquino[2,1-b]-2,6-naphthyridine nucleus[64] **99.** Similarly, the 2-azaanthracene **100** framework can be obtained efficiently (Scheme 34).



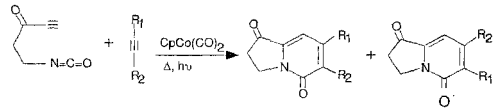
SCHEME 34.

Cocyclization of bis (trimethylsilyl) **101a** or bis (trimethylstannyl) di-2-propynyl ether **101b** with acetonitrile provides a synthetic route to 1,3-dihydro-6-methyl-4,7 bis (trimethylsilyl) **102a** or bis (trimethylstannyl)-furo[3,4-c] pyridines **102b.** This methodology has been used for the total synthesis of Vitamin B_6 **103**[90] (Scheme 35).



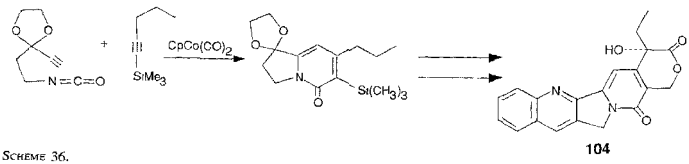
SCHEME 35.

Employment of isocynates[91,92] in place of nitrile on cocyclization with alkynes afforded polyheterocyclic systems (eqn 23). In simple cocyclizations leading to substituted pyridone,

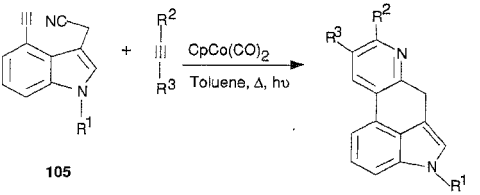


(23)

regioselectivity was not observed, whereas when bulky substituent at the α-position of ω-alkynyl isocyanates was present (*e.g.*, trimethylsilyl) good chemo- and regioselectivity were observed. Application of the above methodology has led to formal synthesis of the antitumor alkaloid camptothecin[93,94] **104** (Scheme 36). Similarly, incorporation of the 6-heptynenitrile **105** unit into the indole gives the basic skeleton of the ergot alkaloids[95] (eqn 24).

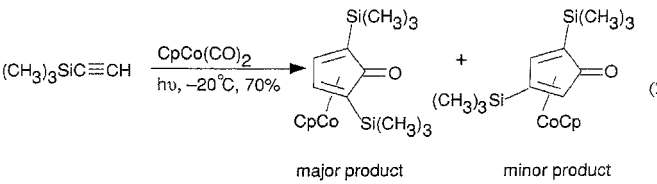


SCHEME 36.

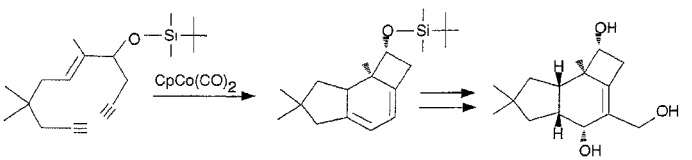


(24)

It has been found that trimethylsilylalkynes undergo [2+2+2] cycloadditions under low-temperature photolytic conditions in the presence of stoichiometric amount of $CpCo(CO)_2$ to afford complexed cyclopentadienones regioselectively[96] (eqn 25). Metallocyclopentadienes[10a] and metallocyclobutenones[97] have been used in the formation of cyclopentadienones from alkynes and carbonylmetal compounds regioselectively.



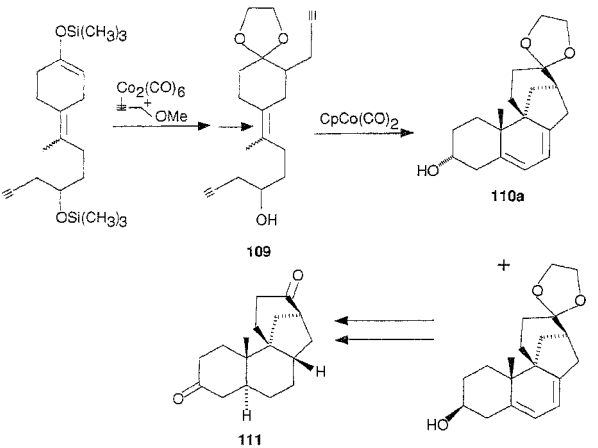
(25)



SCHEME 37.

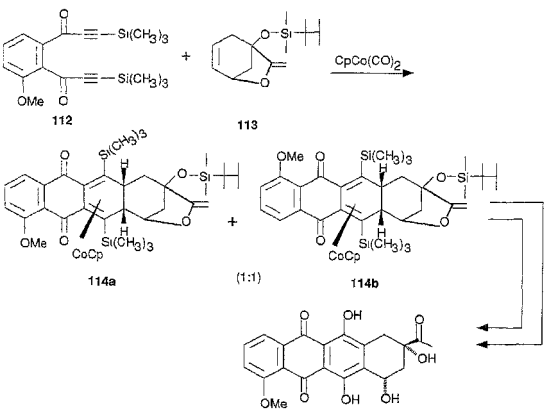
Sesquiterpene illudol[98] **108** was obtained from **107** *via* intramolecular [2+2+2] cyclization of **106** (Scheme 37). It is interesting to note that [5.6.4] ring system is constructed during cyclization from an acyclic precursor.

Vollhardt and co-workers have shown that intramolecular cyclization of enedyene **109** (prepared by Nicholas reaction), containing a tetrasubstituted double bond, provides a diastereomeric mixture of spirocyclic diene **110a** and **110b** which can be converted *via* routine functional group manipulation to the antimicrobial diterpene stemodine[99] **111** (Scheme 38).



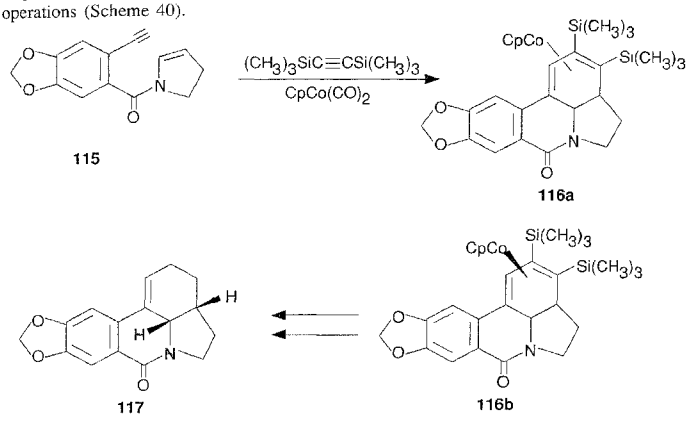
SCHEME 38.

Vollhardt has demonstrated that the precursor **114a** and **114b** for daunomycinone[100] can be synthesised by reacting diyne **112** with alkene **113** in the presence of $CpCo(CO)_2$ (Scheme 39).



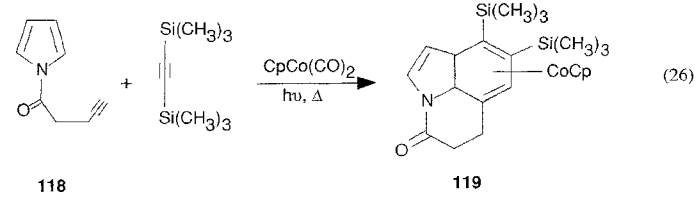
SCHEME 39.

Interestingly, enamide **115** and bis(trimethylsilyl) acetylene (BTMSA) were cocyclized in the presence of $CpCo(CO)_2$ to form diastereomeric complexes **116a** and **116b**, providing galanthan ring systems. These intermediates were transformed to γ-lycorane[101] **117** by routine synthetic operations (Scheme 40).



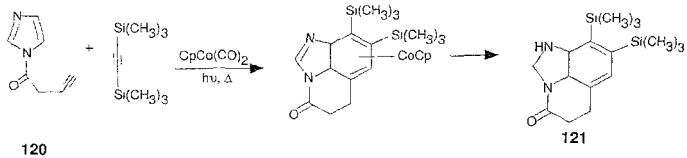
SCHEME 40.

