

Hydrocobaltation–Dehydrocobaltation Reactions in Synthesis: A New Approach to the Controlled Cross-Coupling between sp^2 Carbon Centres leading to Functionalised Alkenes

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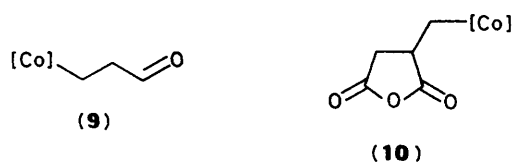
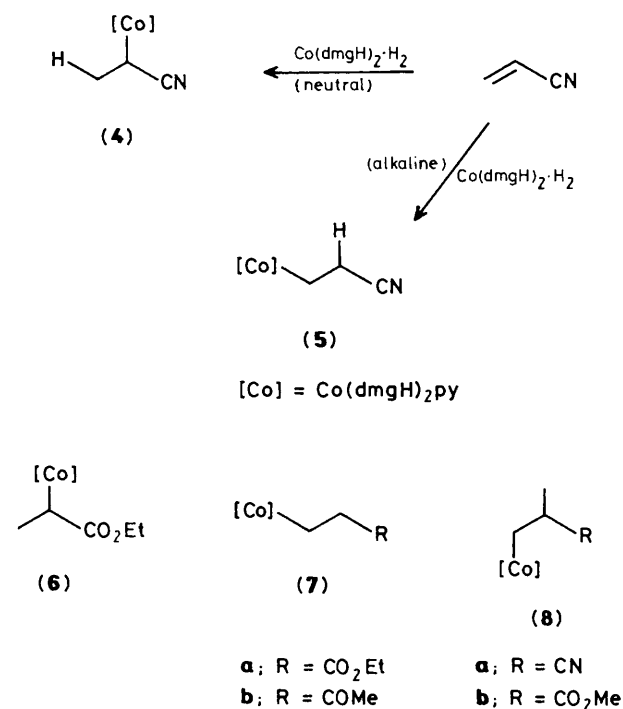
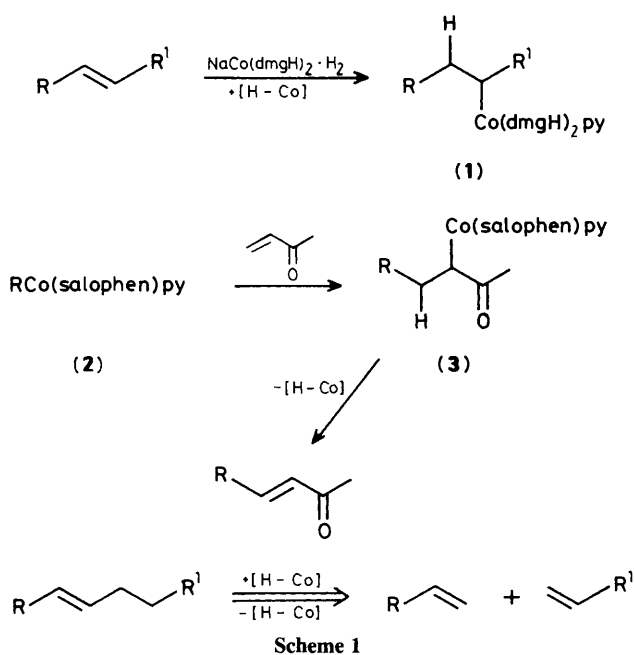
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Cross-coupling reactions between two alkenes, leading to new functionalised alkenes, can be brought about *via* 'hydrocobaltation' of one of the alkenes followed by irradiation of the resulting organocobalt reagent in the presence of the second alkene substrate.

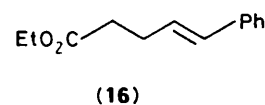
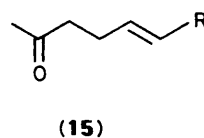
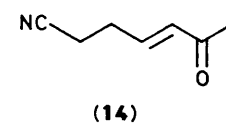
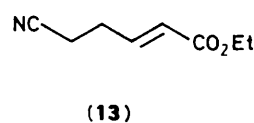
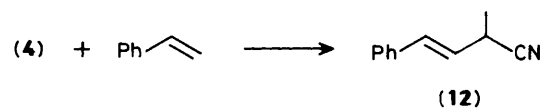
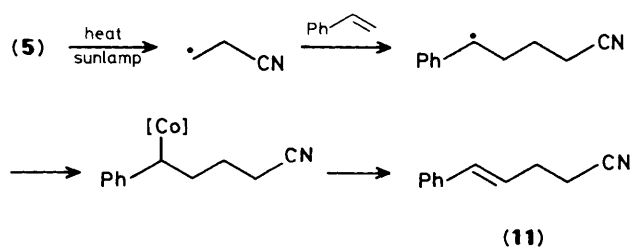
A considerable body of highly innovative synthetic chemistry has emerged in the past few decades, with the finding that olefinic and acetylenic linkages can be converted directly into organometallic species by 'hydrometallation' reactions.¹ The impact that hydroboration chemistry has had on synthesis, for example, is now almost legendary. Less exploited perhaps, but still of immense use in synthesis, are hydrometallation reactions involving a number of transition elements, *e.g.* Zr, Ni, Pd, Rh, and elements other than boron in Groups III and IV, *e.g.* Al, Si, and Sn.¹ Some years ago, Schrauzer *et al.*² described the reactions between deactivated alkenes and reduced cobaloxime species leading to alkylcobaloximes (**1**) *via* 'hydrocobaltation' processes. In recent work³ we have investigated the radical reactions between alkylcobalt (and acylcobalt) complexes (**2**) and a range of C=C bonds, which

lead to new alkene products (also enones and functionalised ring systems) *via* a sequence involving 'dehydrocobaltation' from short-lived organocobalt species (**3**). We here demonstrate how we have brought together the principles of 'hydrocobaltation' of alkenes and 'dehydrocobaltation' of organocobalt complexes to provide a new approach to the controlled cross-coupling between sp^2 carbon centres, leading to functionalised alkenes (Scheme 1).

