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COBALT(II)CHLORIDE CATALYSED CLEAVAGE OF ETHERS WITH ACYL HALIDES : SCOPE AND MECHANISM

Javed Iqbal* and Rajiv Ranjan Srivastava
Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India

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Abstract : Cobalt(II) chloride in acetonitrile catalyses the cleavage of a wide variety of ethers with acyl halides under mild conditions to give the corresponding esters in good yields. Acyclic aliphatic ethers are cleaved to the corresponding ester and chlorides whereas the cyclic aliphatic ethers give rise to the ω -chloroesters. The benzyl ethers can be converted to the corresponding esters along with the formation of benzyl chloride and benzyl acetamide. A comparative study for the cleavage of allyl and benzyl ether has revealed that benzyl ether can be selectively cleaved in presence of the allyl ethers. The oxiranes can be cleaved in highly regioselective manner to the corresponding-β-chloroesters. The vinyl ethers undergo sp^2-hybridised carbon-oxygen bond cleavage under these conditions. Based on product analysis, a mechanism involving electron transfer followed by O-acylation and S_N1 or S_N2 attack by chloride-ion is discussed.

INTRODUCTION

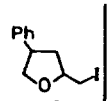
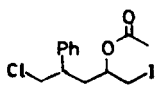
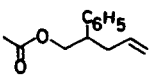
Ethers are very routinely used as protecting groups for hydroxyl functions during organic synthesis and besides a large number of ethers that are known as good blocking groups[1], the role of aliphatic, benzylic and allylic ethers are particularly noteworthy. The unmasking of ethers to alcohols can be performed in numerous ways, although the success of this transformation largely depends upon a judicious choice[2] of the deblocking reagent that is compatible with other functional groups present in the ether molecule. Recently, boron[3], aluminium[4] and silicon[5] based reagents have been employed for the cleavage of ethers and a review has highlighted[6] the merits and demerits of these reagents. Ethers can also be deprotected to the corresponding esters in presence of acylating reagents and it has been shown earlier that such a transformation can be achieved efficiently in presence of transition metal complexes[7]. We here report a novel method involving cobalt(II) chloride catalysed acylative cleavage of a variety of ethers which surpasses the earlier methods in terms of versatility and mild reaction conditions.

RESULTS AND DISCUSSIONS

In a preliminary communication we have shown[8] that aliphatic acylic and cyclic ethers can be cleaved with acid chloride in presence of catalytic cobalt(II) chloride in acetonitrite at 30°C. This reaction is quite efficient and general as a variety of aliphatic ethers can be converted to the corresponding esters and chlorides in high yields (Table I). Thus diethyl ether, which is used very often as a solvent can be cleaved to the ethyl ester by a variety of acid chlorides and the moderate yield of this reaction may be due to the volatility of ether (Table I entries 1-2). The cyclic ethers can be cleaved and acylated in high yields under very mild condition. The cleavage of

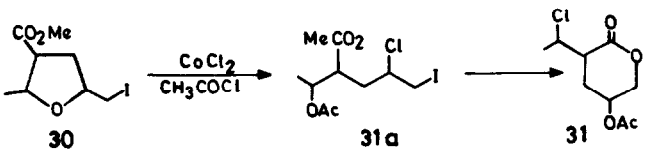
Table I : Cobalt(II) Chloride Catalysed Acylative Cleavage of Aliphatic Ethers With Acyl Chloride.

Entry	Ether	Acyl Halide	Product(s) (% Yield)[a]		
1	$(C_2H_5)_2O$ 5	H_5C_6(C=O)Cl 1	H_5C_6(C=O)OC_2H_5 6(49)	H_5C_6(C=O)C_6H_5 7(27)	
2		$H_7C_3^n$(C=O)Cl 2	$H_7C_3^n$(C=O)OC_2H_5 8(52)	$H_3C_7^n$(C=O)$C_3H_7^n$ 9(17)	
3	$(C_4H_9^n)_2O$ 10	H_3C(C=O)Cl 3	H_3C(C=O)$OC_4H_9^n$ 11(70)	$C_3H_7^nCH_2Cl$ 12(11)	13(10)
4		1	H_5C_6(C=O)$OC_4H_9^n$ 14(65)	12(10)	7(12)
5		2	$H_7C_3^n$(C=O)OC_4H_9 15(68)	12(-)	9(10)
6	$(C_3H_7^i)_2O$ 16	1	H_5C_6(C=O)$OC_3H_7^i$ 17(78)	7(5)	
7	O 18	3	H_3C(C=O)O-$(CH_2)_3$-CH_2Cl 19(90)	13(10)	
8		1	H_5C_6(C=O)O-$(CH_2)_3$-CH_2Cl 20(89)	7(12)	
9		2	$H_7C_3^n$(C=O)O-$(CH_2)_3$ CH_2Cl 21(78)	9(5)	
10	O 22	3	H_3C(C=O)O-$(CH_2)_4$-CH_2Cl 23(55)	13(21)	
11		1	H_5C_6(C=O)O-$(CH_2)_4$-CH_2Cl 24(30)	7(8)	
12	O, I 25	3	Cl, I, O(C=O) 26 (89) (ratio;1:1)	O(C=O), Cl, I 27	
13	I, O, I 28	3	Cl, I, O(C=O) 29 (96.4)		
14	CO_2Me, O, I 30	3	Cl, O, O, O(C=O) 31(88)		

15	 32	3	 33 (98) (ratio;3:1)  33a

a) Yield of the isolated product.

tetrahydrofuran (Table I entires 7-9) is of interest as it is very often used as a solvent during reaction with cobalt complexes on the assumption that it is unreactive. The cleavage of 2-iodomethyltetrahydrofurans **25**,**28**,**30** and **32** with acetyl chloride is quite clean and the corresponding chloroesters are obtained in excellent yields (Table I; entires 12-15). The carbon-iodine bond is compatible with this reaction condition and mainly one regioisomer is obtained in all the cases. However, tetrahydro-furan **32** gave the olefin **33a** as a byproduct in small amounts. The olefin may be formed by a cleavage of carbon-iodine bond from the oxonium ion via a chloride induced fragmentation. Interestingly, the compound **30** underwent acylative cleavage at 80°C to give lactone **31** in high yields (Table I; entry 14). The lactone **31** may be formed from the cleaved acylic intermediate **31a** by an attack of ester group on the carbon-iodine bond (Eqn. 1).



