Cobalt-Mediated Intermolecular Radical Additions to Carbon-to-Carbon Double Bonds leading to New Functionalised Alkenes

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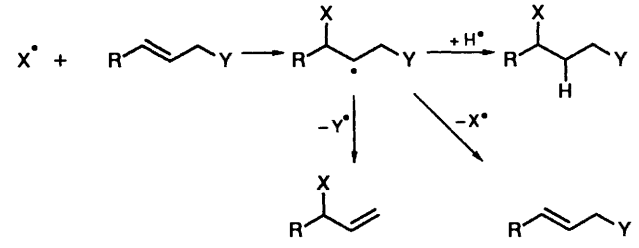
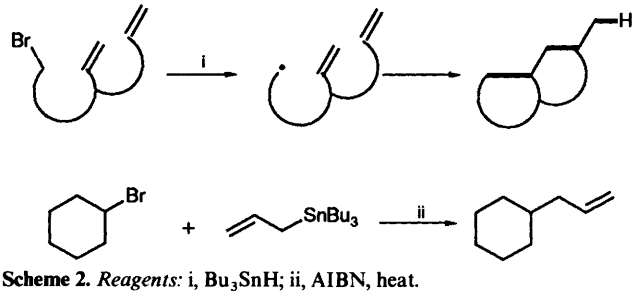
Alkyl radicals generated by photolytic homolysis of cobalt salophen reagents, *e.g.* (**6**) and (**15**), are shown to add to activated carbon-to-carbon double bonds, *i.e.* ethyl acrylate, methyl vinyl ketone, acrylonitrile, and styrene, producing preparatively useful yields of new alkene products, *viz.* (**9**), (**10**), (**12**) and (**14**) [from (**6**)], and (**16**) [from (**15**)]. The reactions proceed *via* radical (Michael) additions, followed by 'dehydrocobaltation' from the presumed organocobalt intermediates (**2**) (Scheme 4). By use of this chemistry, in combination with the Schrauzer 'hydrocobaltation' reaction of alkenes, a new method for the cross-coupling reactions between two alkenes, leading to new functionalised alkenes, *e.g.* (**24**), (**25**), (**26**), (**27**), (**28**), and (**29**), is developed [Equation (2)].

The addition of carbon radicals to alkenes has proven to be one of the most powerful methods for the formation of carbon-to-carbon bonds. These reactions lead to product carbon radicals which either react further with a radical donor (frequently H$^{\bullet}$; leading to quenching) or undergo elimination, depending on the substitution pattern, producing new alkene products (Scheme 1). A number of publications attest the preparative value of



Scheme 1.

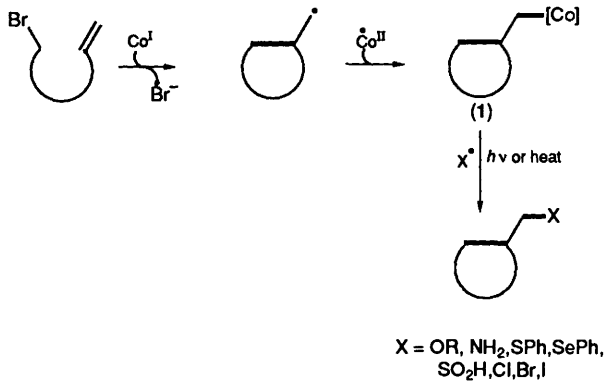
these reactions in synthesis,[1] and particular illustrations of the use of the entropy-favoured intramolecular carbon-to-carbon cyclisations, including tandem cyclisations (Scheme 2) leading to carbo- and hetero-cyclic molecules, abound in the con-



Scheme 2. *Reagents:* i, Bu_3SnH; ii, AIBN, heat.

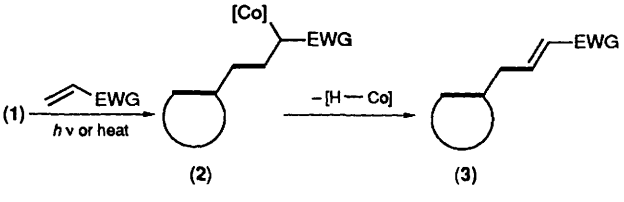
temporary literature.[1a] By contrast, *intermolecular* additions of carbon radicals to an unactivated carbon-to-carbon double bond are not generally useful, and alkenes containing electron-withdrawing groups need to be used. The allylation of carbon radicals using allylstannanes, which proceeds *via* elimination (fragmentation) from the intermediate carbon radical, however, is a great asset in synthesis (Scheme 2).[2] The comprehensive studies of intermolecular additions by Giese *et al.*[3] have resulted in the enumeration of useful guidelines for determining the relative efficiency of radical additions to carbon-to-carbon double bonds, and a number of examples of their use in synthesis have been illustrated.

In the accompanying publications we have described the use of cobalt(I) reagents in intramolecular radical cyclisations leading to product carbon radicals which can be trapped *in situ* leading to isolatable organocobalt intermediates, *viz.* (**1**).[4] We have also described the homolysis of the organocobalt compounds (**1**) in the presence of radical-trapping agents, which lead to oxygen-, nitrogen-, sulphur-, selenium-, and halogen-functionalised radical cyclisation products (Scheme 3).[5] We



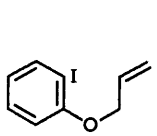
Scheme 3.

describe here the outcome of studies of the homolysis of the aforementioned cobalt compounds in the presence of deactivated carbon-to-carbon double bonds.[6,7] These reactions are shown to lead to new alkene products (**3**) which result from radical (Michael) addition to the carbon-to-carbon double bonds followed by dehydrocobaltation from the presumed organocobalt intermediates (**2**) (Scheme 4).[8]

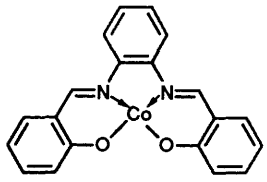


Scheme 4.

