Cobalt Mediated Radical Addition–Elimination Carbon–Carbon Bond Forming Reactions in Synthesis

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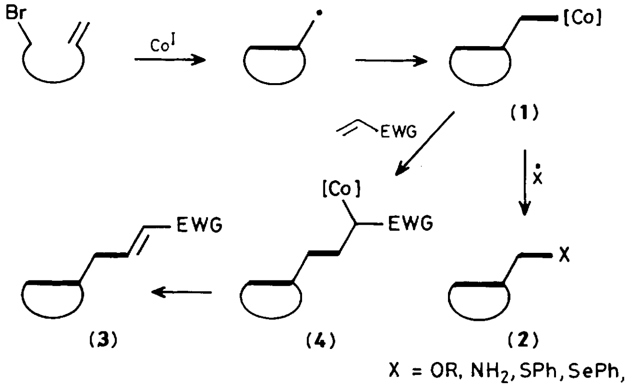
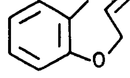
Alkyl radicals generated by photolytic homolysis of cobalt 'salophen' reagents add to activated carbon–carbon double bonds producing preparatively useful yields of new alkene products; the reactions proceed *via* radical (Michael) addition, followed by elimination of H–Co.

The addition of carbon radicals to alkenes is one of the most powerful methods for the formation of carbon–carbon bonds. These reactions lead to product carbon radicals which either react further with a radical donor (frequently H$^\bullet$) or undergo elimination, depending on the substitution pattern, producing new alkene products. A number of publications attest the preparative value of these reactions in synthesis.[1,2] We have recently described the use of cobalt(I) reagents in intramolecular radical cyclisations leading to product radicals which can be trapped *in situ* leading to isolable organo-cobalt intermediates, *viz.* (**1**).[3,4] We have also found that photolytic homolysis of the organo-cobalt compounds in the presence of radical trapping agents provides novel routes to functionalised radical cyclisation products (**2**) (Scheme 1).[5] We describe here the outcome of studies of the photolytic homolysis of the aforementioned cobalt compounds in the presence of activated carbon–carbon double bonds. These novel reactions are

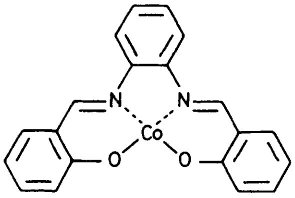


X = OR, NH$_2$, SPh, SePh, SO$_2$H, Cl, Br, I

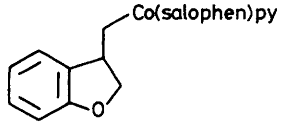
Scheme 1. (EWG = electron withdrawing group)



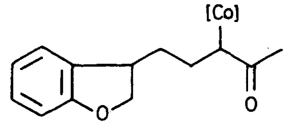
(5)



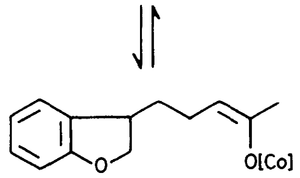
(6)
Co-salophen



(7)



(8)



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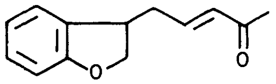

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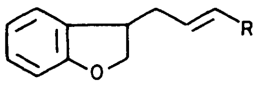
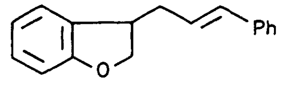
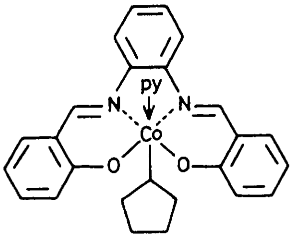


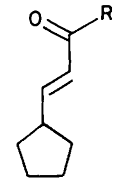
(10)
a; R = CO_2Et
b; R = CN



(11)



(12)



(13)
a; R = Me
b; R = OEt

shown to lead to new alkene products (3) which result from radical (Michael) addition to the C–C double bonds followed by 1,2-elimination of H–Co from the presumed organo-cobalt intermediates (4) (Scheme 1).[6]

Thus, radical cyclisation of the iodoaryl allyl ether (5) in the presence of the cobalt 'salophen' reagent (6) [1% NaHg, tetrahydrofuran (THF), 25 °C, dark] first led to the black crystalline organo-cobalt compound (7). When a refluxing solution of (7) in methylene dichloride was irradiated (300 W sunlamp, 36 h) in the presence of methyl vinyl ketone (5 equiv.), work-up and chromatography led to the separation of a single adduct (50%) whose spectroscopic data, ν_{max} (film) 1680, 1630, 1600 cm^{-1}, δ_H 7.1—7.2 (m, 2 × ArH), 6.8—7.0 (m, 2 × ArH), 6.77 (dt, *J* 7 and 16 Hz, $CH_2CH:CH$), 6.13 (dt, *J* 16 and 1.4 Hz, $CH_2CH:CH$), 4.62 (t, *J* 9 Hz, OC*H*H), 4.22 (dd, *J* 5.8 and 9 Hz, OCH*H*), 3.6 (m, ArCH), 2.6 (m, $CH_2CH:CH$), 2.25 (COMe), were consonant with the (*E*)-enone (9). In a similar manner, irradiation of (7) in the presence of ethyl acrylate or acrylonitrile led to the corresponding adducts (**10a**) (65%) and (**10b**) (30%) respectively.† The adducts (9), (**10a**), and (**10b**) result from Michael addition of the alkyl radical, generated from homolysis of (7), to the acceptors, followed by 1,2-elimination of H–Co from the presumed intermediate organo-cobalt compounds [*viz.* (8)]. Attempts to effect preparative 'one-pot' syntheses of the adducts (9) and (10), following treatment of (5) with Co^I 'salophen' and then with the Michael acceptors were not successful; <5% of the corresponding adducts were produced by this procedure.

Significantly higher yields in the addition–elimination sequence (1) → (4) → (3) (Scheme 1) were realised when styrene was used as the 'Michael' acceptor. Thus, yields of 75—80% of the adduct (11) were produced when the organo-cobalt compound (7) was irradiated in the presence of styrene. This result may well reflect the ease of elimination of H–Co in the second step of the sequence, over those cases involving methyl vinyl ketone, ethyl acrylate, and acrylonitrile.

Secondary alkyl radicals were found to behave in a similar manner to primary radicals in the addition–elimination sequence, as evidenced by studies with the organo-cobalt 'salophen' (12) derived from bromocyclopentane. Like (7), the cobalt 'salophen' (12) underwent photolytic homolysis in the presence of both methyl vinyl ketone and ethyl acrylate producing the corresponding (*E*)-adducts (**13a**) and (**13b**) in 45% and 55% yield, respectively.†

It seems clear that the cobalt-mediated radical addition–elimination sequence highlighted here offers considerable scope in the synthesis of carbon-to-carbon double bonds. It is also clear that the method both complements, and provides a satisfactory alternative to, similar radical methods based on the use of β-stannyl substituted acrylates and related Michael acceptors.[1]

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6 For an example using vitamin B_{12} in organocobalt-mediated C–C bond forming reactions (without H–Co elimination) see: R. Scheffold, in 'Modern Synthetic Methods,' Vol. 3, Ed. R. Scheffold, John Wiley and Sons Ltd., Chichester, 1983.

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† Satisfactory spectroscopic data, together with microanalytical and/or mass spectroscopic data, were obtained for all new compounds.