Further exploration of this reaction by Vollhardt and co-workers has shown that one aromatic double bond of many heterocyclic ring systems is capable of incorporation into cyclohexadiene ring. Reaction with N-substituted heterocycles, imidazole, pyrrole, indole and uracil derivatives has shown that aromatic double bond can function as the alkene component in the cyclization. A [2+2+2] cycloaddition of pyrrole[102] **118** was carried out to afford fused dihydro indole **119** (eqn 26).



(26)

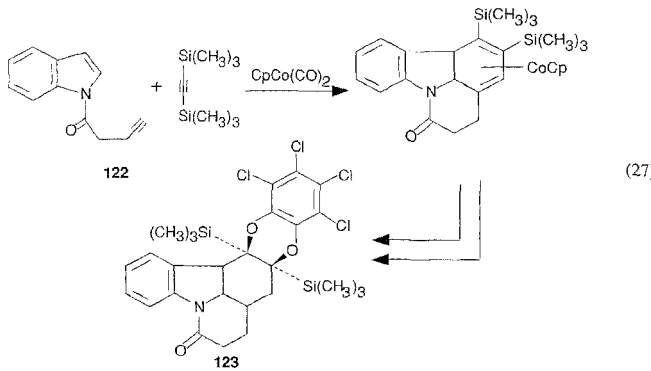
N-substituted imidazole[103] **120** was reacted with BTMSA to give cycloadduct **121** in high yields (Scheme 41).



120 121

SCHEME 41.

N-substituted indole **122** also reacts with BTMSA to provide CpCo-complex. This reaction provides an entry to 4a, 9a-dihydro 9H carbazole[104] **123** (eqn 27).



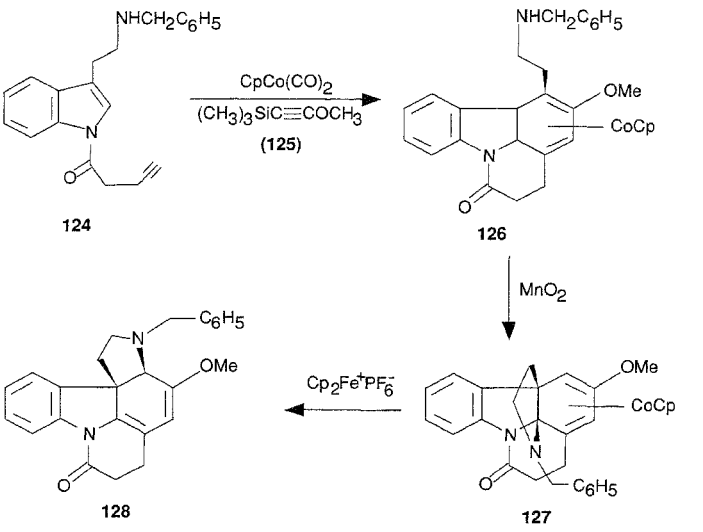
122 123 (27)

Indole derivative **124** on cocyclization with **125** gives cobalt complex **126** which on treatment with MnO_2 furnishes propellane[105] **127**, and the latter rearranges to spirofused compound **128** on oxidative removal of the metal (Scheme 42).

Substituted uranil[106] **129** undergoes cycloaddition to give Co-complexes **130** which can lead to various nucleoside derivatives (eqn 28).

A novel synthesis of fused 2H-pyrans[107] **132** has been achieved *via* η^5-cyclopentadienylcobalt complex-induced [2+2+2] cycloadditions of the alkynes **131** with ketones both inter as well as intramolecularly (eqn 29).

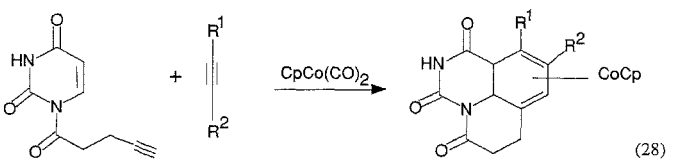
Vollhardt and co-workers[108] have synthesised enantiomerically pure cyclopentadienyl cobalt complexes from chiral ligands obtained from naturally occurring terpenes and acids. The chiral cobalt complexes **133a–c** were efficient catalysts in providing high diastereomeric excess. They have used these complexes for the photolytic cyclization of unsymmetrical α,ω-diynes **134** to metal-complexed cyclopentadienones **135** (eqn 30).



124 126 127 128

SCHEME 42.

Later, these complexes were also exploited for diastereoselective enedine cyclization to complexed cyclohexadienes. Prochiral α,δ,ω-enediynes **136** cyclize to chiral tricyclidiene complex **137** in the presence of **133a** as diastereomeric complexes in 58:42 ratio (eqn 31).

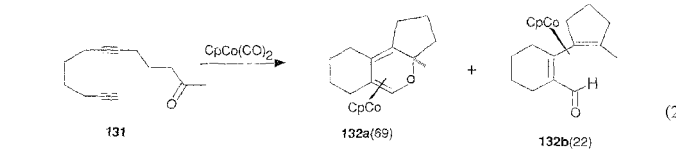


(28)

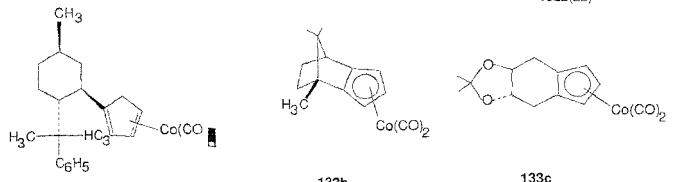
129 **130**

$R^1 = R^2 = Si(CH)_3$ (35%, *syn* /anti=10)

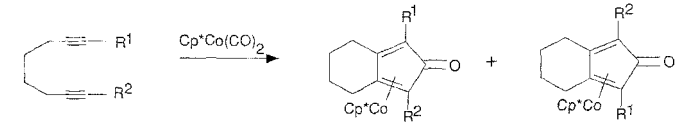
$R^1 = R^2 = CO_2CH_3$ (73%, *anti*)



131 132a(69) 132b(22) (29)



133a 133b 133c

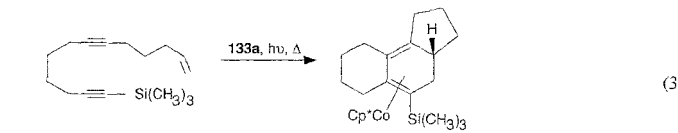


134 135a 135b (30)

cat **133a** (74%, 60:40)

$R^1 = Si(CH_3)_3$, $R^2 = CH_3CH_2$

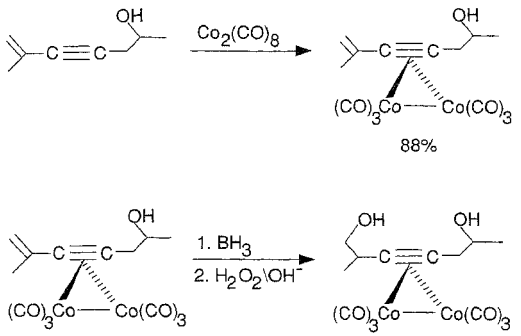
cat **133c** (64%, 50:50)



136 137 (31)

2. Nicholas reaction

A phenomenon of long-standing interest in organometallic chemistry is the tremendously enhanced stability of carbonium ion flanked by organometallic metal moieties[109]. While considerable attention has been focussed on the various possible modes of these stabilizations, the potential applications of these cations in organic synthesis have largely remained an uncharted area. The use of dicobalt octacarbonyl for the protection of a triple bond is well known and the realisation that triple bond-coordinated $Co_2(CO)_6^+$ moiety dramatically enhances stability of propargylic carbocations[110–112] has led to the growth of the synthetic transformations now known as Nicholas reaction (Scheme 43). This methodology has found numerous applications in organic synthesis and some of the salient features of its utility are discussed.