Our earlier work had shown that radical cyclisation of the iodoaryl allyl ether (**4**) in the presence of the cobalt 'salophen' reagent (**5**) (1% NaHg; THF; 25 °C; in dark under nitrogen) leads to the black, crystalline organocobalt compound (**6**) in high yield.[4] When a refluxing solution of compound (**6**) in

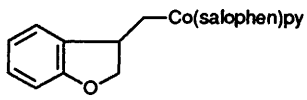


(4)



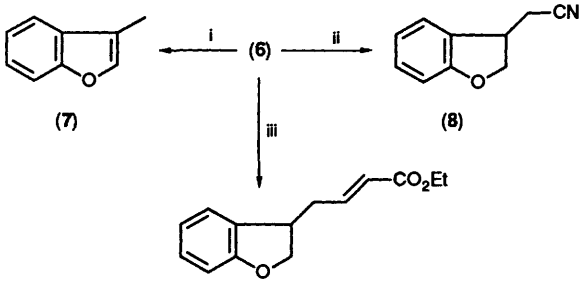
Co^{II}(salophen)

(5)



(6)

dichloromethane was irradiated by a 300 W sunlamp in the presence of cyclohexene, only the benzofuran (**7**) resulting from dehydrocobaltation–isomerisation was isolated. In addition, when compound (**6**) was irradiated in the presence of t-butyl isocyanide (10 mol equiv.), only a modest yield of the nitrile (**8**) was obtained, whose formation was also accompanied by that of the benzofuran (**7**). By contrast, when the furanylcobalt salophen (**6**) was treated with ethyl acrylate under the same conditions, work-up and chromatography led to a high (65%) yield of the *E*-unsaturated ester (**9**) containing only small amounts (~8%) of the benzofuran (**7**).

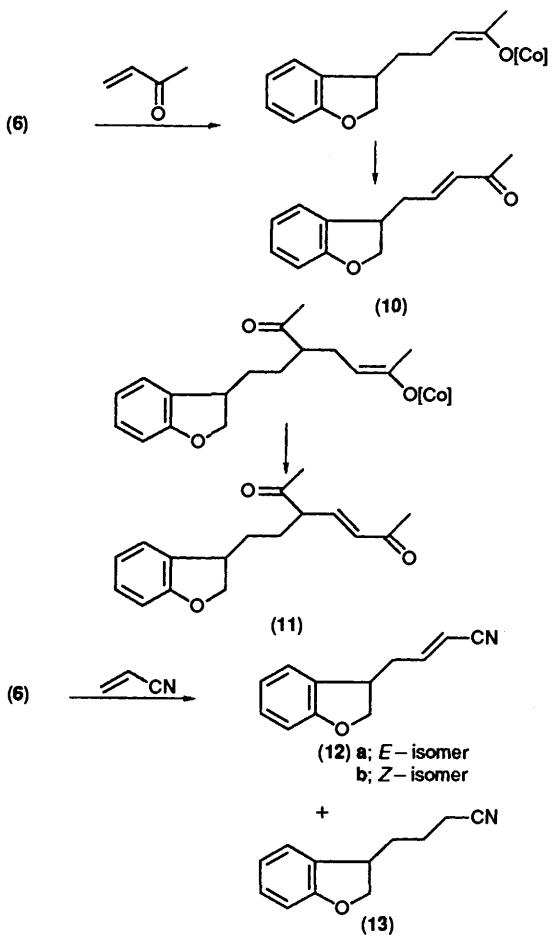


(7) (8) (9)

Reagents and conditions: i, heat or *hν*; ii, heat, Bu^tNC; iii, $H_2C{=}CHCO_2Et$, *hν*.

In a similar manner, irradiation of compound (**6**) in the presence of methyl vinyl ketone or acrylonitrile led to the corresponding adducts (**10**) (56%) and (**12**) (24%) respectively. Two separate features of these latter reactions are worth noting. Thus, in the case of the reaction between compound (**6**) and methyl vinyl ketone, data from mass spectrometry provided evidence for the co-formation of small amounts (<2%) of a 1:2 adduct tentatively assigned structure (**11**). Furthermore, the coupling between compound (**6**) and acrylonitrile produced a 1:1 mixture of (*E*)-(**12a**) and (*Z*)-(**12b**) isomers of the adduct together with small amounts of the product (**13**) resulting from H•-quenching of the product radical.[9]

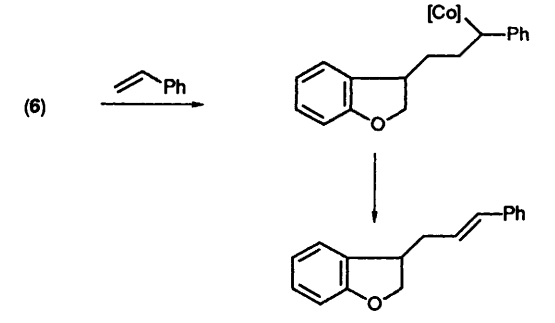
The adducts (**9**), (**10**), and (**12**) result from 'Michael' addition of the alkyl radical generated from homolysis of compound (**6**) to the alkene acceptors, followed by dehydrocobaltation (1,2-elimination) from the presumed intermediate organocobalt



(10) (11) (12) a; *E*–isomer b; *Z*–isomer (13)

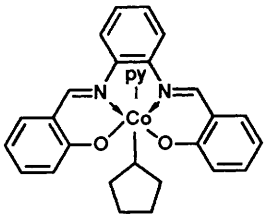
compounds [*viz.* (**2**); Scheme 4]. Attempts to effect preparative 'one-pot' syntheses of the adducts following treatment of compound (**4**) with Co^I salophen and then with the Michael acceptors were not successful, and low yields (<5%) of the corresponding adducts (**9**), (**10**), and (**12**) were produced by this procedure.

Significantly higher yields in the addition–elimination sequence shown in Scheme 4 were realised when styrene was used as the Michael acceptor. Thus high yields (of the order of 75–80%) of the *E*-adduct (**14**) were produced when the organocobalt compound (**6**) was irradiated in the presence of styrene. This result may reflect the relative ease of elimination of H–Co in the second step of the sequence over those cases involving ethyl acrylate, methyl vinyl ketone, and particularly acrylonitrile. Neither ethyl crotonate nor cyclopent-2-enone reacted with the organocobalt salophen (**6**) to give products of addition. This observation is consistent with the work of others* but interestingly contrasts with the observations of

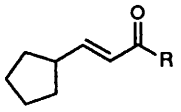


(14)

* See under ref. 3 for extensive discussions.



