

Cobalt-catalysed Oligomerisation of Methyl Methacrylate; Reactivation of Oligomers by Hydrocobaltation

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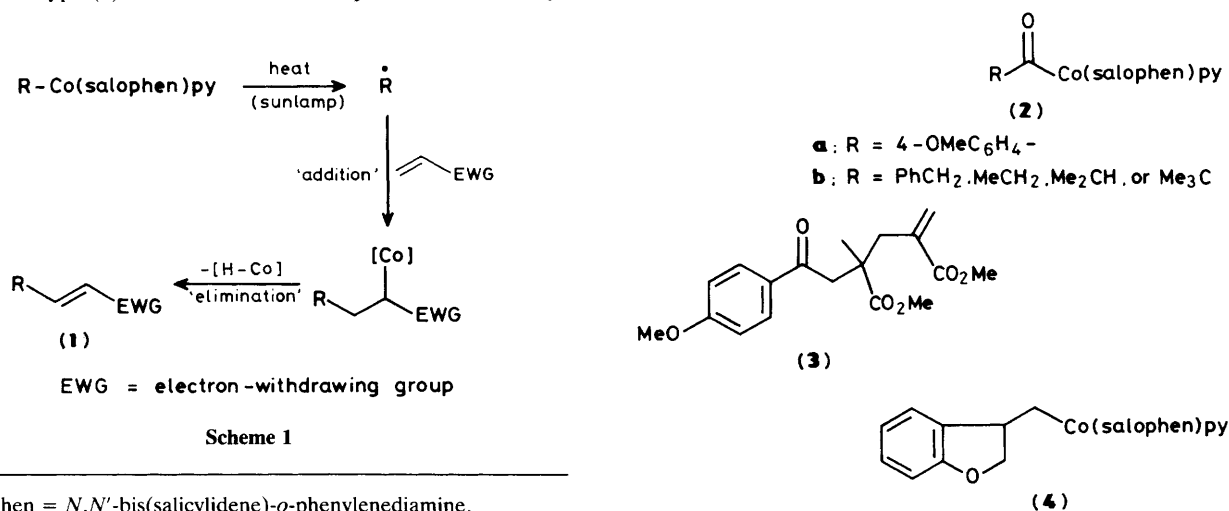
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Irradiation of methyl methacrylate (MMA) in the presence of acyl- and alkyl-cobalt 'salophen' reagents leads to good yields of oligomers [(11)–(13)] by way of a novel catalytic 'hydrocobaltation–dehydrocobaltation' sequence; hydrocobaltation of the dimer (11) [to (14)] followed by conversion of the latter into (15) in the presence of styrene demonstrates the possibilities for 'reactivation' of oligomers of MMA for further chemical studies.