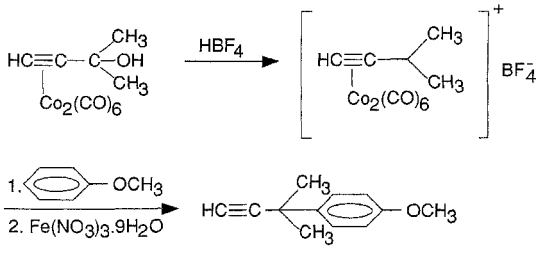
SCHEME 43.

2.1. Reaction with nucleophiles

The enhanced stability of (propargyl) $Co_2(CO)_6^+$ cations has made them an attractive intermediate for a new bond formation on reaction with a wide range of nucleophiles. In all cases, attack by nucleophile occurs exclusively at the propargylic carbon, resulting in a versatile propargylation method subsequent to mild oxidative demetallation.

2.2. Aromatics

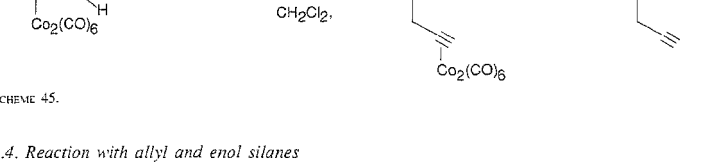
Electron-rich aromatic compounds[113] including anisole, phenol, N, N-dimethylaniline, etc., react at room temperature or even below with the (propargyl) $Co_2(CO)_6^+$ complexes to afford C-propargylated aromatic compounds (Scheme 44).



SCHEME 44.

2 3. Reaction with X-dicarbonyls

Propargylated cobalt complexes as salts with HBF_4 or $TiCl_4$ react easily with β-diketones and β-ketoesters affording mono C-propargylated products in good yields[114] (Scheme 45). This selective reaction reflects the reversibility of coupling reaction and the steric bulk of the (propargyl) $Co_2(CO)_6$ group[115,116]. Reactions of chiral cobalt complexes with the prochiral β-diketones were found to proceed with diastereoselectivities of 2:1 to 15:1.

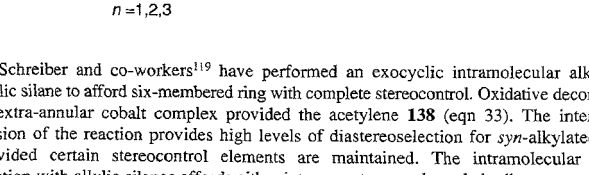


SCHEME 45.

2.4. Reaction with allyl and enol silanes

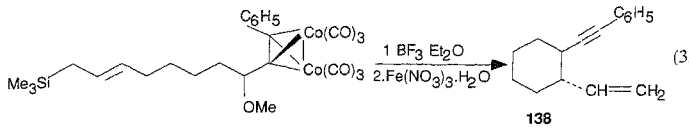
Propargyl dicobalt hexacarbonyl cations couple with allylsilanes to give complexes of 1,5-enynes in satisfactory yields[117,118] (Scheme 46). In the presence of BF_3 etherate a cobalt-complexed propargylic ether can undergo an intramolecular alkylation with an allylic silane to provide six-, seven- and eight-membered complexed cycloalkynes[45] (eqn 32).

SCHEME 46.



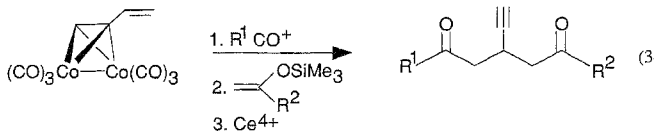
(32)

Schreiber and co-workers[119] have performed an exocyclic intramolecular alkylation of allylic silane to afford six-membered ring with complete stereocontrol. Oxidative decomplexation of extra-annular cobalt complex provided the acetylene **138** (eqn 33). The intermolecular version of the reaction provides high levels of diastereoselection for *syn*-alkylated products provided certain stereocontrol elements are maintained. The intramolecular alkylation reaction with allylic silanes affords either intra or extra-annular cobalt alkyne complexes[45,110].



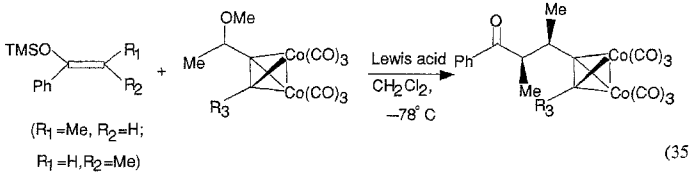
138 (33)

Caple and Smit[120] have reported the trapping of the cation formed by electrophilic addition to 1,3-enyne complexes with trimethylsilyl enol ethers or allylsilanes (eqn 34).



(34)

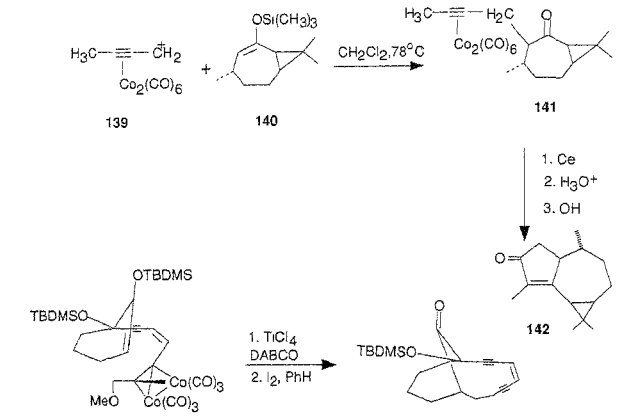
The alkylation of silyl enol ether[45] with the cobalt complex of propargylic methyl ether affords alkylated ketone. Cobalt complex can be removed from the products using trimethylamine-N-oxide or ferric nitrate while the stereochemical nature of the product is being preserved (eqn 35).



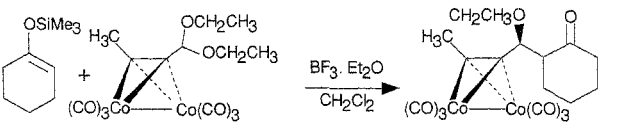
(R_1 =Me, R_2=H;
R_1 =H, R_2=Me) (35)

Cobalt-mediated cyclopentanone annulation was used as a new methodology to give the guaiane sesquiterpene skeleton **142** as in cyclocolorenone[121] which was synthesised from the intermediate **141** derived by the reaction of enol silane **140** with cobalt complex **139**. Magnus and co-workers have carried out[122] an intramolecular Nicholas reaction on cobalt-complexed propargylic methyl ether to provide an access to calicheamicinone model systems (Scheme 47).

In the same way, α-alkoxy cations derived from acetylenic acetals[123] have been found to combine effectively with the enol derivatives, allyl silanes and enol silanes in the presence of BF_3Et_2O to afford the β-alkoxyacetylenic ketone derivatives in excellent yield and modest to excellent *syn* stereoselectivity (eqn 36). The uncomplexed acetals do not undergo reaction at–78°C but between – 20 and O°C reaction did occur affording the corresponding acetylenic ketone as a 1:1 mixture of *syn* and *anti* diastereomers. It is clear therefore that the metal fragment not only facilitates coupling but also has categorical effect on diastereoselectivity.



SCHEME 47

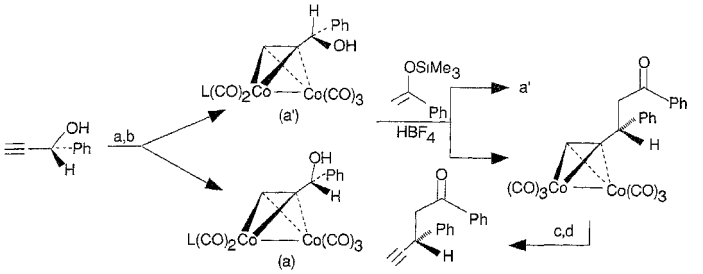


(36)

Although highly diastereoselective products have been achieved from complexed aldehyde or acetal precursors with enol and allyl nucleophiles[124] as mentioned above, facile racemization of these cations has previously thwarted attempts to develop general, enantioselective route to the diastereomers. In order to get enantioselective propargylation, Nicholas and co-workers[125] have used enantiomerically pure propargylic alcohol and converted them to diastereomeric dicobalt propargylium $Co_2(CO)_5L$ complexes, where L may be PPh_3 or $P[OCH(CF_3)_2]_3$. After demetallation of the resulting alkylated complex, enantiomerically pure compounds were obtained (Scheme 48).