(15)



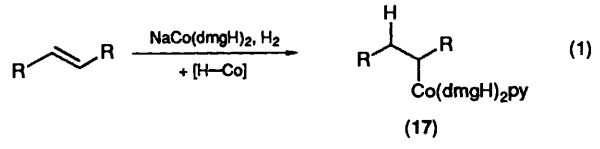
(16) a; R = Me
b; R = OEt

Scheffold *et al.*[8a] who found that alkyl halides do react with ethyl crotonate in the presence of reduced vitamin B_{12}, generated *electrochemically*, leading to a chain-extended product in 72% yield.

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 organocobalt salophen (**15**) derived from bromocyclopentane. Like compound (**6**), the cobalt salophen (**15**) underwent photolytic homolysis in the presence of both methyl vinyl ketone and ethyl acrylate, producing the corresponding *E*-adducts (**16a**) and (**16b**) in 45 and 55% yield respectively.

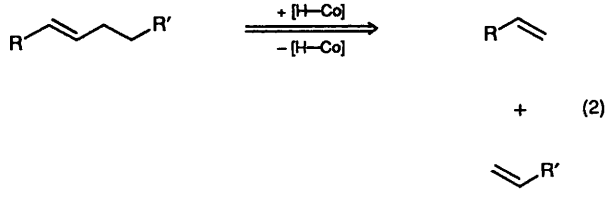
It seems clear that the cobalt-mediated radical addition–elimination sequence highlighted above offers considerable scope in the synthesis of carbon-to-carbon double bonds. It is also clear that the method both complements, and provides a satisfactory alternative to, similar radical methods based on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

Several years ago Schrauzer *et al.*[10] described the reactions between a range of deactivated alkenes and reduced cobaloxime species leading to alkylcobaloximes (**17**) *via* 'hydrocobaltation' processes [equation (1)]. Since this unusual chemistry con-



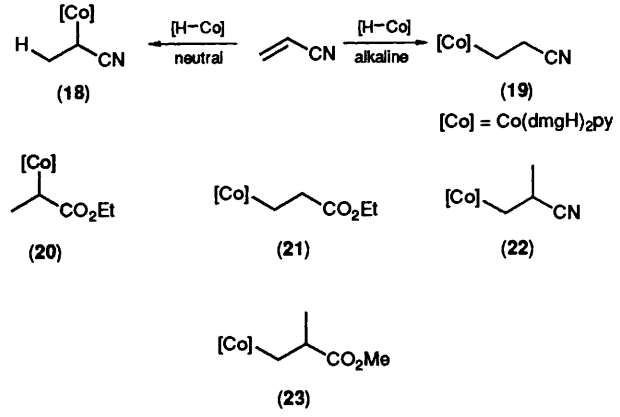
(17) (1)

stituted the reverse of the second, 'dehydrocobaltation' step in the overall addition–elimination sequence shown in Scheme 4 *leading* to new alkenes, we decided to bring together the principles of 'hydrocobaltation' of alkenes and 'dehydrocobaltation' of organocobalt complexes and examine a new approach to the controlled cross-coupling between sp^2-carbon centres [equation (2)].



(2)

The regiochemistry of hydrocobaltation of alkenes, as described by Schrauzer *et al.*,[10] is critically dependent on the pH of the medium. Thus, treatment of acrylonitrile with $Co(dmgH)_2{\cdot}2H_2O$ in the presence of hydrogen, followed by work-up with pyridine, led to the crystalline, α-substituted cobaloxime (**18**). The same reaction, under alkaline conditions, *i.e.* aq. sodium hydroxide, instead leads to the β-substituted cobaloxime (**19**). In a similar manner, hydrocobaltations of ethyl acrylate led to esters (**20**) and (**21**) under neutral and alkaline conditions, respectively. Using a range of pH conditions, we were also able to secure the β-substituted cobaloximes (**22**) and (**23**) from hydrocobaltation reactions of methylacrylonitrile and methyl methacrylate.*

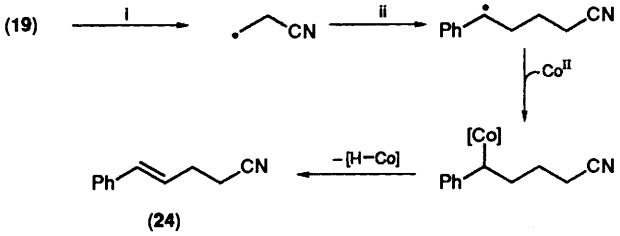


(18) (19)
[Co] = $Co(dmgH)_2py$

(20) (21) (22)

(23)

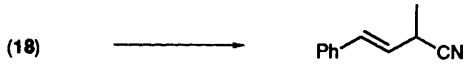
Irradiation of solutions of any of the alkylcobaloximes (**18**)–(**23**) in dichloromethane in the presence of deactivated alkenes (5–10 mol equiv.), using the procedures described above for the syntheses of compounds (**9**), (**10**), (**12**), (**14**), and (**16**), then led to new alkene products, following the now familiar sequence summarised in Scheme 5. Thus, the β-substituted cobaloxime



(24)

Scheme 5. *Reagents and conditions:* i, *hν* or heat; ii, $PhCH{=}CH_2$.

(**19**) derived from acrylonitrile was coupled to styrene to afford compound (**24**) (55%), whereas the isomeric cobaloxime (**18**) reacted with styrene under the same conditions to give the positional isomer (**25**) of compound (**24**) (~40%).

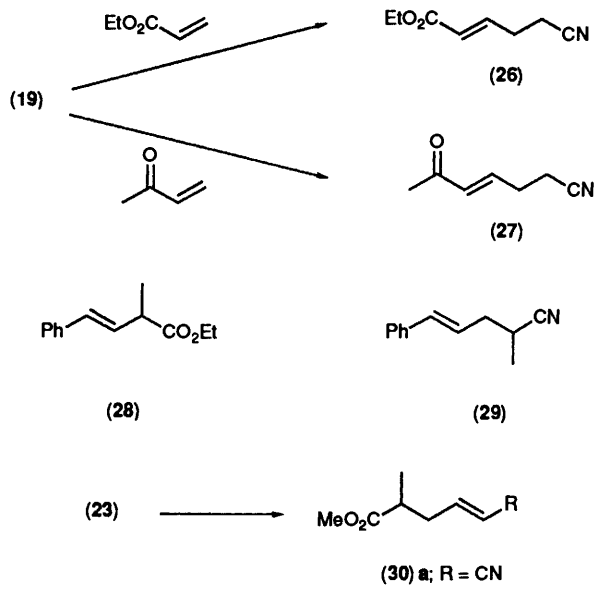


(25)

Reagents and conditions: $PhCH{=}CH_2$, heat, *hν* (sunlamp).