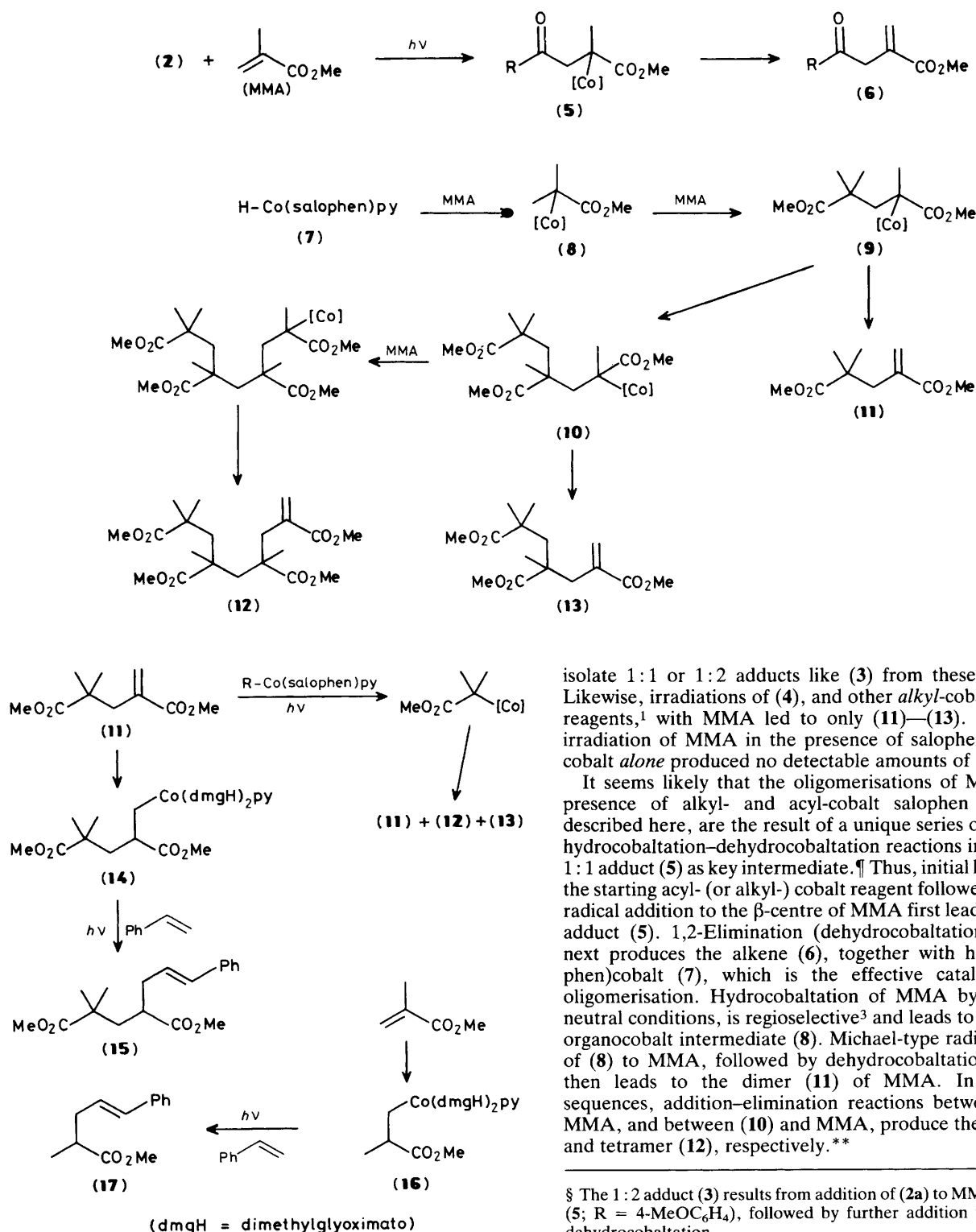
In recent publications we have described the reactions between a range of C → C double bonds and alkyl and acyl radical intermediates, which were generated by photolytic homolysis of the corresponding cobalt 'salophen' reagents.^{1,2†} These reactions led to new alkene products *via* a sequence involving Michael-type addition of the radicals to the alkenes followed by dehydrocobaltation, *i.e.* 1,2-elimination of [H–Co] from short-lived organocobalt intermediates (Scheme 1). We have now examined a number of corresponding reactions using methyl methacrylate, together with other more substituted (both α- and β-) alkene substrates. The reactions were found to be uniformly less efficient in the synthesis of 1:1 adducts of type (1). Furthermore, in the special case of methyl

methacrylate (MMA) the reactions led largely to the formation of oligomers of MMA by way of an interesting and unusual photoinduced catalytic 'hydrocobaltation–dehydrocobaltation' sequence. In this paper we summarise the details of this cobalt-catalysed oligomerisation of MMA, and with the dimer (11) of MMA as an example, we also demonstrate the possibilities for 'reactivation' of oligomers using the principle of hydrocobaltation.