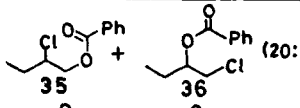
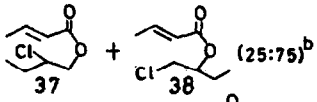
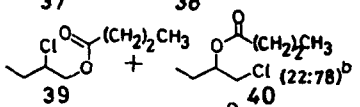
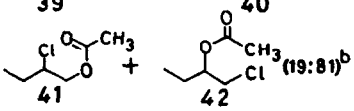
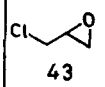
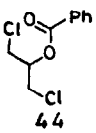
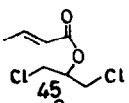
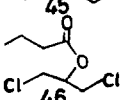
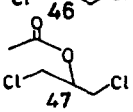
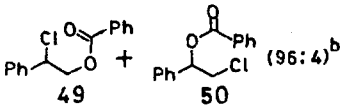
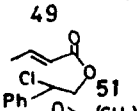
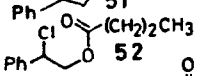
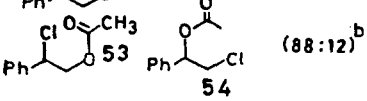
30 **31a** **31** Eqn. 1

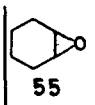
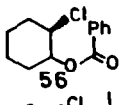
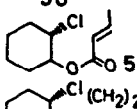
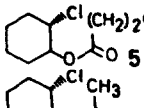
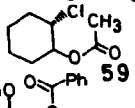
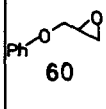
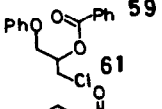
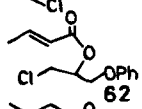
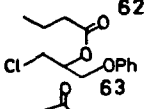
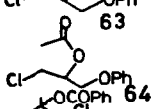
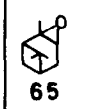
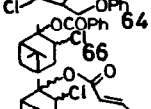
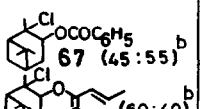
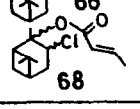
The cleavage of tetrahydropyran can be achieved in moderate yields by prolonging the reaction time (Table I; entires 10 & 11). In all the reactions, biacyl **7**,**9** and **13**, derived from the corresponding acyl chloride, is obtained as a minor product in varying amounts (5-10%).

The oxiranes can be efficiently cleaved in a highly regioselective manner to give the corresponding β-chloroesters in excellent yields (Table II). Oxiranes are acylated[7c] without a catalyst, however the regiochemistry of the non-catalysed reaction is very poor and a mixture of β-chloroesters are obtained. In contrast, the cobalt(II) chloride catalysed acylative cleavage of oxiranes yield mainly one regioisomer that is obtained due to attack of chloride ion on the less substituted carbon atom, although, 1,2-epoxybutane yield a mixture of both regioisomers (Table II; entires 1-4). Cyclohexene oxide gave only the trans β-chloroester (Table II; entries 13-16). However, in case of pinene oxide a mixture of regioisomers are obtained whose relative stereochemistry could not be ascertained by ^{1}H-NMR (Table II; entries 21 & 22). The acylative cleavage of oxiranes with crotyl chloride yield β-chlorocrotonates (Table II) which are useful substrates

for the synthesis of lactones via a intramolecular free radical cyclisation. These reactions also yield biacyls 7,9 and 13 in minor amounts (ca. 5-10%).

Table II : **Cobalt(II) Chloride Catalysed Acylative Cleavage of Oxiranes With Acyl Chlorides**

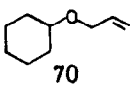
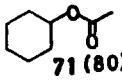
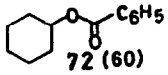
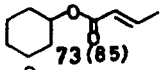
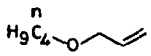
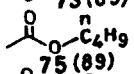
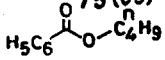
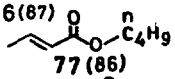
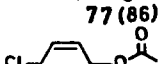
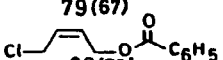
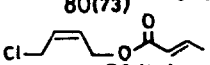
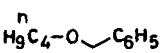
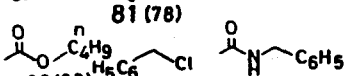
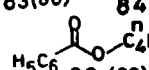
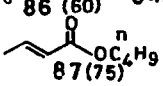
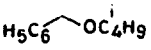
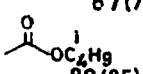
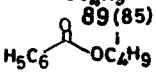
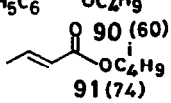
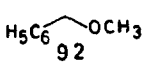
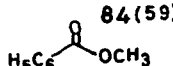
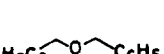
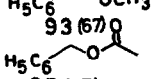
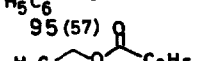
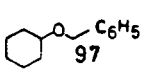
Entry	Oxirane	Acyl Chloride	Product (s)	Yield[a] (%)
1	 34	1	 35 + 36 (20:80)[b]	78
2	 4		 37 + 38 (25:75)[b]	74
3		2	 39 + 40 (22:78)[b]	70
4		3	 41 + 42 (19:81)[b]	75
5	 43	1	 44	85
6		4	 45	80
7		2	 46	72
8		3	 47	78
9	 48	1	 49 + 50 (96:4)[b]	80
10		4	 51	78
11		2	 52	72
12		3	 53 + 54 (88:12)[b]	74

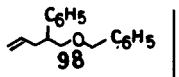
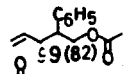
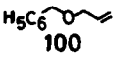
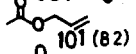
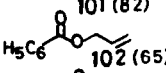
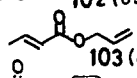
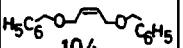
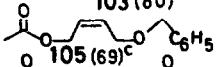
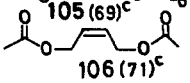
13	 55	1	 56	87
14		4	 57	81
15		2	 58	79
16		3	 59	85
17	 60	1	 61	85
18		4	 62	80
19		2	 63	80
20		3	 64	82
21	 65	1	 66  67 (45:55)[b]	78
22		4	 68 69 (60:40)[b]	72

a) Combined yield of the isolated product. b) Ratio of the regioisomer obtained from the ^{1}H-NMR of the crude mixture.