The previously mentioned reactions were successful with a range of alkene radical-acceptor molecules. For example, the organocobalt reagent (**19**) also reacted with ethyl acrylate and methyl vinyl ketone to produce the adducts (**26**) (60%) and (**27**) (62%) respectively. In similar manner, adducts (**28**) and (**29**)

* In the preliminary communication, ref. 7, we described the successful hydrocobaltations of methyl vinyl ketone and acrolein (acrylaldehyde), and the chemistry of the resulting cobaloximes. In more recent work we have been unable to confirm these observations, and we must therefore withdraw the earlier claims.



Reagents and conditions: $RCH{=}CH_2$, heat, *hν* (sunlamp).

were produced from styrene and the organocobalt compounds (**20**) and (**22**), respectively, and the β-cobaloxime (**23**) from ethyl methacrylate reacted with acrylonitrile and styrene to give rise to adducts (**30a**) and (**30b**), respectively.

The foregoing results illustrate a new approach to the cross-coupling of sp^2-carbon centres, which provides a useful, complementary alternative to the ubiquitous Heck reaction. In principle the method, with appropriate design of ligands around the cobalt centre, should be amenable to fine tuning to allow the coupling of any alkene to a second alkene at either of their α- or β-site, thus leading to several types of cross-coupled products. Studies of aspects of this proposal are now in progress in our laboratory. In the accompanying paper we describe complementary investigations of the selectivity of hydrocobaltation reactions of 1,3-dienes, and the uses of the resulting allylcobalt complexes in preparative chemistry.[11]

Experimental

For general experimental details see ref. 4.

(2,3-*Dihydrobenzofuran*-3-*yl*)*acetonitrile* (**8**).—A solution of the alkylcobalt complex (**6**)[4] (333.9 mg, 0.571 mmol) and t-butyl isocyanide (322 μl, 2.86 mmol) in dichloromethane (85 ml) was irradiated under reflux for 44 h, according to the general procedure.[5] A further portion of the isocyanide (322 μl, 2.86 mmol) was added after 28 h. The solvent was evaporated off *in vacuo* and the brown residue was then purified by chromatography (silica; 1:1 diethyl ether–light petroleum) to give: (i) the furan (**7**) (13.0 mg, 10%) (eluted first) as an oil whose spectral data were identical with those obtained previously,[4] and (ii) the *nitrile* (**8**) (49 mg, 31%) (eluted second) as a pale yellow oil, which darkened on storage at room temperature; $\nu_{max}(CHCl_3)$ 2 900s, 2 260w, 1 670m, 1 600s, 1 590s, 1 460s, 1 330w, and 980s cm^{-1}; δ_H 7.2 (m, 2 × ArH), 6.9 (m, 2 × ArH), 4.7 (dd, *J* 8.7 and 9.5 Hz, OC*H*H), 4.3 (dd, *J* 4.9 and 9.5 Hz, OCH*H*), 3.8 (m, ArC*H*), 2.7 (app. s, C*H*HCN), and 2.6 (d, *J* 0.5 Hz, CH*H*CN) (Found: M^+, 159.0706. $C_{10}H_9NO$ requires *M*, 159.0684).

Photolysis of Alkylcobalt(III) *Pyridinato Salophens in the Presence of Deactivated Olefins. General Procedure.*—A solution of the alkylcobalt complex (1.00 mmol) and the freshly distilled olefin (20–40 mmol) in dry, deoxygenated dichloromethane (120–180 ml) was irradiated under reflux, using a 300 W sunlamp (*d* 12–15 cm) for 24–73 h, under nitrogen. The solvent and the excess of olefin were evaporated off *in vacuo*, and the residue was then purified by chromatography.

(E)-*Ethyl* 4-(2,3-*Dihydrobenzofuran*-3-*yl*)*but*-2-*enoate* (**9**).—A solution of the alkylcobalt(III) complex (**6**)[4] (1.17 g, 2.00 mmol) and ethyl acrylate (8.6 ml, 80 mmol) in dichloromethane (120 ml) was irradiated for 73 h, according to the general procedure, to give, after purification by chromatography (silica; 1:10 diethyl ether–light petroleum): (i) the benzofuran (**7**) (eluted first) (23.1 mg, 8.8%) whose spectral data were consistent with those obtained previously, and (ii) the unsaturated *ester* (**9**) (295 mg, 65%) as a yellow oil; ν_{max}(film) 2 950m, 1 720s, 1 660w, 1 600w, 1 580w, 1 480m, 1 235m, 1 165m, and 755m cm^{-1}; δ_H(250 MHz) 7.1 (m, 2 × ArH), 6.9 (dt, *J* 15.6 and 7.2 Hz, CH=), 6.9 (m, 2 × ArH), 5.9 (dt, *J* 15.6 and 1.5 Hz, =C*H*CO_2Et), 4.6 (dd, *J* ~ 8.9 Hz, OC*H*H), 4.2 (dd, *J* 6.2 and 9.0 Hz, OCH*H*), 4.2 (q, *J* 7.2 Hz, CH_2Me), 3.6 (m, ArC*H*), 2.6 (m, C*H*HC=), 2.5 (m, CH*H*C=), and 1.3 (t, *J* 7.2 Hz, Me); δ_C(62.9 MHz) 166.1, 159.9, and 128.6 (C); 145.3, 129.4, 124.3, 123.6, 120.6, 109.8, and 40.8 (CH); 75.9, 60.4, and 37.5 (CH_2); and 14.4 (CH_3) (Found: C, 72.3; H, 7.2%; M^+, 232.1090. $C_{14}H_{16}O_3$ requires C, 72.4; H, 6.9%; *M*, 232.1099).

