Cobalt(II) Chloride Catalysed Coupling of Acetic Anhydride with Aldehydes. A Novel Synthesis of Asymmetrical 1,2-Diones

Saeed Ahmad and Javed Iqbal*

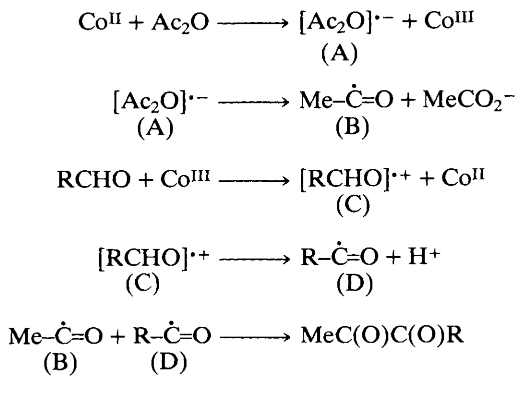
Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India

Cobalt(II) chloride in acetonitrile efficiently catalyses the coupling of acetic anhydride with various aldehydes to the corresponding 1,2-diones in very high yields.

We have recently shown[1] that cobalt(II) chloride efficiently catalyses the acylation of thiols, alcohols, and amines in very high yields. In an attempt to acylate an aldehyde with acetic anhydride in the presence of cobalt(II) chloride we observed the unusual formation of unsymmetrical 1,2-diones in very high yields. Although there are various methods[2] available for the general synthesis of 1,2-diones, very few of them are suitable for the synthesis of unsymmetrical diones having a methyl group attached to one of the carbonyl groups. The oxidation of α-methylene carbonyl compounds by selenium dioxide[2a] is a good general route to 1,2-diones. However, this method is not suitable for the synthesis of a methyl dione as the methyl ketone moiety present in these molecules also undergoes oxidation to the corresponding glyoxal. Methods suitable for the synthesis of unsymmetrical methyl diones, such as oxidation of carbon–carbon multiple bonds by ruthenium tetraoxide,[2c] and the oxidative hydrolysis[2g] of α-ketodithione by silver salts, although efficient are uneconomical on a large scale owing to the use of expensive metal salt. 1,2-Diones are also accessible by the oxidation of acyloin[2a] and α-bromoketones[2e] but the latter method is not suitable for the synthesis of methyl diones as there is no regiochemical control during the bromination of unsymmetrical aliphatic ketones under these conditions. The synthetic utility[2a,3] of 1,2-diones coupled with their application in conformational analysis[4] and photochemistry[5] led us to study the cobalt chloride catalysed coupling of aldehydes with acetic anhydride.

When a catalytic amount (5 mol%) of anhydrous cobalt(II) chloride dissolved in degassed dry acetonitrile was stirred with a mixture of acetic anhydride (3 equiv.) and an aldehyde (1 equiv.) for 24 h at ambient temperature, after the usual work-up very high yields of unsymmetrical 1,2-diones were obtained. Our results are shown in Table 1.

The formation of 1,2-diones can be explained by invoking the intermediacy of an electron transfer process. Thus, an electron transfer from the cobalt(II) complex to acetic anhydride may lead to the formation of a radical anion (A) (Scheme 1) which can undergo fragmentation to the acetyl radical (B) and the acetate anion. The cobalt(III) species thus formed will oxidise the aldehyde to give the cobalt(II) complex back and a radical cation (C), which splits into an acyl radical (D) and a proton. Acetyl radical (B) and the acyl radical (D) then undergo coupling to the observed 1,2-dione. The oxidation of an aldehyde by a cobalt(III) complex to the corresponding acyl radical[6] is fairly well precedented in the



$$\mathrm{Co^{II}} + \mathrm{Ac_2O} \longrightarrow \underset{\text{(A)}}{[\mathrm{Ac_2O}]^{\cdot-}} + \mathrm{Co^{III}}$$

$$\underset{\text{(A)}}{[\mathrm{Ac_2O}]^{\cdot-}} \longrightarrow \underset{\text{(B)}}{\mathrm{Me{-}\dot{C}{=}O}} + \mathrm{MeCO_2^-}$$

$$\mathrm{RCHO} + \mathrm{Co^{III}} \longrightarrow \underset{\text{(C)}}{[\mathrm{RCHO}]^{\cdot+}} + \mathrm{Co^{II}}$$

$$\underset{\text{(C)}}{[\mathrm{RCHO}]^{\cdot+}} \longrightarrow \underset{\text{(D)}}{\mathrm{R{-}\dot{C}{=}O}} + \mathrm{H^+}$$

$$\underset{\text{(B)}}{\mathrm{Me{-}\dot{C}{=}O}} + \underset{\text{(D)}}{\mathrm{R{-}\dot{C}{=}O}} \longrightarrow \mathrm{MeC(O)C(O)R}$$

Scheme 1

Table 1. Cobalt(II) chloride catalysed coupling of acetic anhydride and aldehydes.[a]

$$(\mathrm{MeCO})_2\mathrm{O} + \mathrm{RCHO} \longrightarrow \underset{(\mathbf{1})}{\mathrm{MeC(O)C(O)R}} + \underset{(\mathbf{2})}{\mathrm{RC(O)C(O)R}} + \underset{(\mathbf{3})}{(\mathrm{MeCO})_2}$$

		% Yield of product(s)[c]		
R	Equiv. $(MeCO)_2O$	(1)	(2)	(3)
Ph	1	12	65	45
Ph	3	81	8	6
Ph	0[b]	0	<5	0
n-C_3H_7	1	12	61	48
n-C_3H_7	3	76	8	8
n-C_5H_{11}	3	81	7	5
MeCH=CH	3	89	0	5
PhCH=CH	3	83	0	7
4-$NO_2C_6H_4$	1	8	78	34
4-$NO_2C_6H_4$	3	82	5	9
4-ClC_6H_4	1	14	59	37
4-ClC_6H_4	3	77	6	7
4-$OMeC_6H_4$	3	65	0	15
4-OHC_6H_4	4	79[d]	0	6
2-OHC_6H_4	4	73[d]	0	8
$\overline{\mathrm{OCH{=}CHCH{=}C}}$–	3	77	0	16

[a] All the reactions were carried out in the presence of a catalytic amount of anhydrous cobalt(II) chloride and acetic anhydride in dry acetonitrile at room temperature for 24 h, unless stated otherwise. [b] No acetic anhydride. [c] Yield of the isolated product. All the products were satisfactorily characterised by ^{1}H n.m.r. and i.r. spectroscopy. [d] The hydroxy group in these products was found to be completely acetylated.

literature. The requirement of cobalt(II) chloride in catalytic amounts and the formation of a mixture of 1,2-diones, together with the observation that no self-coupling of aldehydes takes place in the absence of acetic anhydride, clearly indicates that the first step of this reaction is an electron transfer from the cobalt(II) complex to the acetic anhydride. The formation of biacetyl† when acetic anhydride is treated with cobalt(II) chloride in acetonitrile further supports the view of initial electron transfer to the acetic anhydride.

In conclusion cobalt(II) chloride catalysed coupling of acetic anhydride with aldehydes is the first one-pot general synthesis of asymmetrical 1,2-diones having a methyl group on one of the carbonyl carbons. This study has also revealed for the first time electron transfer from a cobalt(II) complex to acetic anhydride.

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† Approximately 10—15% of biacetyl was isolated when an equimolar mixture of anhydrous cobalt(II) chloride and acetic anhydride was stirred in acetonitrile at ambient temperature for 24 h.