The allylic ethers can be cleaved with a variety of acyl chlorides to the corresponding esters (Table III). Thus allyl ethers derived from primary and secondary alcohols can be smoothly converted into esters and allyl chlorides (Table III; entries 1-6). Unlike acyclic aliphatic ethers, the allylic ethers undergo acylative cleavage at a comparatively faster rate. The cyclic allylic ether underwent rapid cleavage to yield the corresponding δ-chloroesters in excellent yield (Table III; entries 7-9). Similarly, the benzylic ethers can be efficiently converted to the corresponding esters alongwith benzyl chloride and benzyl acetamide (Table III; entries 10,13,17,18 and 19). The benzyl ethers derived from primary and secondary alcohols can be cleaved with equal ease and they seem to react even faster than the corresponding allyl ethers (see later). No trace of any benzyl ester was observed in these reactions. The benzyl ester (Table III; entry 24) containing an olefinic group is smoothly debenzylated to the corresponding ester in very high yields. This mode of debenzylation is certainly advantageous over the usual method[9] for removal of a benzyl protecting group. A benzyl allyl ester can be selectively debenzylated to the corresponding allyl ester and benzyl chloride (Table III; entries 24-28) and the presence of any benzyl ester was not observed in these reactions. Interestingly the dibenzyl allyl ether **104** can be selectively debenzylated to the corresponding monobenzyl allyl ether with 1.1 equivalent of the acyl chloride whereas it can

Table III : Cobalt(II) Chloride Catalysed Acylative Cleavage of Allylic And Benzylic Ethers With Acyl Halides.

Entry	Ethers	Acyl chloride	Product(s) (% Yield)
1	 70	3	 71 (80)
2		1	 72 (60)
3		4	 73 (85)
4	 74	3	 75 (89)
5		1	 76 (87)
6		4	 77 (86)
7	 78	3	 79 (67)
8		1	 80 (73)
9		4	 81 (78)
10	 82	3	 83 (80) 84 (15) 85 (21)
11		1	 86 (60) 84 (20) 85 (15)
12		4	 87 (75) 84 (15)
13	 88	3	 89 (85) 84 (15)
14		1	 84 (21)
15		4	 90 (60) 91 (74) 84 (18)
16	 92	3	84 (59) 85 (33)
17		1	 93 (67) 84 (12) 85 (10)
18	 94	3	 95 (57) 84 (22) 85 (12)
19		1	 96 (89) 84 (8)
20	 97	3	71 (80) 84 (13)
21		1	72 (60) 84 (27)
22		4	73 (75) 84 (17)

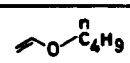
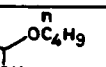
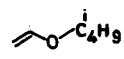
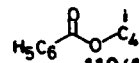
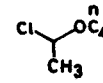
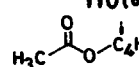
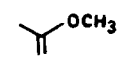
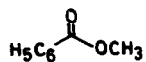
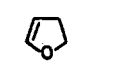
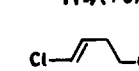
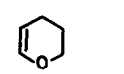
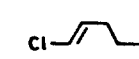
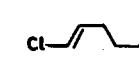
23	 98	3	 99(82)	84 (11)
24	 100	3	 101 (82)	84 (8)
25		1	 102 (65)	84 (19)
26		4	 103 (80)	84 (11)
27	 104	3	 105 (69)[c]	84 (12)
28		3	 106 (71)[c]	84 (10)

a) The biacyl was formed (5-10%) in all the reactions, however no attempt was made to optimise their yield. b) The volatile products could not be identified. c) A minor amount of unidentified products were obtained during this reaction.

be smoothly converted to the diester with 2.5 equivalent of acyl chloride. This kind of selective cleavage of a benzyl allyl ether is unprecedented and hence this route to ether cleavage may turn out to be an extremely useful synthetic methodology.

The cleavage of vinyl ethers give rise to corresponding esters in very good yields (Table IV) although contrary to the expectation, it is the sp^2-hybridised carbon-oxygen

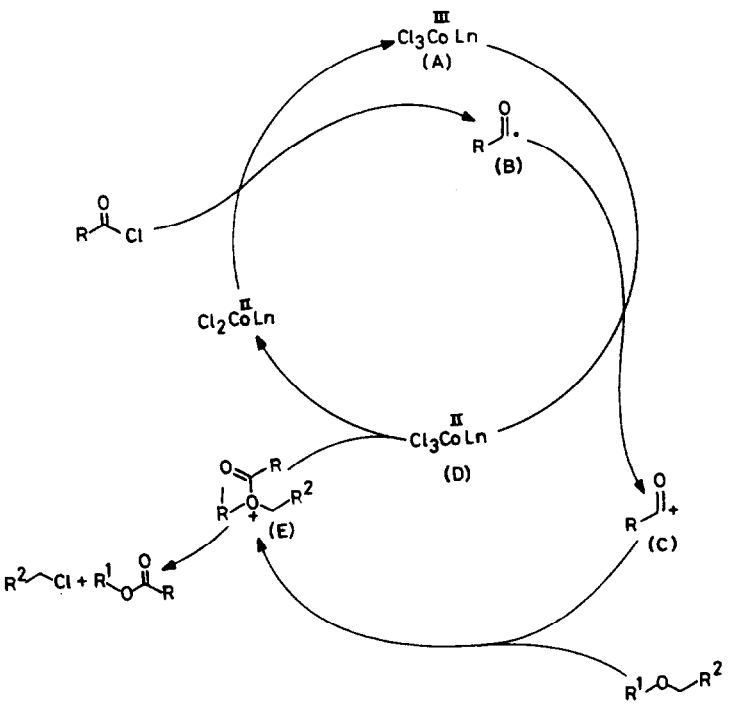
Table IV : Cobalt(II) Chloride Catalysed Cleavage of Vinyl Ethers With Acyl Chlorides

Entry	Vinyl ether	Acyl helide	Product(s) (% Yield)
1	 107	1	11(85)  108(10)
2		3	14(79)
3	 109	1	 110(81)  111(8)
4		3	 112(77)
5	 113	1	 114(78)
6	 115	1	 116(10)
7	 117	3	 118(15)
8		1	 119(12)

bond that is cleaved to yield the ester. The cyclic vinyl ethers, 2,3-dihydrofuran and pyran gave mainly polymeric materials although the corresponding chloroesters were obtained in small amounts (Table IV; entries 6-8). These reactions gave only a trace of biacyl. The mechanism of these reactions is presently unclear, however a preliminary mechanistic proposal can be offered as discussed in the following section.