(E)-5-(2,3-*Dihydrobenzofuran*-3-*yl*)*pent*-3-*en*-2-*one* (**10**).—A solution of the alkylcobalt(III) complex (**6**)[4] (1.17 g, 2.00 mmol) and methyl vinyl ketone (3.9 ml, 37 mmol) in dichloromethane (120 ml) was irradiated for 60 h, according to the general procedure, to give, after purification by chromatography (silica; 1:20 diethyl ether–light petroleum): (i) the benzofuran (**7**) (eluted first) (19.8 mg, 7.5%) as an oil whose spectral data were consistent with those obtained previously, and (ii) the *enone* (**10**) (223 mg, 56%) as a pale yellow oil; ν_{max}(film) 2 950m, 1 680s, 1 630m, 1 600m, 1 370m, 1 265m, 1 240m, 990m, and 765s cm^{-1}; δ_H(250 MHz) 7.2 (m, 2 × ArH), 6.8 (m, 2 × ArH), 6.8 (dt, 15.8 and 7 Hz, CH=), 6.1 (dt, *J* 15.9 and 1.4 Hz, =CHCO), 4.6 (dd, *J* ~ 9 Hz, OC*H*H), 4.2 (dd, *J* 5.8 and 9.1 Hz, OCH*H*), 3.6 (m, ArC*H*), 2.6 (m, CH_2CH=), and 2.2 (Me); δ_C(62.9 MHz) 197.8, 160.0, and 129.4 (C); 143.7, 133.2, 128.8, 124.3, 120.7, 109.9, and 41.1 (CH); 76.0 and 37.7 (CH_2); and 27.2 (CH_3) (Found: M^+, 202.0992. $C_{13}H_{14}O_2$ requires *M*, 202.0994).

4-(2,3-*Dihydrobenzofuran*-3-*yl*)*but*-2-*enenitrile* (**12**).—A solution of the alkylcobalt(III) complex (**6**)[4] (1.00 g, 1.71 mmol) and acrylonitrile (4.6 ml, 70 mmol) in dichloromethane (150 ml) was irradiated for 18 h, according to the general procedure to give, after purification by chromatography (silica; 1:20 diethyl ether–light petroleum): (i) the benzofuran (**7**) (eluted first) (29.4 mg, 13.0%), whose spectral data were consistent with those obtained previously, and (ii) an inseparable 1:1 mixture of the *E* and *Z* isomers of the *nitrile* (**12**) (eluted second) (75 mg, 24%), as a pale yellow oil; $\nu_{max}(CHCl_3)$ 2 930m, 2 860m, 2 230m, 1 600s, 1 455s, 1 100s, 970s, and 910s cm^{-1}; δ_H(250 MHz) 7.1 (m, 2 × ArH), 6.9 (m, 2 × ArH), 6.7 (dt, *J* 16.3 and 7.3 Hz, =CH, *E*-isomer), 6.4 (dt, *J* 11.0 and 7.7 Hz, =CH, *Z*-isomer), 5.4 (dt, *J* 10.9 and 1.4 Hz, =CH, *Z*-isomer), 5.44 (dt, *J* 16.3 and 1.6 Hz =CH, *E*-isomer), 4.6 (dd, *J* ~ 9.1 Hz, 2 × OC*H*H), 4.2–4.6 (m, OCH_2), 3.6 (m, 2 × ArC*H*), 2.8 (m, 2 × C*H*HC=), and 2.6 (m, 2 × CH*H*C=) (Found: M^+, 185.0851. $C_{12}H_{11}NO$ requires *M*, 185.0840).

(E)-3-(2,3-*Dihydrobenzofuran*-3-*yl*)-1-*phenylpropene* (**14**).—A solution of the alkylcobalt(III) complex (**6**)[4] (1.17 g, 2.00 mmol) and excess of styrene (9.15 ml, 80 mmol) in dichloromethane (125 ml) was irradiated for 71 h, according to the general procedure to give, after purification by chromatography (silica; 1:100 diethyl ether–light petroleum): (i) the benzofuran (**7**)

(eluted first) (89.6 mg, 3%), whose spectral data were consistent with those obtained previously, and (ii) the *styrene* (**14**) (346 mg, 75%) as a viscous oil; ν_{max}(film) 3 020s, 2 920s, 1 600s, 1 590s, 1 480s, 1 225s, 960s, 745s, and 690s cm^{-1}; δ_H(250 MHz) 7.3–7.1 (m, 7 × ArH), 6.8 (m, 2 × ArH), 6.4 (d, *J* 15.8 Hz, =C*H*Ph), 6.1 (dt, *J* 15.9 and 7.1 Hz, CH=), 4.6 (dd, *J* ~ 9.1 Hz, OC*H*H), 4.3 (dd, *J* 6.1 and 9.1 Hz, OCH*H*), 3.6 (m, ArC*H*), 2.6 (m, C*H*HC=), and 2.5 (m, CH*H*=); δ_C(62.9 MHz) 161.1, 138.2, and 129.3 (C); 133.4, 129.9 (2 C), 129.1, 128.0, 127.8, 126.9 (2 C), 125.2, 121.1, 109.8, and 42.0 (CH); and 76.6 and 38.6 (CH_2) (Found: M^+, 236.1202. $C_{17}H_{16}O$ requires *M*, 236.1201).

Cyclopentylcobalt(III) *Pyridino Salophen Complex* (**15**).—By the general procedure[4] bromocyclopentane (4.69 g, 0.0315 mol) was treated with sodium cobalt(I) salophen (0.0252 mol), and then the crude product was recrystallised from aq. pyridine to give the *title complex* (**15**) (6.4 g, 48%) as a black, crystalline solid; ν_{max}(KBr) 1 610, 1 575, 1 520, 1 145, 1 340, 1 190, 1 150, 925, and 750 cm^{-1}; δ_H(400 MHz) 8.6 (2 × CH=N), 8.0–6.6 (m, 17 × ArH), 4.2 (quintet, *J* 7.2 Hz, CHCo), 1.4–1.2 (m, 2 × ring CH), 0.8 (m, C*H*HCHCo), and −0.1 (m, CH*H*CHCo); δ_C(100.62 MHz) 168.2, 166.0, 144.8, 142.8, 142.8, and 118.8 (C); 162.2, 156.1, 151.7, 139.5, 135.0, 134.8, 134.1, 134.0, 129.8, 127.7, 126.8, 125.3, 124.0, 123.6, 123.3, 118.5, 117.0, 115.5, and 114.6 (CH); and 35.0, 32.4, 22.7, and 21.0 (CH_2) [*m/z* (FAB) 443 (*M*H − py)$^+$. $C_{25}H_{24}CoN_3O_2$ requires *m/z*, 443].

