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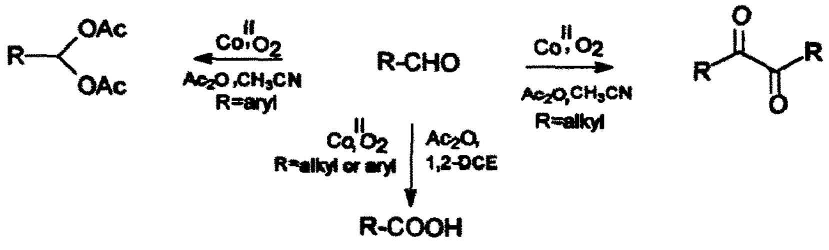
Cobalt Catalysed Synthesis of 1,2-Diones from Aromatic Aldehydes in the Presence of n-Butanal

T.Punniyamurthy, Swinder Jeet Singh Kalra and Javed Iqbal*
Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, INDIA

Abstract: *Cobalt(II) chloride catalyses the oxidative coupling of a wide range of aromatic aldehydes in the presence of dioxygen to afford 1,2-diones or carboxylic acids. Aromatic aldehydes may be transformed to 1,2-diones in the presence of n-butanal whereas the presence of acetic anhydride and n-butanal lead to the formation of the corresponding carboxylic acids.*

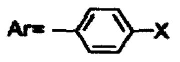
Metal catalysed oxidative coupling of aldehydes is known to provide an easy access[1] to 1,2-diones, however, it has been a relatively unexplored pathway to this type of compounds. We have recently demonstrated[2] that cobalt(II) chloride catalyses the coupling of aliphatic aldehydes in the presence of acetic anhydride and dioxygen to afford 1,2-diones. However, the aromatic aldehydes behaved quite differently under these conditions, and depending upon the reaction medium, they were either oxidised to the corresponding carboxylic acid or underwent transformation to acylals (scheme I). We now report that an aliphatic aldehyde (n-butanal) has an interesting effect on the reactivity of aromatic aldehydes as the latter can be transformed to the corresponding symmetrical 1,2-diones in high yields. Thus, the reaction of aromatic aldehydes (10 mmol) and n-butanal (1 mmol) in the presence of dioxygen and catalytic cobalt(II) chloride in acetonitrile at ambient temperature afforded the corresponding 1,2-dione 1 in high yields (table I). It is interesting to note that the 4-substituted benzaldehydes undergo the 1,2-dione formation quite readily whereas benzaldehyde or 4-methoxy benzaldehyde are mainly transformed to the corresponding carboxylic acids 2. Similarly, pyridine aldehyde also provides high yield of 1,2-dione and acid 2 under these conditions (scheme II). Surprisingly, no 1,2-diones are observed when these reactions are carried out in the presence of 3 fold excess of acetic

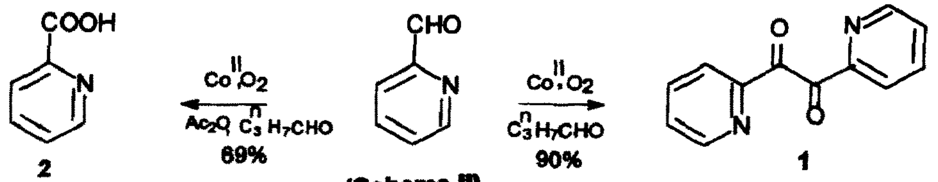


(Scheme I)

anhydride and n-butanal, and instead the corresponding carboxylic acids **2** are obtained in good yields (table I). This difference in the behaviour of the aromatic aldehydes is clearly due to the presence of n-butanal as our earlier studies have indicated[2] that the reaction of aromatic aldehydes with excess of acetic anhydride and cobalt(II) chloride in acetonitrile afford the corresponding acylal in high yield (scheme I). It is interesting to note that compound **1** or**2** can also be obtained in good yield by using catalytic amount of n-butanal(5 mol %) as no significant difference in the yield of 1,2-dione is observed by increasing the quantity of n-butanal. A non-aqueous analysis of the reaction mixture reveals that n-butanal undergoes transformation to butyric acid under these conditions and there is no observable cross or homo coupling between the two aldehydes.

Table I. Cobalt (II) Catalysed Reaction of Aromatic Aldehydes with Molecular Oxygen in the Presence of n-Butanal

entry	Ar= 	product(s) (% yield)	
		1,2-dione 1	Acid 2
1	X=H	-	71
2	F	70	68
3	Cl	81	65
4	Br	65	63
5	CN	33	69
6	Me	52	75
7	OAc	–	62
8	OMe	–	71



(Scheme II)

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