MECHANISM

The presence of biacyl clearly suggests that these reactions are proceeding via an acyl radical which can be obtained from the corresponding acyl chloride. The acyl radical can be derived via a catalytic cycle involving electron transfer process as shown in Scheme 1. Thus cobalt(II) chloride may transfer an electron[10] to acyl halide

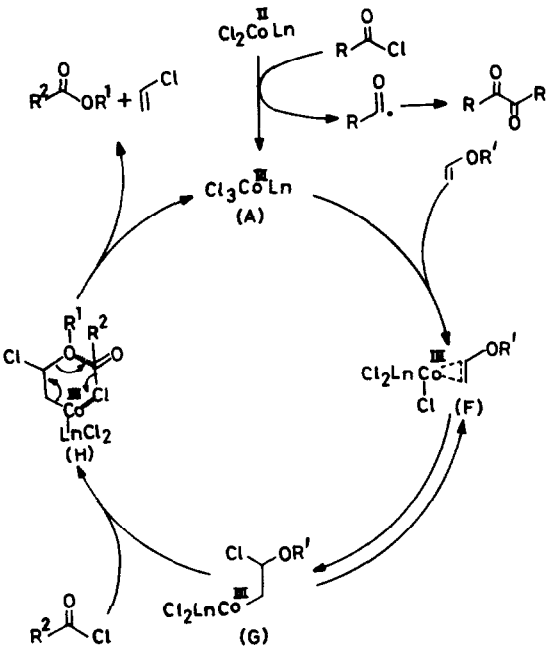


Scheme 1

to yield a cobalt(III) complex (A) and acyl radical (B). The acyl radical (B) may not be responsible for the cleavage of ester, however, it may undergo oxidation by cobalt(III) complex (A) to give an acyl cation (C) and the cobalt(II) species (D). The cation (C) will acylate the ethereal oxygen to give oxonium ion (E). The attack of chloride ion (D) in an S_N2 manner will lead to the ester and alkyl chloride. Alternatively the ion (E) may give rise to the benzylic cation which may undergo the S_N1 attack by chloride ion or solvent acetonitrile to give alkyl chloride or acetamide respectively. The oxida-

tion of an acyl radical by copper(II) complexes to give an acyl cation is known from the earlier studies[11]. We have also observed recently that cobalt(III) complexes are capable of oxidising radical to the corresponding cations[12]. The presence of benzylacetamide 85 during the cleavage of benzylic ethers clearly suggests that their cleavage is mainly proceeding via an S_N1 pathway.

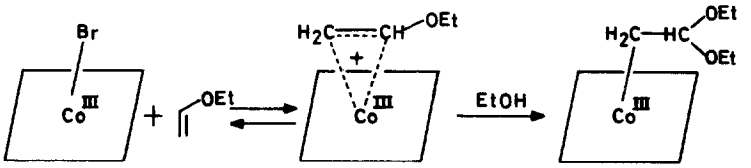
The acylative cleavage of vinyl ethers seems quite intriguing as it involves the breaking of a sp^2 hybridised carbon-oxygen bond. However, this mode of cleavage can be explained if we assume that the sp^2-hybridised carbon changes to sp^3-hybridised state via an initial electrophilic attack of cobalt(III) complex to vinyl ether (Scheme 2). An initial electron transfer to acyl halide will give rise to cobalt(III) complex (A) and an acyl radical as shown in scheme. The cobalt(III) species (A) and vinyl ether may form a complex (F) which will eventually lead to a sigma complex (G). The complex G may undergo O-acylation with acyl halide to give the ester vinyl chloride and cobalt(III) complex (A)[13].



Scheme 2

The presence of cobalt(III) species (A), a better Lewis acid than cobalt(II) may activate the carbon-chloride bond of acyl halide leading to a six membered cyclic transition state (H) which may undergo a concerted O-acylation and β-elimination process to yield the ester and regenerate the cobalt(III) complex (A). The sigma complex is

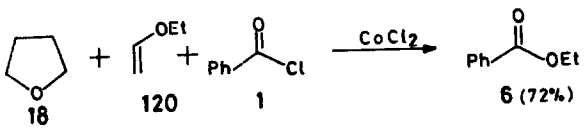
also known from cobaloxime-vinyl ether reaction as shown earlier[14] by Dolphin et al (Eqn. 2).



Eqn. 2

The presence of a carbon-cobalt bond in the complex (H) is also indicated by isolating an small amount of the chloroester **108** and **111** during the acylative cleavage of vinyl ether **107** and **109**. The carbon-cobalt bond has sufficient radical[15] character and therefore the chloroether **108** and **111** may form due to hydrogen atom abstraction by sigma complex. We were unable to trap the vinyl chloride due to its volatile nature, however, vinyl chloride **116**, **118** and **119** were isolated from cyclic vinyl ethers **115** and **117**. These reactions give a trace of biacyl which is in agreement with our proposed mechanism as the initial electron transfer will only generate small amount of acyl radical and hence lead to very little formation of biacyl. The cobalt(III) complex obtained due to electron transfer does not oxidise the acyl radical to acyl cation but it preferentially form a π-complex with vinyl ether. Such electron rich olefin π-complex of trivalent cobalt are speculated[14] during model studies on vitamin B_{12}-coenzyme dependent rearrangement.

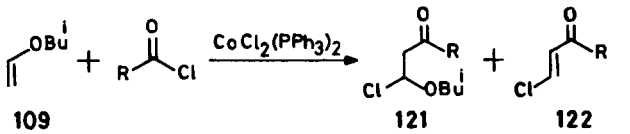
The acylative cleavage of aliphatic ethers and vinyl ethers proceed *via* a different pathway. Thus, when a mixture of tetrahydrofuran and ethyl vinyl ether were subjected to cobalt(II) chloride catalysed acylation with benzoyl chloride (2 equivalents) only the vinyl ether **120** reacted to give corresponding ester 6 alongwith a trace of cleaved tetrahydrofuran (Eqn. 3).



Eqn. 3

This experiment clearly suggests that as soon as the cobalt(III) complex (A) is formed it preferentially reacts with vinyl ether to give a π or σ complex and therefore no complex (A) is available for oxidising the acyl radical to the corresponding cation. It is also clear that any acyl cation generated during the cleavage of vinyl ethers will react at the carbon rather than oxygen in vinyl ether to give β-chloroketones. However, no such compound is obtained during this reaction. On the other hand the complex $CoCl_2(PPh_3)_2$ catalysed the acylation of vinyl ether to give only the β-chloroketones **121** in good yields (Eqn. 4). A careful analysis of the reaction mixture revealed

that no biacyl is formed in this reaction. The later observation indicates that the $CoCl_2(PPh_3)_2$ catalysed acylation does not involve electron transfer and this catalyst may be ionizing the acyl chloride to the acyl cation as a typical Lewis acid.