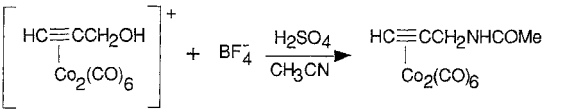
2.5. Reaction with amines

The Nicholas reaction with carbon nucleophiles[111] has been explored to a great extent and apart from this, the oxygen-centered nucleophiles[126] were also used frequently. However, only little is known about Nicholas reaction with nitrogen nucleophiles. The earliest example, an unoptimized reaction of propargylic cobalt salt of HBF_4 with acetonitrile in the presence of sulfuric acid, dates from 1981[127] (eqn 37).



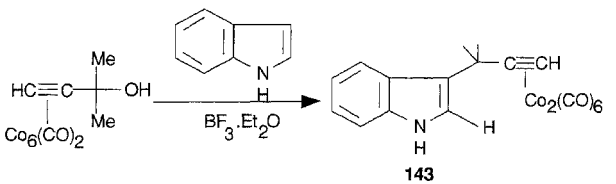
(a) $Co_2(CO)_8$; (b) $P[OCH(CF_3)_2]$; (c) CO; (d) $(NH_4)_2Ce(NO_3)_6$

SCHEME 48.



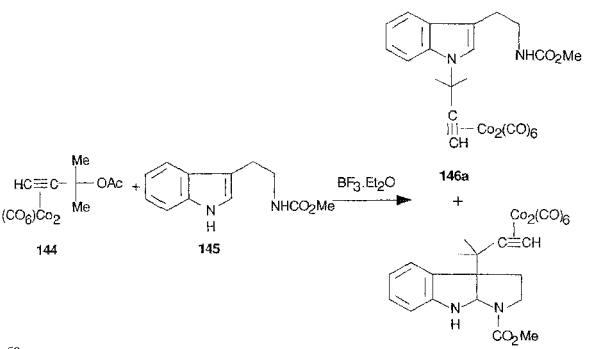
(37)

In 1990, Japanese group[128] reported the N-propargylation of indole and a few other heterocycles. Indole reacted with propargylic alcohol-$Co_2(CO)_6$ complexes to give 3-(1,1-dimethylpropargyl) indole **143** (Scheme 49) whereas N-methoxycarbonyl-tryptamine **145** gave the corresponding N- and C-substituted derivative **146a,b** with (propargyl acetate) $Co_2(CO)_6$ complex **144** (Scheme 50).



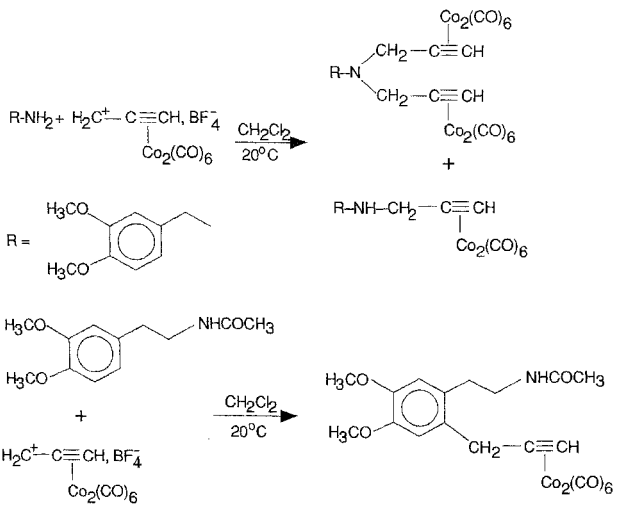
143

SCHEME 49.



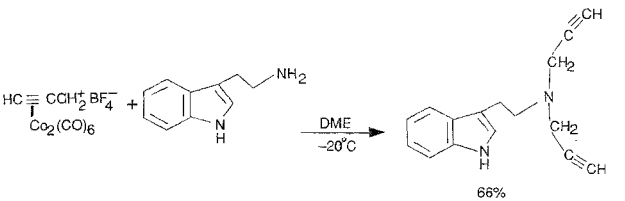
SCHEME 50.

The reactions of the $[(HC{\equiv}CCH_2)Co_2(CO)_6]BF_4$ have been carried out with a wide range of amines to give the corresponding propargylic amines[129, 130] (Scheme 51). The primary amines were simultaneously C-alkylated by protecting the $-NH_2$ group.



SCHEME 51.

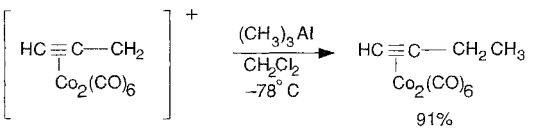
Recently, tertiary amines[131] have been synthesised by a selective reaction from cobalt-complexed propargyl cation using primary and secondary amines as nucleophiles (eqn 38).



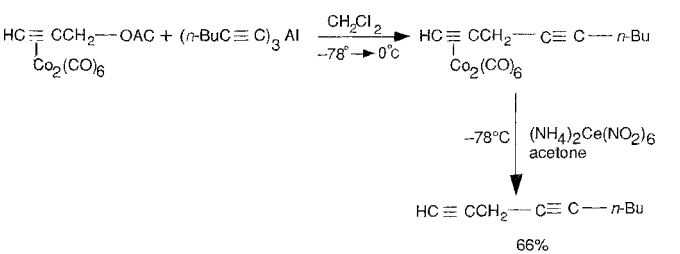
(38)

2.6. Reaction with other organometallic nucleophiles

The reaction of several methyl-metallic compounds $(CH_3)_3\,ML_n$ with the propargylated cobalt complexes had been tried to produce the methylated derivatives of propargyl group containing compounds[132,133] (eqn 39). The most efficient method of coupling of propargyl cations with acetylenic group was *via* the reaction (alkyne)$_3$Al with complexed propargyl acetates to form 1,4-diyne complexes[134] (Scheme 52).



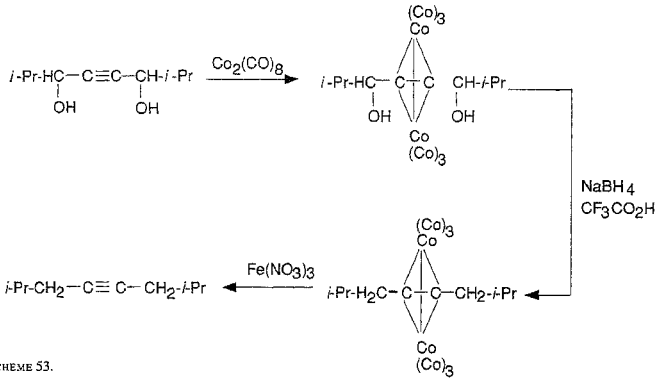
(39)



SCHEME 52.

2.7 *Miscellaneous nucleophiles*

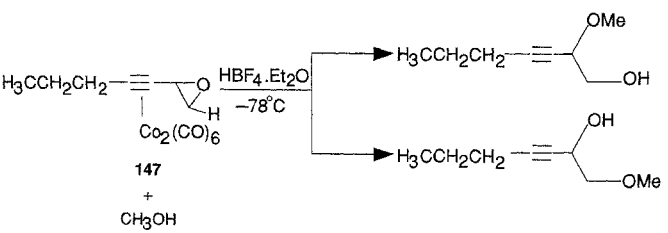
Although not much work has been done on the reaction of propargyl $Co_2(CO)_6^+$ cation with non-carbon-centered nucleophiles, Siegel *et al*[134,135] found that secondary alkyl acetylenes can be prepared through the reduction of the corresponding cobalt-complexed α-acetylenic alcohols with $NaBH_4/CF_3COOH$ in dichloromethane (Scheme 53). Deuterium-labelled diisopropylacetylene prepared by this method has been used in the synthesis of (hexaisopropyl-d_6) benzene.



SCHEME 53.