(E)-4-*Cyclopentylbut*-3-*en*-2-*one* (**16a**).—A solution of the cyclopentylcobalt(III) complex (**15**) (521 mg, 1.00 mmol) and methyl vinyl ketone (2.80 g, 40 mmol) in dichloromethane (180 ml) was irradiated for 25 h, according to the general procedure, to give, after purification by chromatography (silica; 1:20 diethyl ether–light petroleum), the enone (**16a**) (62 mg, 45%) as a volatile, pale yellow oil; $\nu_{max}(CHCl_3)$ 1 675s and 1 630m cm^{-1}; δ_H 6.8 (dd, *J* 7.7 and 15.9 Hz, CH=), 6.0 (dd, *J* 0.7 and 15.9 Hz, =CHCO), 2.6 (m, ring CH), 2.2 (COMe), and 2.0–1.2 (m, 8 H, 4 × ring CH_2), consistent with the literature data.[12]

(E)-*Ethyl* 3-*Cyclopentylpropenoate* (**16b**).—A solution of the cyclopentylcobalt(III) complex (**15**) (521 mg, 1.00 mmol) and ethyl acrylate (1.50 g, 15.0 mmol) in dichloromethane (150 ml) was irradiated for 28 h, according to the general procedure, to give, after purification by chromatography (silica; 1:20 diethyl ether–light petroleum), the ester (191 mg, 55%) as a sweet smelling, yellow oil; $\nu_{max}(CHCl_3)$ 1 710m and 1 650w cm^{-1}; δ_H(250 MHz) 6.9 (dd, *J* 8.0 and 15.4 Hz, CH=), 5.0 (dd, *J* 1.7 and 15.4 Hz, =C*H*CO_2Et), 4.2 (q, *J* 6 Hz, OCH_2), 2.6 (m, ring CH), and 2.3–1.3 (m, 11 H, OCH_2Me and 4 × ring CH_2), consistent with the literature data.[13]

β-*Hydrocobaltation of Alkenes. General Procedure.*—The alkene (8 mmol) was added to a solution of cobalt(II) chloride hexahydrate (8 mmol), dimethylglyoxime (16 mmol), and pyridine (8 mmol) in methanol (40 ml) at room temperature. The solution was degassed with nitrogen (20 min), then aq. sodium hydroxide (10M; 3 ml) was added, and the solution was degassed for a further 15 min. The nitrogen gas was exchanged for hydrogen gas, and the progress of the reaction was then monitored by TLC for disappearance of the alkene (reaction times were generally < 1 h). Water (10 ml) was added, and the mixture was then extracted with dichloromethane (2 × 20 ml). The combined extracts were dried ($MgSO_4$) and then evaporated to leave a crude product, which was purified by chromatography on silica gel and/or by recrystallisation from dichloromethane–light petroleum. The alkylcobaloxime reagents all melted erratically with decomposition, and satisfactory, reproducible microanalytical data could not be obtained from most compounds.*

α-*Hydrocobaltation of Alkenes. General Procedure.*—The α-hydrocobaltation of alkenes was achieved by the same general procedure as that employed for β-hydrocobaltation, except that the reactions were carried out in the absence of aq. sodium hydroxide.

α-*Cyanoethylpyridinatocobaloxime* (**18**). According to the general procedure, hydrocobaltation of acrylonitrile gave the α-alkylcobaloxime (**18**) (1.64 g, 48%) as a yellow-orange solid, $\nu_{max}(CHCl_3$ solution) 2 210 cm^{-1}; δ_H 8.56 (2 × pyr. CH), 7.82 (m, pyr. CH), 7.4 (m, 2 × pyr. CH), 2.2 (4 × Me), 2.2 (m under s, 1 H, CHCo), and 0.55 (d, *J* 7 Hz, Me); *m/z* (FAB) 368 (M^+ − C_3H_4N), 339, 290 [Co(dmgH)$_2$ + 1], and 289.

β-*Cyanoethylpyridinatocobaloxime* (**19**). According to the general procedure, hydrocobaltation of acrylonitrile gave the β-alkylcobaloxime (2.8 g, 83%) as a cinnamon brown powder, ν_{max}(solution) 2 235 cm^{-1}; δ_H 8.5 (m, 2 × pyr. CH), 7.7 (m, pyr. CH), 7.3 (m, 2 × pyr. CH), 2.2 (4 × Me), 1.8 (t, *J* 7 Hz, CH_2Co), and 1.55 (t, *J* 7 Hz, CH_2CN); *m/z* (FAB) 423 (M^+ + 1), 422 (M^+), 344 (M^+ + 1 − pyr.), 343, 290 [Co(dmgH)$_2$ + 1], and 289.

α-(*Ethoxycarbonyl*)*ethylpyridinatocobaloxime*(**20**). According to the general procedure, hydrocobaltation of ethyl acrylate gave the α-alkylcobaloxime (**20**) (2.0 g, 54%) as an orange solid, $\nu_{max}(CHCl_3$ solution) 1 690, 1 230, and 1 100 cm^{-1}; δ_H 8.5 (m, 2 × pyr. CH), 7.7 (m, pyr. CH), 7.3 (m, 2 × pyr. CH), 3.9 (m, OCH_2), 2.2 (4 × Me), 2.1 (q, *J* 7 Hz, CHCo), 1.2 (t, *J* 7 Hz, OCH_2Me), and 0.4 (d, *J* 7 Hz, Me); δ_C 180.6 (C=O), 150.8 (q), 150.2 (CH), 137.7 (CH), 125.2 (CH), 59.5 (CH_2), 29.0 (CH), 16.9 (CH_3), 14.2 (CH_3), and 12.4 (CH_3).

β-(*Ethoxycarbonyl*)*ethylpyridinatocobaloxime*(**21**). According to the general procedure, hydrocobaltation of ethyl acrylate gave the β-alkylcobaloxime (**21**) (3.2 g, 87%) as an orange solid, $\nu_{max}(CHCl_3$ solution) 1 715, 1 555, and 1 090 cm^{-1}; δ_H 8.56 (m, 2 × pyr. CH), 7.7 (m, pyr. CH), 7.3 (m, 2 × pyr. CH), 3.6 (OCH_2), 2.1 (4 × Me), 1.9 (br m, CH_2Co), 1.7 (br m, CH_2CO_2Et) and 1.2 (t, *J* 7Hz, Co_2CH_2*Me*); δ_C 173.2 (C=O), 149.9 (CH), 149.6 (q), 137.6 (CH), 125.3 (CH), 51.3 (CH_3), 35.0 (CH_2), 21.5 (CH_2), and 12.1 (CH_3); *m/z* (FAB) 456 (M^+ + 1), 391, 390, 377 (M^+ + 1 − pyr.), 368 (M^+ + 1 − $C_4H_7O_2$), 290 [Co(dmgH)$_2$ + 1], and 289.