109 121 122

(a) R = C_6H_5 1 (a) 65% (a) 15%

(b) R = CH_3 3 (b) 47% (b) —

Eqn. 4

In conclusion cobalt(II) chloride is a versatile catalyst for acylative cleavage of a wide variety of ethers and the study described here reveals that these reactions are proceeding via an electron transfer process. The cleavage of vinyl ethers suggests that the reaction is proceeding via a cobalt sigma complex.

EXPERIMENTAL

MATERIALS AND METHODS : Infrared spectra were recorded on Perkin-Elmer 683 spectrometer. Proton magnetic resonance spectra were recorded on Varian EM-390, Bruker WP-80 and Jeol PMX-60 in $CDCl_3$ and CCl_4. The presence of volatile products was confirmed by comparing them with the authentic samples on Shimadzu LC-6A HPLC. Flash chromatography was performed by using Merck and Acme thin-layer chromatography silica gel. Acetonitrile and acyl chlorides were purified by the standard procedures. Cobalt(II) chloride was purchased from LOBA India Ltd., Bombay and dried at 120°C for 2-3 hours prior to use. The ethers were made by the standard procedures. Dibutyl ether and all the vinyl ethers used in this study were obtained commercially and purified prior to use. The iodotetrahydrofurans were prepared[16] by the iodocyclisation of the corresponding hydroxy olefins.

General Procedure for Cobalt(II) Chloride Catalysed Acylation of Ethers with Acyl Chloride : Ether (15 mmol) and acyl halide (25 mmol) were added to a stirred solution of anhydrous cobalt(II) chloride (2 mol%) in anhydrous acetonitrile (70 mL). The mixture was stirred at room temperature under nitrogen for 8-12 h. The solvent was evaporated in vacuum and the residue was dissolved in ether and the ether layer was washed successively with saturated solution of ammonium chloride (3x25 mL), sodium bicarbonate (3x25 ml) and water (3x20 mL). Drying ($MgSO_4$) and evaporation of the solvent gave the crude product, which was purified by flash chromatography on silica gel (pet. ether-diethyl ether).

2-Acetoxy-5-chloro-1-iodohexane(26) and 5-Acetoxy-2-chloro-1-iodohexane(27) : The compound 25 (0.45 g, 2 mmol) and acetyl chloride (0.3 mL, 4 mmol) were reacted according

to the general procedure to give 0.59 g (89%) of **26** and **27** in a 1:1 ratio. These compounds had the following spectral characteristics :**26**: IR(CH_2Cl_2)ν_{max}: 1735 cm^{-1}; ^{1}H-NMR-(CCl_4) :δ : 5.57(m, 1 H), 3.91(m, 1 H), 3.42(m, 2 H), 2.01(s, 3 H), 1.27-1.87(m, 4 H), 1.17(d, 3 H, J = 7 Hz). **27** : IR(CH_2Cl_2)ν_{max}: 1733 cm^{-1}; ^{1}H-NMR(CCl_4) δ ; (5.18 m, 1 H), 4.13(m, 1 H), 3.37(m, 2 H), 1.98(s, 3 H), 1.22-1.89(m, 2 H), 1.21(d, 3 H, J = 7 Hz).

2,5-Diiodomethyltetrahydrofuran (28) : Iodine (5.5 g, 22 mmol) and saturated solution of sodium bicarbonate in water (5 mL) were dissolved in tetrahydrofuran (20 mL) and to this ether (10 mL) and 1,5-hexadiene (0.82 g, 10 mmol) were added. The mixture was stirred at 20°C for 4 hr. and organic solvent was removed under vacuum to give a residue which was dissolved in ether (80 mL) and washed successively with saturated solution of sodium thiosulphate (2x20 mL) and water (2x20 mL). Drying ($MgSO_4$) and evaporation gave an oil which on column chromatography (SiO_4 ether-pet.ether) yielded **28** (3.41 g, 97%). ^{1}H-NMR(CCl_4) δ : 4.01(m, 2 H), 3.11(br s, 2 H), 2.97(m, 2 H), 1.37-2.21(m, 4 H). Anal. Calcd. for $C_6H_{10}I_2$: C, 21.43; H, 2.97. Found : C, 21.39; H, 3.01.

2-Acetoxy-5-chloro-1,2-diiodohexane (29) : Compound **28** (0.7 g, 2 mmol) and acetyl chloride (0.3 mL, 4 mmol) were reacted according to the general procedure to give **29** (0.82 g,96%). IR(thin film)ν_{max}:1735 cm^{-1} ^{1}H-NMR(CCl_4)δ : 5.01(m, 1 H), 4.12(m, 1 H), 3.1-3.67-(m, 4 H), 2.05(s, 3 H), 1.5-1.9(m, 4 H). Anal. Calcd. for $C_8H_{13}O_2I_2Cl$: C, 22.29; H, 3.02. Found : C, 22.21; H, 3.08.

2-Iodomethyl-4-methoxycarbonyl-5-methyltetrahydrofuran (30) : Iodine (3.04 g, 12 mmol), saturated solution of sodium bicarbonate (5 mL) and 5-hydroxy-4-methoxycarbonylhex-1-ene (1.58 g, 10 mmol) were reacted according to the above procedure (as described for the synthesis of **28**) to give **30** (2.7 g, 97%). IR (CH_2Cl_2) ν_{max}: 1738 cm^{-1}; ^{1}H-NMR(CCl_4) δ : 3.81-4.39(m, 2 H), 3.72(s, 3 H), 3.25(m, 2 H), 2.69(m, 1 H), 1.82-2.52(m, 2 H), 1.15(m, 3 H). Anal. Calcd. for $C_8H_{13}O_3I$: C, 33.80; H, 4.58. Found : C, 33.76; H, 4.61.

δ-Lactone (31) : The tetrahydrofuran **30** (0.37 g, 2 mmol) and acetyl chloride (0.78 g, 10 mmol) were reacted according to general procedure to give **31** (0.25 g, 88%). IR(CH_2Cl_2) ν_{max}: 1751, 1735 cm^{-1}; ^{1}H-NMR(CCl_4)δ : 5.17(m, 1 H), 3.78(d, 2 H, J = 7 Hz), 3.57(m, 1 H), 3.36(m, 1 H), 2.18(m, 2 H), 1.96(s, 3 H), 1.27(m, 3 H). Anal. Calcd. for $C_9H_{13}O_4Cl$: C, 48.98; H, 5.89. Found : C, 48.90; H, 5.81.