2.8. *α-Alkoxy cations*

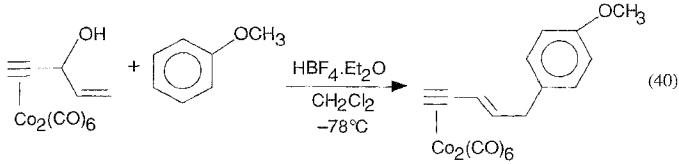
The highly reactive (1,2-epoxy alkyne) dicobalt hexacarbonyl complexes **147** had been generated *in situ* by treatment of 1,2 epoxy-3-alkyne (from 1-octene-3-yne/MCPBA) and with a slight deficiency of $Co_2(CO)_8$ in benzene solution at 5°C. The epoxide reacts with several nucleophiles (*i.e.*, CH_3OH, H_2O, Cl_3COOH) under acidic conditions to produce the 1-substituted 2-hydroxy products[136,137] in good yields (Scheme 54).



SCHEME 54.

2.9. α-Vinyl cations

In order to further elucidate the steric and eletronic properties of the propargylic carbonium ion stabilized with $Co_2(CO)_6$, the reactions of various nucleophiles with the vinylogous cations[138] were examined. Accordingly, it was demonstrated that anisole[139] reacts regio- and stereoselectively with **148** to give (E)-1,3-enyne **149** derivative in good yields (eqn 40).



148

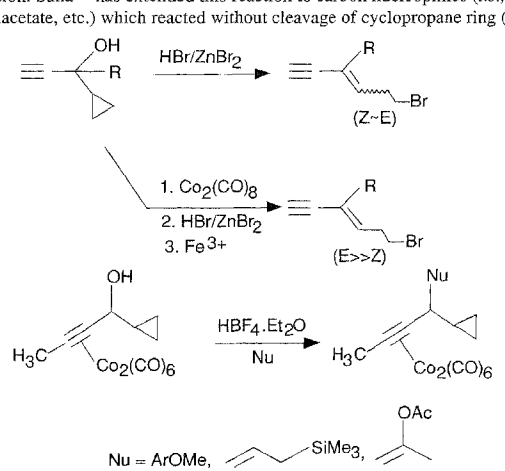
82% *trans*

149

(40)

2.10. α-Cyclopropyl cations

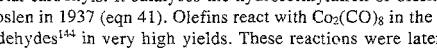
Descoins and Samain[140] have shown the contrast between the stereoselectivities of the reaction with the free and complexed cyclopropyl carbinols. It shows that attachment of complex not only facilitates the reaction but also provides a highly stereoselective (E)-1,3-enyne formation. Saha[141] has extended this reaction to carbon nucleophiles (*i.e.*, allyl silanes, anisole, vinylacetate, etc.) which reacted without cleavage of cyclopropane ring (Scheme 55).



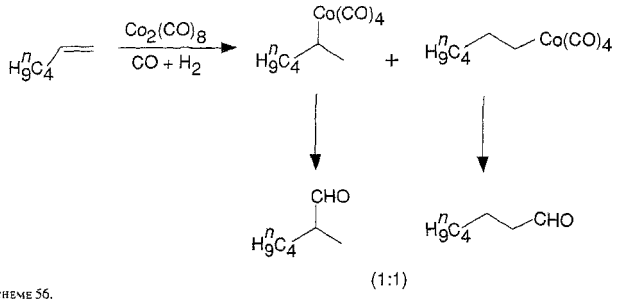
SCHEME 55.

3. Carbonylation reaction

Carbonylation[1,13], as the name suggests here, involves the process of introducing CO into the molecule. Transition metal-promoted carbonylation[142,143] of olefins, acetylenes, halides, alcohols, amides, nitro compounds, etc., are very important in both industrial and academic research. Cobalt carbonyls have been widely used and most extensively studied among the metal carbonyls. It catalyses the hydroformylation of olefin, and was first discovered by Roslen in 1937 (eqn 41). Olefins react with $Co_2(CO)_8$ in the presence of CO/H_2 to provide aldehydes[144] in very high yields. These reactions were later on developed into an useful industrial process[145] for the synthesis of aldehydes from alkenes (Scheme 56).

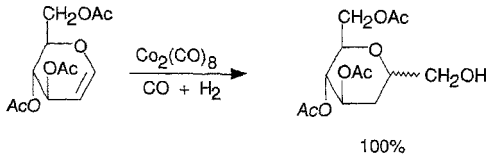


(41)

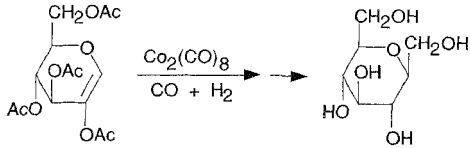


SCHEME 56.

The carbonylation process using $Co_2(CO)_8$ is more useful with vinyl ethers[146] or vinyl acetates which leads to the formation of mainly one regioisomer (eqn 42). These reactions have found widespread application on carbohydrate substrates owing to their high regioselectivity and mild conditions (eqn 43).

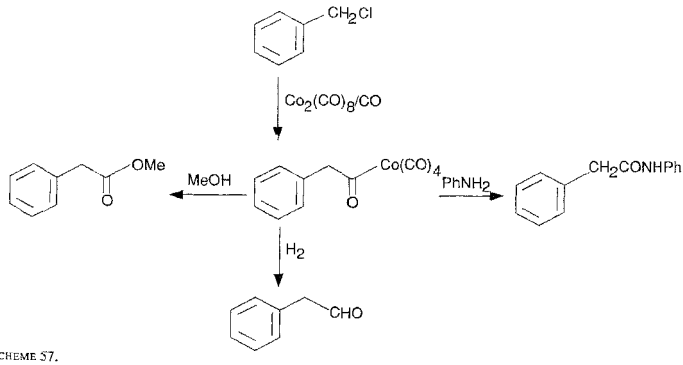


(42)



70% (43)

Heck and co-workers have developed a novel route to alkyl-$Co(CO)_4$ complex[147] from the reaction between alkyl halide or sulphonates and $Co_2(CO)_8$. The alkyl cobalt complex thus prepared underwent CO insertion to give acyl cobalt complex which was converted to aldehydes, amides or esters on reaction with hydrogen, amine or alcohols, respectively (Scheme 57).



SCHEME 57.

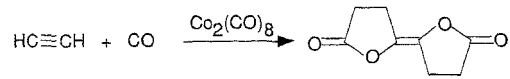
Conjugated dienes undergo reductive hydroformylation to yield saturated monoaldehyde[148] whereas non-conjugated dienes are prone to form ketones as byproduct (eqn 44).

$$CH_2{=}CH\text{-}CH{=}CH_2 + CO + H_2 \xrightarrow{Co_2(CO)_8} CH_3(CH_2)_3CHO + CH_3CH_2CH(CH_3)CHO \quad (44)$$

Secondary and tertiary alcohols readily undergo hydroformylation presumably *via* the corresponding olefins (eqn 45).

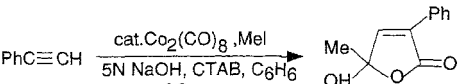
$$PhCH_2OH + H_2 + CO \xrightarrow{Co_2(CO)_8} \underset{31\%}{PhCH_2CH_2OH} + \underset{63\%}{PhCH_3} \quad (45)$$

Dilactone[149] can be synthesised by Co-catalysed carbonylation of acetylenes *via* the isolable complexes $Co_2(CO)_6C_2H_2$ and $Co_2(CO)_9C_2H_2$ as intermediates (eqn 46).



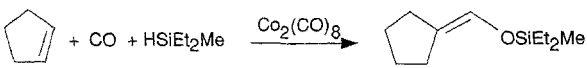
70% (46)

Alper and co-workers[150] have synthesised γ-hydroxy lactone using acyl-Co-complexes derived from the reaction of $Co_2(CO)_8$ with CH_3I and CO. Co-complex reacts with alkyne to give 4-keto-3-alkenoyl cobalt intermediate, using phase transfer catalyst. This complex gives unsaturated keto acid that cyclised to give γ-hydroxy lactone (eqn 47).