Thus, irradiation of a deaerated solution of the acylcobalt salophen (2a)² and MMA (5 equiv.) in methylene dichloride, using light from a 300 W sunlamp (48 h), followed by work-up



† Salophen = *N,N'*-bis(salicylidene)-*o*-phenylenediamine.



and chromatography, led largely to a mixture of the dimer (11) (25%), the trimer (13) (20%), and the tetramer (12) (20%) of MMA, accompanied by small amounts (*ca.* 10%) of the 1:2 adduct (3).[‡] Similar reactions with a range of alternative acylsalophen reagents, *i.e.* (2b),² led to comparable yields of the MMA oligomers (11)–(13), but in no case were we able to

isolate 1:1 or 1:2 adducts like (3) from these reactions.[§] Likewise, irradiations of (4), and other *alkyl*-cobalt salophen reagents,¹ with MMA led to only (11)–(13). Conversely, irradiation of MMA in the presence of salophen(pyridine)-cobalt *alone* produced no detectable amounts of oligomers.

It seems likely that the oligomerisations of MMA in the presence of alkyl- and acyl-cobalt salophen complexes, described here, are the result of a unique series of controlled hydrocobaltation–dehydrocobaltation reactions involving the 1:1 adduct (5) as key intermediate.[¶] Thus, initial homolysis of the starting acyl- (or alkyl-) cobalt reagent followed by carbon radical addition to the β-centre of MMA first leads to the 1:1 adduct (5). 1,2-Elimination (dehydrocobaltation) from (5) next produces the alkene (6), together with hydrido(salophen)cobalt (7), which is the effective catalyst for the oligomerisation. Hydrocobaltation of MMA by (7), under neutral conditions, is regioselective³ and leads to the reactive organocobalt intermediate (8). Michael-type radical addition of (8) to MMA, followed by dehydrocobaltation from (9), then leads to the dimer (11) of MMA. In alternative sequences, addition–elimination reactions between (9) and MMA, and between (10) and MMA, produce the trimer (13) and tetramer (12), respectively.^{**}

[§] The 1:2 adduct (3) results from addition of (2a) to MMA, leading to (5; R = 4-MeOC₆H₄), followed by further addition to MMA and dehydrocobaltation.

[¶] *Cf.* the formation of (3) from (2a) *via* (5; R = 4-MeOC₆H₄).

^{**} The cobalt-catalysed dimerisation of MMA has also been investigated recently by Abbey *et al.*⁴ and by Kijima *et al.*⁵ These groups have shown that in the presence of cobaloxime or alkylcobaloximes, MMA is converted only into the dimer (11); subsequent treatment of the dimer (11) with azobisisobutyronitrile was then shown⁴ to lead to the trimer (13) and the tetramer (12) together with the positional isomer MeO₂C·CMe₂·CH=C(CO₂Me)CH₂·CMe₂·CO₂Me (*Z*- and *E*-forms) of (13).

[‡] Satisfactory spectroscopic data, together with microanalytical and/or mass spectrometric data, were obtained for all new compounds.

In separate experiments, we were able to initiate further polymerisation of the dimer (**11**) by simple irradiation in methylene dichloride in the presence of an alkyl- or acyl-cobalt salophen complex; thus, the dimer (**11**) with (**2b**) led to a 2:1:1 mixture of (**11**), (**12**), and (**13**) (total yield 76%).

As a corollary, and as an extension of our other work,³ we have also demonstrated that it is possible to 'reactivate' the oligomers of MMA for further chemical studies, by applying the principle of hydrocobaltation.⁶ Thus, treatment of the dimer (**11**) with $\text{Co}(\text{dmgH})_2 \cdot 2\text{H}_2\text{O}$ (from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, dimethylglyoxime, pyridine, and MeOH) under alkaline conditions (aq. NaOH) in the presence of hydrogen, followed by work-up, led to the crystalline cobaloxime (**14**).^{††} Irradiation of (**14**) in the presence of styrene (10 equiv.) then led to the adduct (**15**) (ca. 10%) resulting from a homolysis-addition-elimination sequence, together with recovered dimer (**11**). The adduct (**15**) showed spectral data closely similar to those of the corresponding adduct (**17**) produced from styrene and the cobaloxime (**16**) obtained from MMA.⁵

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