2-Iodomethyl-4-phenyltetrahydrofuran (32) : An oven dried three necked round bottom flask equipped with reflux condenser and dropping funnel was charged with 1.32 g (55 mmol) of magnesium turning in 50 mL of dry ether. Ice cold water was circulated through the reflux condenser followed by nitrogen flushing of the reaction system. 6.05 g (50 mmol) allyl bromide in 20 mL of dry ether was added dropwise over a period of 20 min. The reaction mixture was allowed to stir at ambient temperature for 30 min. followed by the dropwise addition of styrene oxide (5.64 g, 47 mmol) as a solution in 10 mL of dry ether at 15°C. After the addition of styrene oxide was over, the reaction mixture was allowed to stir for additional 2 h at r.t. The reaction was then quenched

with 5 mL of saturated solution of NH_4Cl. Organic layer was then washed successively with $NaHCO_3$(2x15 mL) and water (2x15 mL) followed by drying ($MgSO_4$). Ethereal solution was then concentrated over rotatory evaporator and briefly placed under vacuum to yield 6.78 g (89%) of 1-hydroxy-2-phenylpentene-4.

Iodine (6.09 g, 24 mmol), saturated solution of sodium bicarbonate (5 mL) and 1-hydroxy-2-phenylpentene-4 (3.2 g, 20 mmol) were reacted according to the procedure described for the synthesis of **25** to give **32** (5.35 g, 94%). ^{1}H-NMR($CDCl_3$) δ : 7.12-7.25 (m, 5 H), 3.78-4.25(m, 3 H), 3.35-3.62(m, 2 H), 1.86-2.76(m, 3 H). Anal. Calcd. for $C_{11}H_{13}OI$: C, 45.83; H, 4.51. Found : C, 45.80; H, 4.49.

2-Acetoxy-5-chloro-4-phenyl-1-iodopentane (33) : The tetrahydrofuran **32** (0.57 g, 2 mmol) and acetyl chloride (0.3 mL, 4 mmol) were reacted according to general procedure to give **33** (0.7 g, 98%). IR(thin film) ν_{max}:1738 cm^{-1}; ^{1}H-NMR(CCl_4) δ : 7.3(m, 5 H), 5.34(m, 1 H), 4.20(d, 2 H, J = 6.8 Hz), 3.55 (m, 2 H), 2.87(m, 1 H), 2.27(m, 2 H), 1.95(s, 3 H). Anal. Calcd. for $C_{13}H_{16}O_2ClI$: C, 40.42; H, 4.40. Found : C, 40.39; H, 4.48.

2-2'-Dichloropropylbenzoate (44) : The reaction between oxirane **43** (0.55 g, 6 mmol) and acid chloride 1 (1.4 g, 10 mmol) according to the general procedure yielded 1.16 g (85%) of **44**. IR(thin film) ν_{max}: 1697 cm^{-1}; ^{1}H-NMR(CCl_4) δ : 8.05(m, 2 H), 7.2-7.56(m, 3 H), 5.39(t, 1 H, J=6Hz), 3.80(d, 4 H, J = 7 Hz).

2,2'-Dichloropropylcrotonoate (45) : The reaction betweent oxirane **43** (0.95 g, 10 mmol) and acid chloride **4** (1.55 g, 15 mmol) according to the general procedure yielded 1.55 g (80%) of **45**. IR(CH_2Cl_2) ν_{max}: 1700 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ : 7.01(m, 1 H), 5.91 (d, 1 H, J = 17 Hz), 5.18(m, 1 H), 3.8(d, 4 H, J = 6.5 Hz), 1.89(d, 3 H, J = 7 Hz).

2,2'-Dichloropropylbutyrate (46) : The reaction between oxirane **43** (0.75 g, 8 mmol) and acid chloride 2 (1.25 g, 12 mmol) according to the general procedure yielded **46** (1.15 g, 72%). IR(CCl_4) ν_{max}: 1735 cm^{-1}; ^{1}H-NMR(CCl_4)δ : 5.17(t, 1 H, J = 6 Hz), 3.8(d, 4 H, J = 6.5 Hz), 2.23(t, 2 H, J = 6.5 Hz), 1.77(m, 2 H), 0.95(t, 3 H, J = 6.5 Hz).

2,2'-Dichloropropylacetate (47) : The reaction between oxirane **43** (0.95 g, 10 mmol) and acid chloride (1.57 g, 20 mmol) according to the general procedure yielded 1.32 g (78%) of **47**. IR(thin layer) ν_{max}: 1731 cm^{-1}; ^{1}H-NMR($CDCl_3$)δ : 5.16(t, 1 H, J = 6 Hz), 3.85(d, 4 H, J = 6.5 Hz), 2.15(s, 3 H).

(2-Chloro-2-phenyl)ethylcrotonoate (51) : The reaction between oxirane **48** (1.2 g, 10 mmol) and acid chloride **4** (1.57 g, 15 mmol) yielded **51** (1.7 g, 78%). IR(CH_2Cl_2) ν_{max}: 1732 cm^{-1}; ^{1}H-NMR(CCl_4) δ : 7.13-7.57(m, 5 H), 6.87(m, 1 H), 5.81(d, 1 H, J = 13 Hz), 5.07(t, 1 H, J = 6.5 Hz), 4.47(d, 2 H, J = 6.5 Hz), 1.89 (d, 3 H, J = 6.7 Hz).

(2-Chloro-2-phenyl)ethylbutyrate (52) : The reaction between oxirane **48** (0.97 g, 8 mmol) and acid chloride 2 (1.28 g, 12 mmol) were stirred with catalytic cobalt(II) chloride (30 mg) in dry acetonitrile. The reaction mixture worked up as described earlier

to give 1.3 g (72%) of 52. IR(CH_2Cl_2) ν_{max}: 1735 cm^{-1}; ^{1}H-NMR(CCl_4) δ : 7.24(br s, 5 H), 5.07(t, 1 H, J = 6 Hz), 4.47(d, 2 H, J = 6.5 Hz), 2.19(t, 2 H, J = 6.5 Hz), 1.76(m, 2 H), 0.87(t, 3 H, J = 6 Hz).

2-Chlorocyclohexylbenzoate (56) : The reaction between oxirane 55 (1.48 g, 15 mmol) and acid chloride 1 (2.54 g, 18 mmol) according to the general procedure yielded 3.1 g (87%) of 56. IR(thin film) ν_{max}: 1695 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ : 8.05(m, 2 H), 7.4(m, 3 H), 5.05(m, 1 H), 4.06(m, 1 H), 1.2-2.27(m, 8 H).