44% (47)

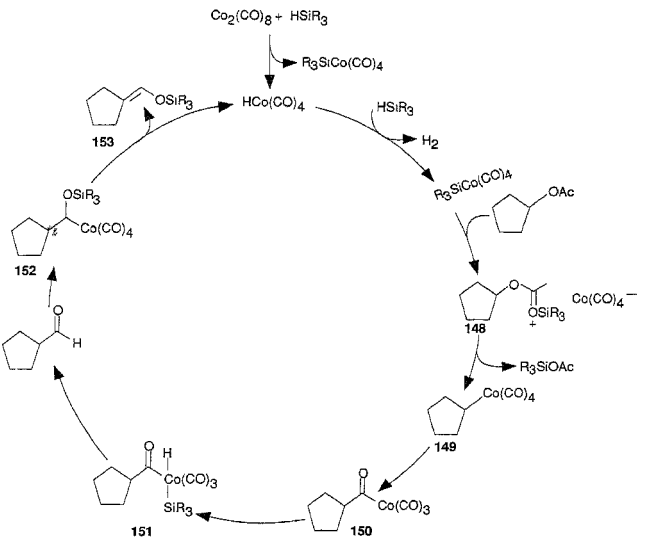
One of the outstanding developments in the area of carbonylation using $Co_2(CO)_8$ is the contribution from Murai and co-workers[151]. They have developed a direct method for the synthesis of enolsilyl ether from cyclic olefins in the presence of CO and diethyl (methyl) silane (eqn 48). They have suggested a catalytic pathway for siloxymethylation.



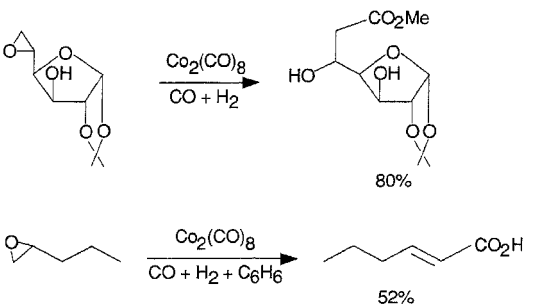
(48)

High affinity of silicon towards oxygen in the key intermediate $R_3SiCo(CO)_4$[152] is the driving force for the cleavage of C–O bond in oxygenated compound **148** to give intermediate **149** having carbon–cobalt bond. Insertion of CO gives acyl cobalt complex **150** which reacts with $HSiR_3$ to give Co-complex **151** and the latter on reductive elimination of $R_3SiCo(CO)_3$ provides aldehyde. Subsequently the reductive addition of $HSiR_3$ gives Co-complex **152**, which on elimination of $HSiCo(CO)_3$ provides enolsilane **153** (Scheme 58).

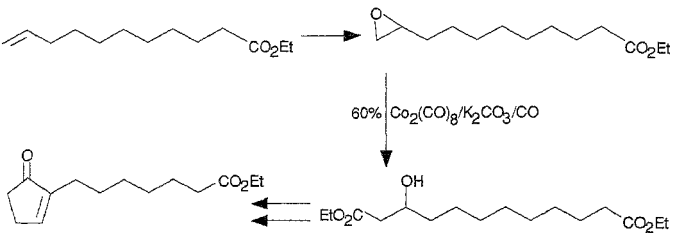
Reaction of epoxides with $Co_2(CO)_8$/CO depends upon the solvent used in the reaction as 3-hydroxy esters[146] were obtained by using MeOH as solvent whereas in aprotic solvent α,β-unsaturated acids were found to be the major products (Scheme 59). This methodology has been used for the synthesis of 2-(6-methoxycarbonylhexyl)-cyclopent-2-ene-1-one **154**. This is a simple and short route for the synthesis of **154** *via* Co-catalysed carbonylation of intermediate epoxide. The reaction does not occur in the absence of base and ethanol was used for achieving the highest selectivity (Scheme 60). When reaction of epoxides was carried out in the presence of H_2, aldehydes or alcohols[153] were obtained as major products (Scheme 61).



SCHEME 58.

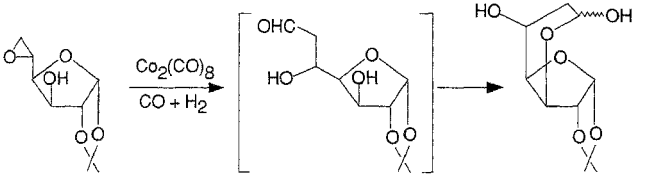


SCHEME 59.



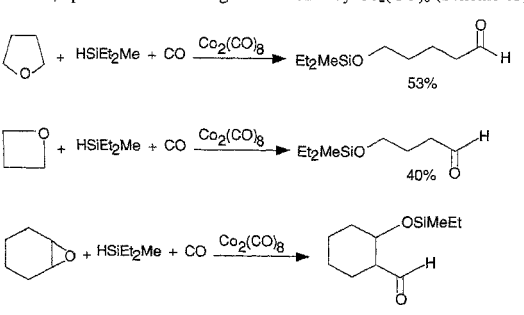
SCHEME 60

Later, Murai and co-workers have reported hydroformylation of cyclic ethers[154] in the presence of hydrosilanes. It has been shown that direct hydroformylation of these molecules suffers from undesirable side reactions.

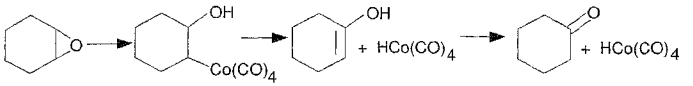


SCHEME 61.

Tetrahydrofuran, oxetane and 1,2-epoxycyclohexane undergo cleavage with diethyl (methyl) silane and CO to give silyl-protected hydroxy aldehydes[155] (Scheme 62). In the absence of CO, epoxides are rearranged to ketone[1] by $Co_2(CO)_8$ (Scheme 63).

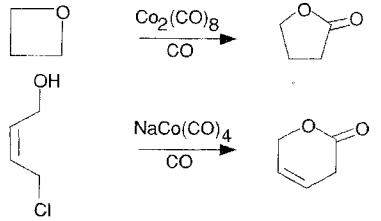


SCHEME 62.

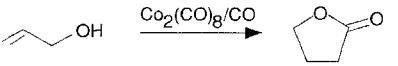


SCHEME 63.

Oxetanes react with $Co_2(CO)_8$ and CO to give 4-hydroxy acyl cobalt tetracarbonyls which decompose to give γ-lactone[156]. Large ring lactones can also be prepared by using chloroalcohol (Scheme 64). Allyl alcohols on intramolecular cyclization give lactones (eqn 49).

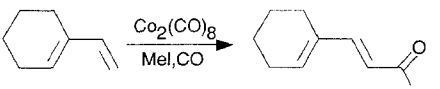


SCHEME 64.



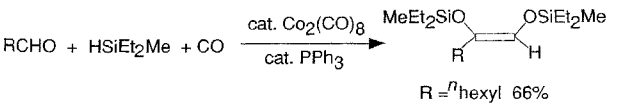
(49)

Alkyl and acyl Co-complexes react with 1,3-dienes to provide η^3-allyl derivatives[150] which decompose to give 1-acyl, 1,3-dienes (eqn 50).



(50)

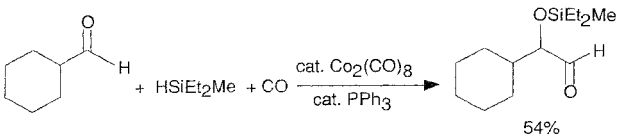
1,2-Bis(siloxy) olefin[157] can be prepared from Co-catalysed reaction of aldehydes with $HSiR_3$ in the presence of PPh_3. The PPh_3 as co-catalyst is necessary to avoid undesired hydrosilylation of aldehydes (eqn 51). In these reactions, 3-fold excess of $HSiEt_2Me$ was used.