β-*Cyanopropylpyridinatocobaloxime* (**22**). According to the general procedure, hydrocobaltation of methylacrylonitrile gave the β-alkylcobaloxime (**22**) (3.19 g, 91%) as an orange-brown solid, δ_H 8.5 (m, 2 × pyr. CH), 7.7 (m, pyr. CH), 7.3 (m, 2 × pyr. CH), 2.1 (4 × Me), 2.1 (m, CH_2Co), 1.8 (m, CHCN), and 1.2 (d, *J* 7 Hz, Me); *m/z* (FAB) 369 (M^+ + 1 − C_4H_6N), 290 [Co(dmgH)$_2$ + 1], and 289.

β-(*Methoxycarbonyl*)*propylpyridinatocobaloxime* (**23**). According to the general procedure, hydrocobaltation of methyl methacrylate gave the β-alkylcobaloxime (**23**) (3.18 g, 85%) as a golden, crystalline solid, δ_H 8.6 (m, 2 × pyr. CH), 7.7 (m, pyr. CH), 7.3 (m, 2 × pyr. CH), 3.6 (OMe), 2.2 (m, CH_2Co), 2.1 (4 × Me), 1.3 (m, CHCO_2Me), and 1.0 (d, *J* 7 Hz, Me); *m/z* (FAB) 391 (M^+ + 1 − pyr.), 390, 368 (M^+ − $C_5H_9O_2$), 290 [Co(dmgH)$_2$ + 1], and 289.

Coupling Reactions between Alkylcobaloximes and Deactivated Alkenes. General Procedure.—A solution of the alkylcobalt (1 mmol) and the alkene (5 mmol) in dichloromethane (170 ml) was degassed for 1 h by bubbling nitrogen through it. The solution was then irradiated under nitrogen with a 300 W UV lamp at a distance of 12 cm for 48 h. The solvent was removed, and the residue was then preloaded on silica gel and eluted with light petroleum–diethyl ether to give the coupled alkene.

* See footnote on p. 2711.

(E)-5-*Phenylpent*-4-*enenitrile* (**24**). According to the general procedure, reaction between β-cyanoethylpyridinatocobaloxime (**19**) and styrene, followed by chromatography on silica gel with light petroleum–diethyl ether (1:1) as eluant, gave the *title alkene* (**24**) (50 mg, 32%) as a liquid; ν_{max}(film) 3 100, 2 200, 1 600, and 980 cm^{-1}; δ_H 7.3 (m, Ph), 6.4 (d, *J* 16 Hz, =CH), 6.1 (m, =CH), and 2.5 (m, 4 H) (Found: M^+, 157.0899. $C_{11}H_{11}N$ requires *M*, 157.0892).

(E)-2-*Methyl*-4-*phenylbut*-3-*enenitrile* (**25**). According to the general procedure, reaction between α-cyanoethylpyridinatocobaloxime (**18**) and styrene, followed by chromatography on silica gel with light petroleum–diethyl ether (1:1) as eluant, gave the alkene (**25**); ν_{max}(film) 3 010, 2 215, and 1 620 cm^{-1}; δ_H 7.3 (m, Ph), 6.7 (d, *J* 16 Hz, =CH), 6.1 (dd, *J* 16 and 7 Hz, =CH), 3.5 (m, 1 H, CHCN), and 1.5 (d, *J* 8 Hz, Me).

(E)-*Ethyl* 5-*cyanopent*-2-*enoate* (**26**). According to the general procedure, reaction between β-cyanoethylpyridinatocobaloxime (**19**) and ethyl acrylate, followed by chromatography on silica gel with light petroleum–diethyl ether (1:1) as eluant, gave the unsaturated ester (**26**) (40 mg, 26%); ν_{max}(film) 2 225, 1 725, and 1 645 cm^{-1}; δ_H 6.8 (m, =CH), 5.8 (d, *J* 16 Hz, =CH), 4.09 (q, *J* 7 Hz, OCH_2), 2.4 (m, 4 H), and 1.2 (t, *J* 7 Hz, OCH_2Me) [Found: *m/z*, 108.0441. C_6H_6NO (M^+ − OEt) requires *m/z*, 108.0449].

(E)-6-*Oxohept*-4-*enenitrile* (**27**). According to the general procedure, reaction between β-cyanoethylpyridinatocobaloxime (**19**) and methyl vinyl ketone, followed by chromatography on silica gel with light petroleum–diethyl ether (1:1) as eluant, gave the *unsaturated nitrile* (**27**) (80 mg, 65%) as an oil; ν_{max}(film) 2 230, 1 710, and 1 628 cm^{-1}; δ_H 6.9 (m, =CH), 6.3 (d, *J* 16 Hz, =CH), 2.6 (m, 4 H), and 2.3 (MeCO) (Found: M^+, 123.0682. C_7H_9NO requires *M*, 123.0684).

(E)-*Ethyl* 2-*methyl*-4-*phenylbut*-3-*enoate* (**28**). According to the general procedure, reaction between α-(ethoxycarbonyl)-ethylpyridinatocobaloxime (**20**) and styrene, followed by chromatography on silica gel with light petroleum–diethyl ether (1:1) as eluant, gave the *unsaturated ester* (**28**) (66 mg, 32%); ν_{max}(film) 3 010, 1 730, and 1 610 cm^{-1}; δ_H 7.2 (m, Ph), 6.5 (d, *J* 16 Hz, =CH), 6.4 (dd, *J* 16 and 7 Hz, =CH), 4.1 (q, *J* 7 Hz, OCH_2), 3.3 (quint., *J* 7 Hz, $CHCO_2Et$), 1.4 (d, *J* 7 Hz, Me), and 1.2 (t, *J* 7 Hz, OCH_2Me) (Found: M^+, 204.1161. $C_{13}H_{16}O_2$ requires *M*, 204.1151).