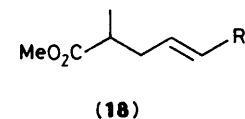
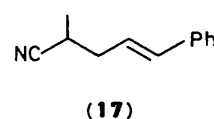
The regioselectivity of hydrocobaltation of alkenes, as described by Schrauzer *et al.*,² is critically dependent on the pH of the medium. Thus, treatment of acrylonitrile with $\text{Co}(\text{dmgH})_2 \cdot 2\text{H}_2\text{O}$ [from $\text{Co}(\text{OAc})_2$ and dimethylglyoxime in MeOH] in the presence of hydrogen, followed by work-up with pyridine, led to the crystalline α -substituted cobaloxime (**4**). The same reaction, under alkaline conditions (aq.



NaOH), instead leads to the β-substituted cobaloxime (5). In a similar manner, hydrocobaltations of ethyl acrylate led to (6) and (7a) under neutral and alkaline conditions, respectively. Using a range of pH conditions, we have only been able to secure the β-substituted cobaloximes (7b), (8a), (8b), (9), and



a; R = CN
b; R = CO₂Et
c; R = Ph



a; R = CN
b; R = Ph



(10) from hydrocobaltation reactions of methyl vinyl ketone, methyl acrylonitrile, methyl methacrylate, acrylaldehyde, and methylenesuccinic anhydride, respectively.†

Irradiation of solutions of any of the alkylcobaloximes (4)–(9) in dichloromethane in the presence of deactivated alkenes (5–10 equiv.), using light from a conventional 300 W sunlamp (24 h), led to new alkene products resulting from: (i) carbon–cobalt bond homolysis, (ii) radical (Michael-type) addition to the alkene substrate, (iii) quenching of the product radical centre with [Co^{III}], and (iv) dehydrocobaltation (β-elimination) (Scheme 2). Thus, the β-substituted cobaloxime (5) derived from acrylonitrile was coupled to styrene, producing (11) (55%), whereas the isomeric cobaloxime (4)

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

reacted with styrene under the same conditions leading to the positional isomer (**12**) of (**11**) (ca. 40%).^{4‡}

The foregoing reactions were successful with a range of alkene radical acceptor molecules. For example, the organocobalt reagent (**5**) also reacted with ethyl acrylate and methyl vinyl ketone (MVK) producing the adducts (**13**) (60%) and (**14**) (62%), respectively.[‡] Likewise, the β -substituted cobaloxime (**7b**) derived from MVK was coupled to acrylonitrile, ethyl acrylate, and styrene leading to (**15a**), (**15b**), and (**15c**) (45–60%), respectively. In similar manner, (**16**) and (**17**) were produced from styrene and the organocobalt compounds (**7a**) and (**8a**), respectively, and the β -cobaloxime (**8b**) from methyl methacrylate reacted with acrylonitrile and styrene giving rise to (**18a**) and (**18b**) respectively. The addition–elimination reaction between the formylethylcobaloxime (**9**) and acrylonitrile, leading to (**19**), is particularly noteworthy.

The foregoing results illustrate a new approach to the cross-coupling of sp^2 carbon centres, based on a novel hydrocobaltation–radical addition–dehydrocobaltation sequence, leading to highly functionalised alkenes. The method,

[‡] All alkene products produced in this study were shown by ¹H n.m.r. data to have the *E* geometries shown (=CH, J_{vic} ca. 16 Hz).

which constitutes a useful, complementary alternative to the ubiquitous Heck reaction, should be amenable to fine ‘tuning’ to allow the coupling of any alkene to a second alkene at either of their α - or β -sites leading to several types of cross-coupled products. This work, together with related studies using vinylcobalt reagents in coupling reactions, is in progress.

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References

- 1 See, for example, ‘Comprehensive Organic Chemistry’ and ‘Comprehensive Organometallic Chemistry,’ Pergamon, Oxford, 1979 and 1982, respectively.
- 2 G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc.*, 1967, **89**, 1999.
- 3 H. Bhandal, G. Pattenden, and J. J. Russell, *Tetrahedron Lett.*, 1986, **27**, 2299; V. F. Patel, G. Pattenden, and J. J. Russell, *ibid.*, p. 2303; V. F. Patel and G. Pattenden, *J. Chem. Soc., Chem. Commun.*, 1987, 871; D. J. Coveney, V. F. Patel, and G. Pattenden, *Tetrahedron Lett.*, 1987, **28**, 5949.
- 4 For some contemporaneous work using styrene as an alkene substrate in similar reactions, see B. P. Branchaud, M. S. Meier, and Y. Choi, *Tetrahedron Lett.*, 1988, **29**, 167.