2-Chlorocyclohexylcrotonoate (57) : The reaction between oxirane 55 (1.15 g, 12 mmol) and acid chloride 4 (1.55 g, 15 mmol) according to the general procedure yielded 1.95 g (81%) of 57. IR(CH_2Cl_2) ν_{max}: 1695 cm^{-1}; ^{1}H-NMR(CCl_4) δ : 6.90(m, 1 H), 5.87(d, 1 H, J = 17 Hz), 4.81(m, 1 H), 3.88(m, 1 H), 1.95(d, 3 H, J = 6.5 Hz).

2-Chlorocyclohexylbutyrate (58) : The reaction between oxirane 55 (1.00 g, 10 mmol) and acid chloride 2 (1.10 g, 11 mmol) according to the general procedure yielded 1.60 g (79%) of 58. IR(CH_2Cl_2) ν_{max}: 1730 cm^{-1}; ^{1}H-NMR(CCl_4) δ : 4.8(m, 1 H), 3.79(m, 1 H), 2.28(t, 2 H, J = 7 Hz), 1.19-1.95(m, 10 H), 0.91(t, 3 H, J = 7 Hz).

2-Chlorocyclohexylacetate (59) : The reaction between oxirane 55 (1 g, 10 mmol) and acid chloride 3 (1.55 g, 20 mmol) according to the general procedure yielded 1.50 g (85%) of 59. IR(CH_2Cl_2)ν_{max} 1733 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ : 4.82(m, 1 H), 3.86(m, 1 H), 2.03(s, 3 H), 1.22-1.9(m, 8H).

(2-Chloro-2'-phenoxy)propylcrotonoate (62) : The reaction between oxirane 60 (0.75 g, 5 mmol) and acid chloride 4 (0.85 g, 8 mmol) according to the general procedure yielded 1.0 g (80%) of 62. IR(thin film) ν_{max}: 1700, 1668 cm^{-1}; ^{1}H-NMR(CCl_4) δ : 6.81-7.49(m, 5 H), 6.76(m, 1 H), 5.85(d, 1 H, J = 17 Hz), 5.31(m, 1 H), 4.12(d, 2 H, J = 6.5 Hz), 3.78(d, 2 H, J = 6.5 Hz), 1.88(d, 3 H, J = 7 Hz).

(2-Chloro-2'-phenoxy)propylbutyrate (63) : The reaction between oxirane 60 (1.2 g, mmol) and acid chloride 2 (1.27 g, 12 mmol) according to the general procedure yielded 1.67 g (82%) of 63. IR(thin layer) ν_{max}: 1730, 1661 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ : 7.21 (m, 2 H), 6.82-(m, 3 H), 5.27(m, 1 H), 4.16(d, 2 H, J = 6.7 Hz), 3.79(d, 2 H, J = 6.5 Hz), 2.25(t, 2 H, J = 7 Hz), 1.77(m, 2 H), 0.91(t, 3 H, J = 7 Hz).

(2-Chloro-2'-phenoxy)propylacetate (64) : The reaction between oxirane 60 (0.75 g, 5 mmol) and acid chloride 3 (1.57 g, 10 mmol) according to the general procedure yielded 0.95 g (82%) of 64. IR(CCl_4) ν_{max}: 1735, 1660 cm^{-1}; ^{1}H-NMR(CCl_4) δ : 7.17(m, 2 H), 6.82-(m, 3 H), 5.18(m, 1 H), 4.1(d, 2 H, J = 6.5 Hz), 3.81(d, 2 H, J = 6.5 Hz), 2.05(s, 3 H).

3-Benzoyloxy-2-chloropinane (66) : The reaction between oxirane 65 (0.75 g, 5 mmol) and acid chloride 1 (1.12 g, 8 mmol) according to the general procedure yielded 1.14 g (78%) of 66. IR(CH_2Cl_2) ν_{max} : 1695 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ : 8.15(m, 2 H), 7.56(m, 3 H), 5.57(m, 1 H), 1.85-2.2(m, 3 H), 1.76(s, 3 H), 1.52(s, 6 H), 1.05-1.33 (m, 3 H).

3-Crotonoyloxy-2-chloropinane (68) : The reaction between oxirane 65 (0.6 g, 4 mmol) and acid chloride 4 (0.62 g, 6 mmol) according to the general procedure yielded 0.7 g (72%) of **68**. IR(CH_2Cl_2)ν_{max}: 1700 cm^{-1}; ^{1}H-NMR($CDCl_3$) δ: 6.95(m, 1H), 5.66(d, 1 H, J = 17 Hz), 1.8-2.2(m, 3 H), 1.78(s, 3 H), 1.55(s, 6 H), 0.98-1.21(m, 3 H).

cis(1-Acetoxy-4-chloro)but-2-ene (79) : IR(thin film) ν_{max}: 1735, 1659 cm^{-1}; ^{1}H-NMR (CCl_4) δ: 5.5-5.76(m, 2 H), 5.37(d, 2 H, J = 6.6 Hz), 4.56(d, 2 H, J = 6.8 Hz).

cis(1-Benzoyloxy-4-chloro)but-2-ene (80) : IR(CH_2Cl_2) ν_{max}: 1700, 1665 cm^{-1}; ^{1}H-NMR (CCl_4) δ: 7.2-7.7(m, 5 H), 5.89(d, 2 H, J = 7 Hz), 5.47-5.81(m, 2 H), 4.45(d, 2 H, J = 7 Hz).

cis(4-Chloro-1-crotoyloxy)but-2-ene (81) : IR(CH_2Cl_2) ν_{max}: 1705, 1657 cm^{-1}; ^{1}H-NMR (CCl_4) δ: 7.37(m, 1 H), 5.94-6.68(m, 3 H), 5.41(d, 2 H, J = 7 Hz), 4.46(d, 2 H, J = 6.8 Hz), 1.85(d, 3 H, J = 6.8 Hz).

General Procedure for the Acylative Cleavage of Vinyl Ethers : Vinyl ethers (12 mmol) and acyl chlorides (8 mmol) were stirred in acetonitrile (60 mL) in the presence of a catalytic quantity of anhydrous cobalt(II) chloride (40 mg) at 30°C for 8-10 h. Removal of acetonitrile under vaccum gave a residue which was dissolved in ether (80 mL) and washed successively with $NaHCO_3$ and water. Drying ($MgSO_4$) and evaporation of solvent gave a residue which was purified by column chromatography (SiO_2).