(E)-2-*Methyl*-5-*phenylpent*-4-*enenitrile* (**29**). According to the general procedure, reaction between β-cyanopropylpyridinatocobaloxime (**22**) and styrene, followed by chromatography on silica gel with light petroleum–diethyl ether (9:1) as eluant, gave the *unsaturated nitrile* (**29**) (65 mg, 38%); ν_{max}(film) 3 010, 2 215, and 1 620 cm^{-1}; δ_H 7.3 (m, Ph), 6.5 (d, *J* 16 Hz, =CH), 6.1 (dt, *J* 16 and 7 Hz, =CH), 2.7 (m, CHCN), 2.5 (dd, *J* ~ 7 Hz, CH_2), and 1.4 (d, *J* 8 Hz, Me) (Found: M^+, 171.1046. $C_{12}H_{13}N$ requires *M*, 171.1049).

(E)-*Methyl* 5-*cyano*-2-*methylpent*-4-*enoate* (**30a**). According to the general procedure, reaction between β-(methoxycarbonyl)propylpyridinatocobaloxime (**23**) and acrylonitrile, followed by chromatography on silica gel with light petroleum–diethyl ether (1:1) as eluant, gave the unsaturated ester (**30a**) (50 mg, 33%); ν_{max}(film) 2 217, 1 727, and 1 630 cm^{-1}; δ_H 6.8 (dt, *J* 16 and 7 Hz, =CH), 5.4 (d, *J* 16 Hz, =CH), 3.7 (OMe), 2.6 (3 H, m), and 1.3 (d, *J* 7 Hz, Me).

(E)-*Methyl* 2-*methyl*-5-*phenylpent*-4-*enoate* (**30b**). According to the general procedure, reaction between β-(methoxycarbonyl)propylpyridinatocobaloxime (**23**) and styrene, followed by chromatography on silica gel with light petroleum–diethyl ether (1:1) as eluant, gave the *unsaturated ester* (**30b**); ν_{max}(film) 3 250, 1 740, and 1 601 cm^{-1}; δ_H 7.3 (m, Ph), 6.4 (d, *J* 16 Hz, =CH), 6.1 (dt, *J* 16 and 7 Hz, =CH), 3.7 (OMe), 2.6 (m, CH_2), 2.3 (m, $CHCO_2Me$), and 1.2 (d, *J* 7 Hz, Me); δ_C 176.2 (C=O), 137.2 (q), 131.9 (CH), 128.2 (CH), 126.9 (CH), 125.9 (CH), 51.4 (CH_3), 39.4 (CH), 36.8 (CH_2), and 16.4 (CH_3) (Found: M^+, 204.1169. $C_{13}H_{16}O_2$ requires *M*, 204.1151).

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References

1 For extensive bibliography, see: (*a*) D. P. Curran, *Synthesis*, 1988, 417, 489; B. Giese, 'Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds,' Pergamon, 1986. See also G. Stork, 'Radical-Mediated Cyclisation Processes,' in 'Selectivity—A Goal for Synthetic Efficiency,' eds W. Bartman and B. M. Trost, Verlag Chemie, Basel, 1984, pp. 281–299; (*b*) J. E. Baldwin and D. R. Kelly, *J. Chem. Soc., Chem. Commun.*, 1985, 682; (*c*) D. H. R. Barton and D. Crich, *Tetrahedron Lett.*, 1984, **25**, 2787; J. E. Baldwin, R. M. Adlington, and A. Basak, *J. Chem. Soc., Chem. Commun.*, 1984, 1284.

2 See G. E. Keck, E. J. Enholm, J. B. Yates, and M. R. Wiley, *Tetrahedron*, 1985, **41**, 4079; G. E. Keck and J. H. Byers, *J. Org. Chem.*, 1985, **50**, 5442.

3 B. Giese, *Angew. Chem.*, 1983, **95**, 771; *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 753; *Angew. Chem.*, 1985, **97**, 555; *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 553; see also ref. 1*a*.

4 H. Bhandal, V. F. Patel, G. Pattenden, and J. J. Russell, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2691.

5 V. F. Patel and G. Pattenden, preceding paper.

6 Preliminary communication: V. F. Patel and G. Pattenden, *J. Chem. Soc., Chem. Commun.*, 1987, 871.

7 Preliminary communication: H. Bhandal and G. Pattenden, *J. Chem. Soc., Chem. Commun.*, 1988, 1110.

8 (*a*) For examples of vitamin B_{12} in organocobalt-mediated C–C bond-forming reactions (without H–Co elimination), see R. Scheffold, S. Abrecht, R. Orlinski, H.-R. Ruf, P. Stamouli, O. Tinembart, L. Walder, and C. Weymuth, *Pure Appl. Chem.*, 1987, **59**, 363; R. Scheffold, *Chimia*, 1985, **39**, 203, and references therein. (*b*) For some contemporaneous studies using styrene as an alkene substrate in similar reactions, see B. P. Branchaud, M. S. Meier, and Y. Choi, *Tetrahedron Lett.*, 1988, **29**, 167; B. P. Branchaud and Y. Choi, *ibid.*, p. 6037; B. P. Branchaud and M. S. Meier, *J. Org. Chem.*, 1989, **54**, 1320; A. Ghosez, T. Gobel, and B. Giese, *Chem. Ber.*, 1988, **121**, 1807. (*c*) For demonstrations of the potential for organocobalt methods in synthesis, see M. J. Begley, H. Bhandal, J. H. Hutchinson, and G. Pattenden, *Tetrahedron Lett.*, 1987, **28**, 1317; J. E. Baldwin and C.-S. Li, *J. Chem. Soc., Chem. Commun.*, 1987, 166, 261; M. J. Begley, D. R. Cheshire, T. Harrison, J. H. Hutchinson, P. L. Myers, and G. Pattenden, *Tetrahedron*, 1989, **45**, 5215.

9 For further discussion of this feature, see D. J. Coveney, V. F. Patel, G. Pattenden, and D. M. Thompson, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2721; O. Tinembart, L. Walder, and R. Scheffold, *Ber. Bunsenges. Phys. Chem.*, 1988, **92**, 1225; B. Giese, J. Hartung, J. He, O. Hüter, and A. Koch, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 325.

10 G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc.*, 1967, **89**, 1999.

11 A. R. Howell and G. Pattenden, following paper.

12 J. Hooz and J. Oudenes, *Synth. Commun.*, 1980, **10**, 667.

13 R. M. Gerkin and B. Rickborn, *J. Am. Chem. Soc.*, 1967, **89**, 5850.

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