R = ^{n}hexyl 66%

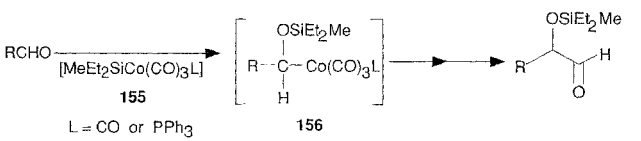
(51)

Later, these authors reported conversion of aldehydes to their higher α-siloxy aldehydes[158] by hydrosilane and CO. Here the use of an excess of starting aldehyde is essential to avoid formation of 1,2-bis(siloxy) alkenes (eqn 52).

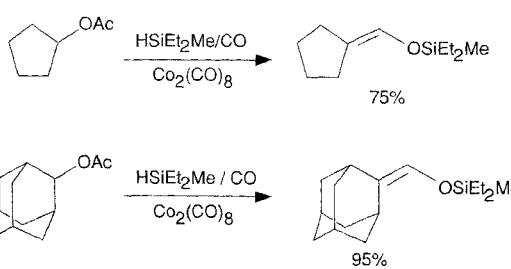


(52)

These reactions may be proceeding *via* silyl cobalt complex **155** formed *in situ* from $Co_2(CO)_8$ with hydrosilane. The intermediate is α-siloxy alkyl cobalt compound **156** formed *in situ* from **155** with aldehyde. The high affinity of silyl group for oxygen may force C–Co bond formation (eqn 53). Murai and co-workers[159] have described transformation of alkyl acetates to [(trialkylsiloxy)methylene]alkanes (Scheme 65).

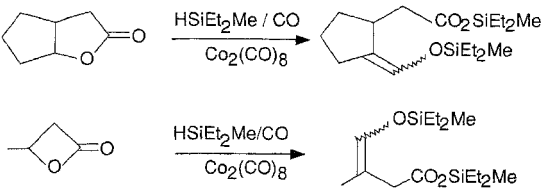


(53)



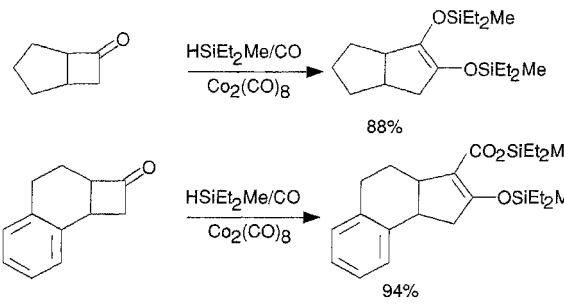
This methodology is also applicable to lactone which is converted to the corresponding silyl enol ethers obtained by reductive opening of the ring (Scheme 66).

Later, these workers have reported a cobalt carbonyl-catalysed ring enlargement of cyclobutanones[160] with hydrosilanes and CO. This was the first example reported for the catalytic incorporation of CO into a ketonic carbon (Scheme 67). This reaction provides a



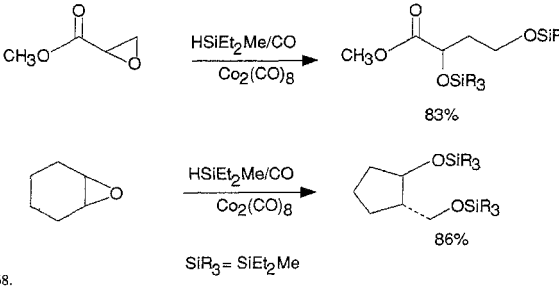
SCHEME 66.

novel method for the formation of five-membered rings containing disiloxy alkene which can be useful in the synthesis of polycyclopentanoids.



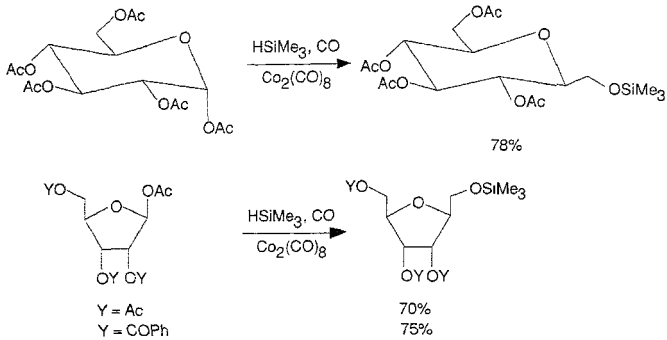
SCHEME 67.

The authors have also reported that $[R_3SiCo(CO)_4]$ is efficient catalyst for nucleophilic oxymethylation[61] of oxiranes to give 1,3-diol derivatives (Scheme 68). It was observed that functional groups present in oxiranes are not affected under these reaction conditions.



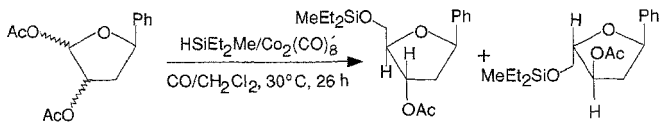
SCHEME 68.

Murai and co-workers have reported a novel route for the synthesis of C-glycosyl compounds from glycosyl acetates *via* glyoxymethylation[162] (Scheme 69). C-Glycosyl compounds are valuable as multipurpose building blocks and also as intermediate for methylene phosphonate and homo-C-nucleosides. This method is useful for one carbon chain extension at the anomeric centre of glycosides.



SCHEME 69

Ito[163] has utilised this methodology for the synthesis of 2-deoxy-C-nucleoside skeletons (Scheme 70). It was noted that siloxymethyl group has been introduced *trans* to the adjacent (C-3) acetate group which is in consonance with Murai's result.

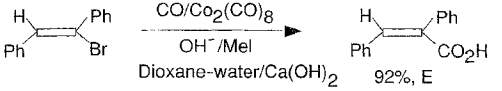


SCHEME 70.

Foa and co-workers[164] have shown that in the presence of appropriate base alkyl tetracarbonyl cobalt complexes catalyse the carboxylation of aryl halides in aliphatic alcohols to provide ester. In contrast, Murai and co-workers have shown that the reaction of aryl halides under phase transfer conditions in the presence of MeI and NaOH have a mixture of aryl methyl ketones and aromatic carboxylic acid (eqn 54). This reaction proceeds *via* methyl tetra carbonyl cobalt complex[165] which can be generated *in situ* from $Co_2(CO)_8$ with MeI. Product composition is highly dependent on base and solvent used.

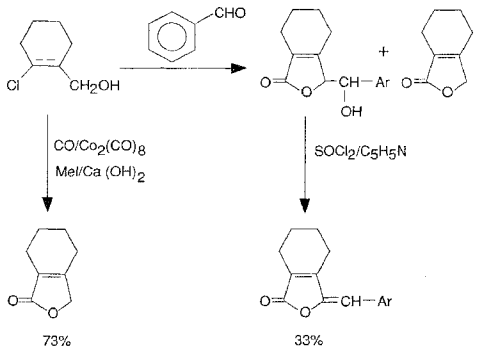
$$ArX \xrightarrow[C_6H_6\text{-}H_2O/CTAB]{Co_2(CO)_8/CO/MeI/NaOH} ArCOMe + ArCO_2H \qquad (54)$$

Later, Miura and co-workers[166] have demonstrated the carbonylation of vinyl halides on the corresponding carboxylic acid under these conditions (eqn 55).



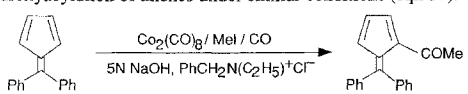
(55)

This methodology can be employed for the synthesis of Furan-2(5H)-ones[167] by carbonylation of 3-chloroprop 2-enols. When carbonylation was carried out in the presence of benzaldehyde using NaOH, an adduct was formed in 70% and furanone in 13% yield. These products were further converted into γ-alkyldenebutenolides on treatment with thionyl chloride in pyridine (Scheme 71).

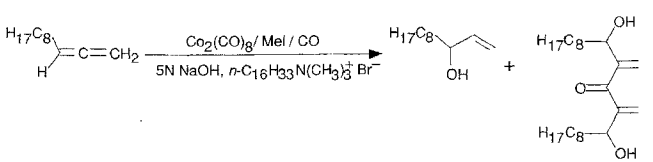


SCHEME 71.

