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ACYLCOBALT SALOPHEN REAGENTS. PRECURSORS TO ACYL RADICAL INTERMEDIATES FOR INTER- AND INTRA-MOLECULAR OXIDATIVE MICHAEL ADDITION REACTIONS

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Summary: Acylcobalt salophens (2) undergo homolytic cleavage (Δ, sunlamp) producing acyl radicals (10) which undergo oxidative additions to activated carbon-to-carbon double bonds leading to enones and functionalised ring systems e.g. (3)→(4); (5)→(6); (7)→(8); (12)→(13); and (14)→(15).

We have previously described the use of a range of cobalt(I) reagents in both inter- and intra-molecular radical addition reactions to carbon-to-carbon double bonds.[1] These reactions lead to product radical centres which can usually be trapped *in situ* producing new isolable alkyl organocobalt reagents. We have also shown that photochemical homolyses of the same organocobalt compounds in the presence of radical trapping agents provides a useful route to functionalised (oxygen, nitrogen, halogen, sulphur, selenium, nitrile, carbon) radical bond-forming products[2]. In further investigations of the scope for stable organocobalt reagents in synthesis we have now prepared a range of acylcobalt salophen compounds and studied their chemistry. In this *Letter* we describe the use of these reagents as precursors to acyl radicals for carrying out oxidative additions to activated carbon-to-carbon double bonds leading to enones and functionalised ring systems.

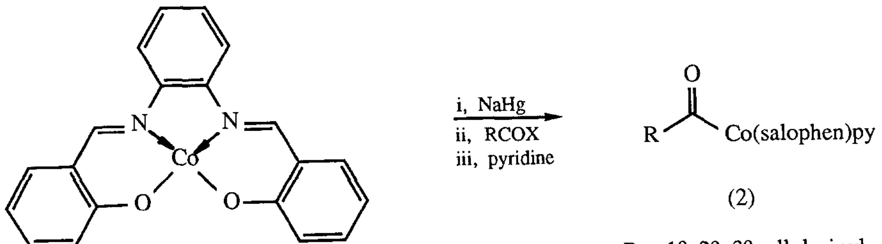
Acylcobalt salophen reagents are conveniently synthesised from carboxylic acid chlorides or the mixed anhydrides with 2,6-dichlorobenzoic acid, following treatment with the sodium derivative produced from reduction of cobalt(II) salophen (1)(1%NaHg,THF,25°C),and chromatographic purification in the presence of pyridine. In this manner, we have prepared a range of primary, secondary, tertiary, allyl, vinyl, aryl and arylmethyl acylcobalt salophens (2), all of which are brightly coloured, stable crystalline materials.[3]

Irradiation of a de-aerated refluxing solution of propionoylcobalt salophen (3) and ethyl propenoate (10 equivs) in methylene dichloride, using light from a conventional 300W sunlamp (20-30 cm distance) for 18-24h (with monitoring by t.l.c.), followed by work-up and chromomatography led to the separation of a single adduct (40%) whose spectroscopic data, ν_{max} 1720, 1700, 1640, 990 cm.$^{-1}$, δ_H 7.08 (d, *J* 16, COC$\underline{H}$:), 6.64 (d, *J* 16 : C$\underline{H}$CO$_2$Et,) 4.26 (q, *J* 7, C$\underline{H}_2$CH$_3$), 2.7 (q, *J* 7.5, CH$_2$CO), 1.32 (t, *J* 7, CH$_3$), 1.13 (t, *J* 7.5, CH$_3$), were consistent with the known E-isomer (4) of ethyl 4-oxo-2-hexenoate. During some experiments we also detected small amounts of the *Z*-isomer corresponding to (4)(δ_H 6.5 and 5.98, AB system, *J* 12) in crude reaction products, which was rapidly isomerised to (4) during attempted purification and chromatography. In a similar manner, irradiation of the acylcobalt reagent (5) derived from cyclopentanecarboxylic acid in the presence of styrene, led to the *E*-isomer (6) of 3-phenyl-2-propenoylcyclopentane (40%), δ_H 6.85 (d, *J* 15, :C$\underline{H}$), 6.28 (d, *J* 15, :C$\underline{H}$), and irradiation of a solution of the 4-methoxybenzoylcobalt derivative (7) and methyl vinyl ketone in methylene dichloride produced (25%) the *E*-2-penten-1,4-dione (8), ν_{max} 1660, 1610 cm.$^{-1}$, δ_H 7.71 (d, *J* 16, :C$\underline{H}$.COAr), 7.06 (d, *J* 16, :C$\underline{H}$.COMe), 2.42 (COMe)[4].