4-Benzoyloxy-1-chloro-but-1-ene (116) : IR(CH_2Cl_2) ν_{max}: 1695, 1660 cm^{-1}; ^{1}H-NMR(CCl_4) δ: 7.2-7.78(m, 6 H), 6.97(m, 1 H), 5.13(t, 2 H, J = 7 Hz), 2.38(m, 2 H).

4-Acetoxy-1-chloro-pent-1-ene (118) : IR(CH_2Cl_2) ν_{max}: 1730, 1665 cm^{-1}; ^{1}H-NMR(CCl_4) δ: 7.21(m, 1 H), 6.77(m, 1 H), 4.36(t, 2 H, J = 6.8 Hz), 2.24(m, 2 H), 1.38(m, 2 H).

4-Benzoyloxy-1-chloro-pent-1-ene (119) : IR(thin layer) ν_{max}: 1700, 1665 cm^{-1}; ^{1}H-NMR (CCl_4) δ: 7.25-7.86(m, 6 H), 6.9(m, 1 H), 5.09(t, 2 H, J = 6.7 Hz), 2.36(m, 2 H), 1.39(m, 2 H).

3-Chloro-3-isobutyloxypropiophenone (121) : The acid chloride 1 (1.4 g, 10 mmol) and vinyl ether **109** (1.5 g, 15 mmol) were added to benzene (50 mL) in the presence of a catalytic amount of $CoCl_2(PPh_3)_2$ (30 mg). The mixture was stirred at 30°C for 14 hr. and benzene was removed under vacuo to give a residue which was chromatographed over silica gel (pet. ether-diethyl ether) to yield **121** (2.3 g, 65%). IR(thin film) ν_{max}: 1695 cm^{-1}; ^{1}H-NMR(CCl_4) δ : 8.13(m, 2 H), 7.52(m, 3 H), 4.67(t, 1 H, J = 7 Hz), 3.48(m, 2 H), 3.18(d, 2 H, 6.8 Hz), 1.89(m, 1 H), 0.89(d, 6 H, J = 7 Hz).

REFERENCE AND NOTES

1. (a) Flowers, H.M. Chemistry of the hydroxyl group; Patai, S., Ed.; Interscience; New York, **1969**; Chapter 7, p. 1001 and references therein. (b) Cunnigham, J.; Gigg, R.; Warren, G.D. Tetrahedron Lett., **1964**, 1196. (c) Tate, M.E.; Bishop, C.D. Can. J. Chem. **1963**, 41, 1801.

2. (a) Fujii, K.; Ichikawa, K.; Node, M.; Fuji, E. J. Org. Chem. **1970**, 44, 1661. (b) Harrison, I.T.; Harrison, S. Compendium of Organic Method; Wiley-Interscience; New York, **1971**; vol. 1, pp. 92-99, 127-128. (c) Hanessian, S.; Guindon, Y. Tetrahedron Lett. **1980**, 2305. (d) Jung, M.E.; Lyster, M.A. J. Org. Chem. **1977**, 42, 3761. (e) Spyroudis, S.S.; Varvoglis, A. J. Chem. Soc. Chem. Comm. **1979**, 615. (f) Narayanan, C.R.; Iynger, K. N. J. Org. Chem., **1965**, 30, 1734.

3. (a) Niwa, H.; Hida, T.; Yamada, K. Tetrahedron Lett. **1981**, 22, 4239. (b) Guindon, Y.; Yoakim, C.; Horton, H.E. Tetrahedron Lett. **1983**, 24, 2969.

4. Johnson, F. "Friedel-Crafts and related reaction". Olah, G.A., Ed.; Interscience; New York, **1965**, 4, pp. 1-109.

5. (a) Jung, M.E.; Lyster, M.A. J. Org. Chem. **1977**, 42, 3761. (b) Olah, G.A.; Narang, S.C.; Gupta, B.G.; Malhotra, R. J. Org. Chem. **1979**, 44, 1247. (c) Bhatt, M.V.; El-Morey, S.S. Synthesis, **1982**, 1048.

6. For a review on ether cleavage see : Bhatt, M.V.; Kulkarni, S.U. Synthesis **1983**, 249.

7. (a) Alper, H.; Huang, C. J. Org. Chem. **1973**, 38, 64. (b) Ganem, B.; Small, R.V. J. Org. Chem. **1974**, 39, 3728. (c) Pri-Bar, I.; Still, J.K. J. Org. Chem. **1982**, 47, 1215. (d) Shibata, I.; Baba, A.; Matsuda, H. Tetrahedron Lett. **1986**, 27, 3021.

8. Ahmad, S.; Iqbal, J. Chem. Lett. **1987**, 953.

9. (a) Raylander, P.N. in "Catalytic hydrogenation over platinum metals"; Academic press : New York, 1967; p. 449. (b) Barton, D.H.R.; Magnus, P.D.; Srecket, G.S.; Furr, D. J. Chem. Soc., Perkin Trans., **1972**, 1, 542. (c) Olah, G.A.; Surya-Prakash, G.K.; Narang, S.C. Synthesis **1978**, 11, 825.

10. For electron transfer involving cobalt(II) complexes see : (a) Ahmad, S., Iqbal, J. J. Chem. Soc., Chem. Comm. **1987**, 692. (b) Iqbal, J.; Pandey, A. Tetrahedron Lett. **1990**, 575. (c) Iqbal, J.; Pandey, A.; Shukla, A.; Srivastava, R.R.; Tripathi, S. Tetrahedron **1990**, 46, 6423.

11. For oxidation of acyl radical to acyl cation see : Kochi, J.K. in "Organometallic mechanism and catalysis", Academic Press, New York, **1978**; Chapter 5 and references therein.

12. Iqbal, J.; Kumar, T.K.P.; Manogaran, S. Tetrahedron Lett. **1989**, 30, 4701.

13. For cobalt(III) and vinyl ether complexes see : Dolphin, D. in "Biomimetic Chemistry"; American Chemical Society, Washington, D.C., **1980**; Chapter 5.

14. Silverman, R.B.; Dolphin, D. J. Am. Chem. Soc., **1976**, 98, 4626.

15. For radical character of carbon-cobalt bond see : Halpern, J. in "Biomimetic Chemistry"; American Chemical Society, Washington, D.C., **1980**, Chapter 9.

16. Rychnovsky, S.D.; Bartlet, P.A. J. Am. Chem. Soc., **1981**, 103, 3963.