Alper and co-workers[168] have developed an efficient method for regiospecific acylation of fulvenes by using phase transfer agent (eqn 56). Later, these workers[169] have shown the hydroxyacylation of allenes under similar conditions (eqn 57).

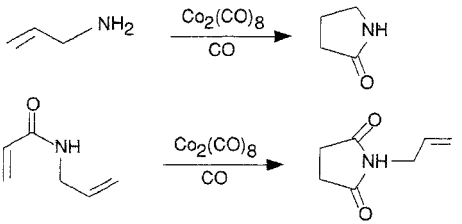


(56)

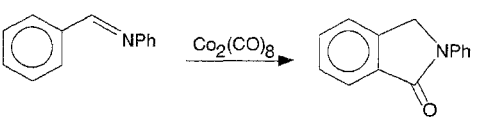


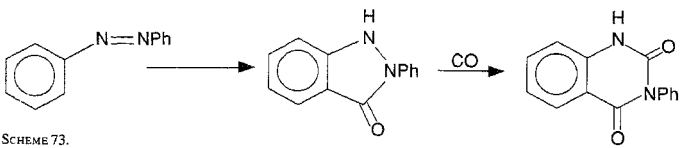
(57)

Cobalt carbonyl is an efficient catalyst for carbonyl insertion reactions betweenC–N and N–N double or triple bond. Unsaturated amines and amides give lactams and imides[170], respectively, under the aegis of cobalt carbonyl and CO (Scheme 72). Schiff bases and azo compounds[171] provide phthalimidines and 2-phenyl indazolone, respectively, by cyclocarbonylation reaction with $Co_2(CO)_8$/CO (Scheme 73). Phenyl hydrazones and oximes also undergo cyclocarbonylation reactions to give cyclic amides (Scheme 74).

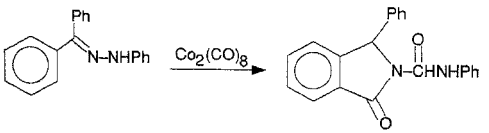


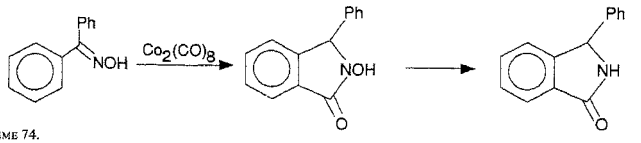
SCHEME 72.





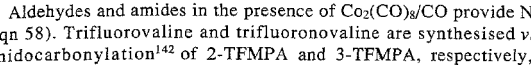
SCHEME 73.



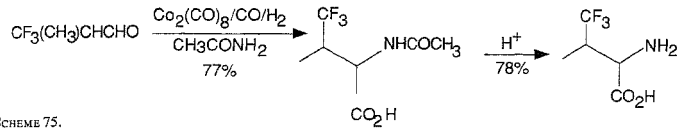


SCHEME 74.

Aldehydes and amides in the presence of $Co_2(CO)_8/CO$ provide N-acyl aminoacids[172] (eqn 58). Trifluorovaline and trifluoronovaline are synthesised *via* cobalt-catalysed amidocarbonylation[142] of 2-TFMPA and 3-TFMPA, respectively, which are further hydrolysed to give free amino acid (Scheme 75).

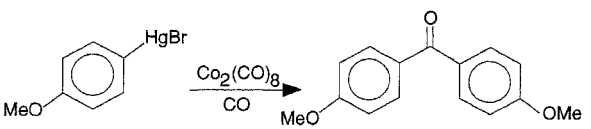


(58)



SCHEME 75.

Ketones can be prepared by the reaction of organomercury compounds[173] in the presence of $Co_2(CO)_8/CO$ (eqn 59).

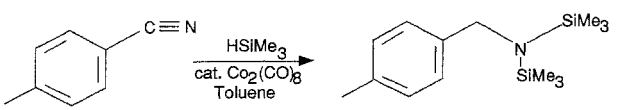


(59)

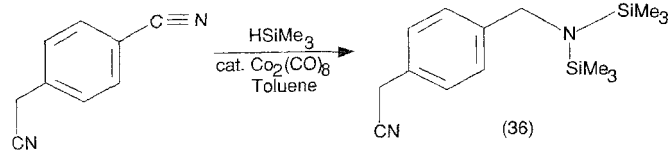
4. Miscellaneous reactions

Murai and co-workers[174] have developed a novel and efficient method for the synthesis of N, N-disilylamines by reduction of aromatic nitriles using cobalt carbonyl-catalysed addition of two molecules of $HSiMe_3$.

Aliphatic nitriles did not react with $HSiMe_3$ whereas in *p*-(cyanomethyl)-benzonitriles, the cyano group adjacent to benzene ring, selectively reacts with $HSiMe_3$. The rate of conversion of aromatic nitriles having electron-withdrawing group or sterically hindered nitriles is rather low (Scheme 76).

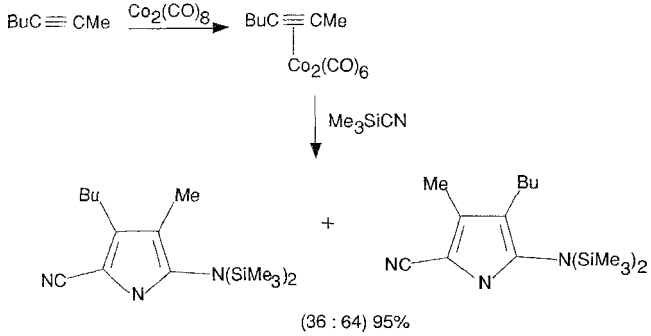


(90)



SCHEME 76.

Chatani and co-workers[175] have developed a method for the formation of pyrrole ring from alkynes and cyanotrimethyl silane in the presence of $CO_2(CO)_8$(Scheme 77).

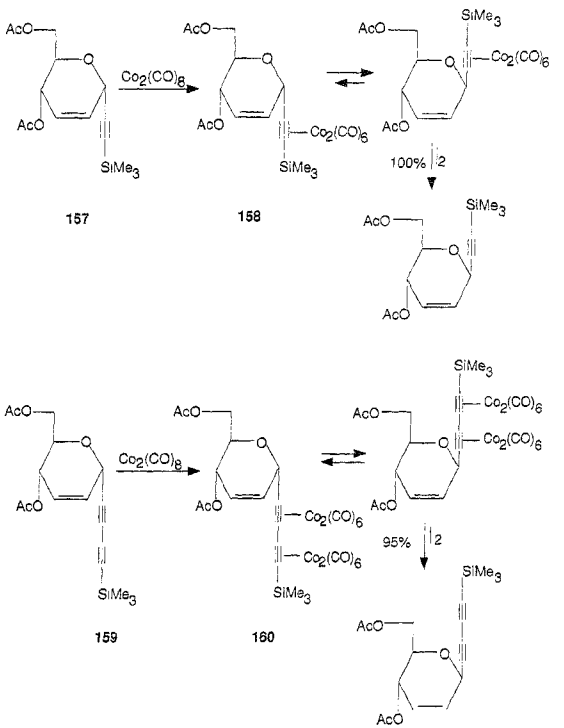


SCHEME 77.

Isobe and co-workers[176] have recently shown the epimerization of C-1 alkynyl group on pyranose ring through cobalt complexes under acidic conditions. Thus, **157** on complexation with $Co_2(Co)_8$ provides Co-complex **158** which was equilibrated under acidic conditions by using TfOH to give the opposite isomer in very high yields. This reaction was carried out under various conditions and best results were obtained at higher temperatures with catalytic amount of iodine which afforded the isomer in very high yields. A similar transformation is also achieved on pyranose ring **159** containing substituent with two triple bonds by epimerisation of bis-cobalt complex **160** (Scheme 78).

5. Conclusion

The foregoing sections have clearly established the versatility of cobalt carbonyl in contemporary synthesis and this development has a very strong bearing on the future attempts towards pursuit of selectivity during the construction of sensitive and complex organic structures. Pauson–Khand, Nicholas and Vollhardt reactions are the outstanding features of these endeavours which will go a long way in achieving the desired efficiency and selectivity which has now become a hallmark of modern synthesis.



SCHEME 78.

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