In each of the above reactions the acylcobalt salophen reagent is behaving as a source of the corresponding acyl radical intermediate (10), which adds in a Michael fashion to the olefin substrate leading to a short lived organocobalt species *viz* (11) which then suffers β-elimination of H-Co producing the conjugated enone products (see Scheme). The acylcobalts therefore assume a dual role, viz nucleophilic acyl reagents with a capacity for the cobalt moiety to effect an oxidation (i.e. elimination of H-Co)[5]. In one instance only, i.e. the addition of (7) to methyl vinyl ketone, were we able to isolate some of the 'saturated' product (9, 20%) corresponding to (8) from the reaction.

To augment the use of acyl radical intermediates for carrying out oxidative additions of the type shown above, we examined corresponding intramolecular cyclisations from the acylcobalt salophen reagents (12) and (14)[6]. Thus, irradiation of (12) in methylene dichloride for 20h, followed by chromatography and crystallisation led to the crystalline *Z*- and oily-*E*-isomer of the benzylidenecyclopentanone (13) in a combined yield of 42%. Similarly, the acyl cobalt reagent (14) derived from ethyl 6-carboxy-2-hexenoate underwent intramolecular oxidative addition on irradiation leading to the 4-keto-2-enoate (15)(25%), whose formation was accompanied by the 4-keto ester product (16)(28%) resulting from intramolecular addition only.

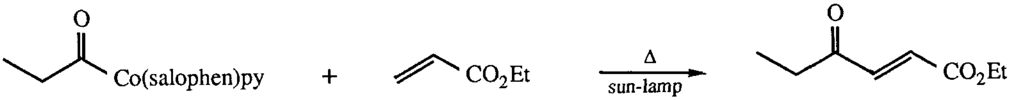
As a corollary we also examined the reactions between the acylcobalt salophen compounds (2) and diphenyldisulphide and diphenyldiselenide. In every case (CH$_2$Cl$_2$ solutions, sunlamp, 18h) the corresponding phenylthio and phenylseleno esters (17) were produced in high yields (70-80%)[7].



(1); Co(salophen)

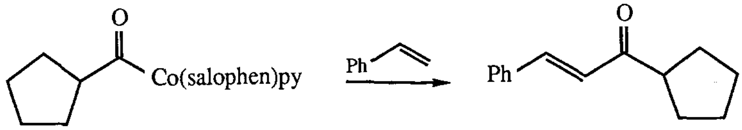
(2)

R = 1°, 2°, 3°, allyl,vinyl, aryl, OR', NR'$_2$ etc.,



(3)

(4)



(5)

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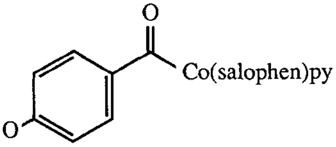

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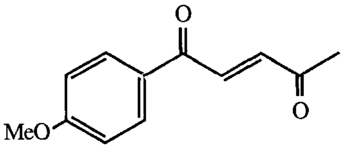

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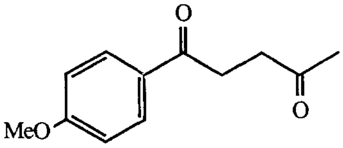

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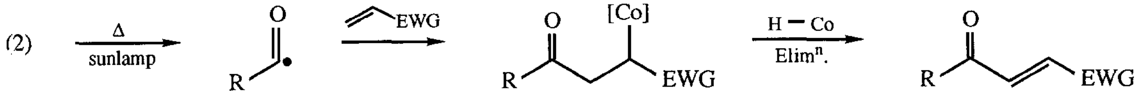
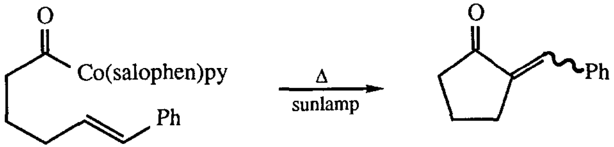


(10)

(11)

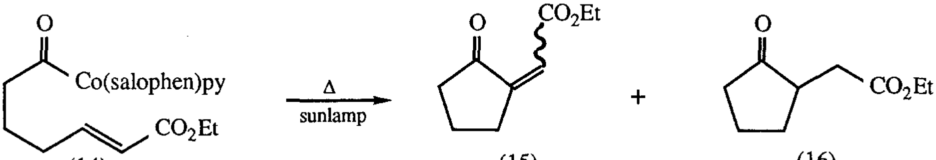
EWG - electron withdrawing group

Scheme



(12)

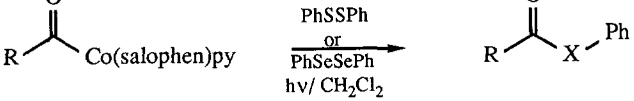
(13)



(14)

(15)

(16)



(2)

(17)

X = S or Se

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