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The $CoCl_2/Ph(Et)_2N{:}BH_3/CO$ system: Reactions of the borane and cobalt carbonyl species

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Abstract

The $CoCl_2/Ph(Et)_2N{:}BH_3/CO$ system is useful for the hydroboration and carbonylation of alkenes to obtain the corresponding dialkyl ketones. The cobalt carbonyl species formed in situ in this way is also useful for hydroacylation–cyclisation of norbornene and for the Pauson–Khand reaction. © 1998 Elsevier Science S.A.

Keywords: Hydroboration; Alkene; Carbonylation; Dialkylketone; Cobalt carbonyl reagents; Carbonylative cyclisations

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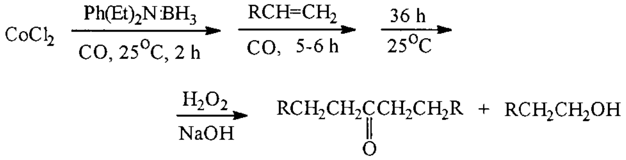
1. Introduction

In recent years, there has been immense interest in the utilisation of transition metal organometallic reagents for organic synthesis [1,2]. Transition metal salts in combination with hydride reagents have been used for many useful new synthetic methods [2]. In this laboratory, several such reagents generated in situ were used for hydrogenation, hydroboration, isomerisation, dimerisation, reductions and for carbonylation in the presence of carbon monoxide [3–11]. In continuation of our studies on the development of useful organometallic reagents for organic synthesis, we report that the boron and cobalt carbonyl reagents, generated in the reaction of BH_3 complexes with anhydrous $CoCl_2$ under carbon monoxide atmosphere, are useful for hydroboration–carbonylation, hydroacylation of norbornene and Pauson–Khand cyclisation.

2. Results and discussion

2.1. Reactivity of borane species generated using $PhN(Et)_2N{:}BH_3/CoCl_2/CO$ system

We have observed that the reagent generated from the $Ph(Et)_2N{:}BH_3$ complex (1 equiv.) in benzene [11] and anhydrous $CoCl_2$ (1 equiv.) in THF in the presence of carbon monoxide, is useful for the hydroboration and carbonylation of alkene (2 equiv.) to obtain the corresponding dialkyl ketones after oxidation with H_2O_2/NaOH [12]. The reaction sequence is represented in Eq. (1).



$$CoCl_2 \xrightarrow[CO,\ 25^{\circ}C,\ 2\ h]{Ph(Et)_2N{:}BH_3} \xrightarrow[CO,\ 5\text{-}6\ h]{RCH{=}CH_2} \xrightarrow[25^{\circ}C]{36\ h} \xrightarrow[NaOH]{H_2O_2} RCH_2CH_2\underset{\underset{O}{\|}}{C}CH_2CH_2R + RCH_2CH_2OH \quad (1)$$

This new method of carbonylation of alkene through borane species works well with various other alkenes and the

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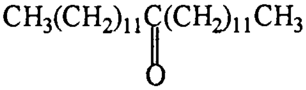
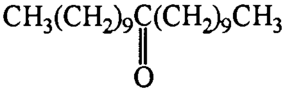
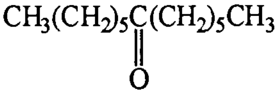
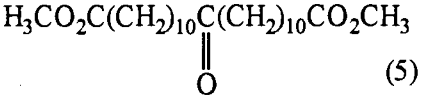
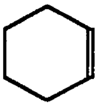
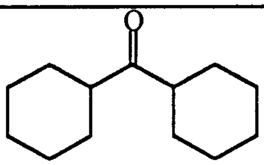
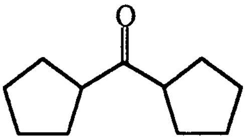
corresponding dialkyl ketones were isolated in 50–70% yield (Table 1). The alcohols (25–35%) are also formed as side products in all cases. However, the dialkyl ketones can be readily separated by column chromatography on silica gel. Evidently, the present reagent system tolerates the presence of an ester group as indicated by the conversion of methyl-10-undecenoate to the corresponding dialkyl ketone (entry 5, Table 1).

The trialkylborane species have been reported to give the corresponding dialkyl ketones with CO in the presence of H_2O at 100–120°C [13]. We have carried out an experiment using 30 mmol of 1-decene to examine whether R_3B is formed under the reaction conditions. In this run, only 20 mmol of the 1-decene reacted and 10 mmol was recovered. This indicates that the species generated in the reaction of the BH_3 complex with $CoCl_2$ reacts with only two equivalents of olefins. Presumably, the BH_3–amine complex on reaction with $CoCl_2$ would give the $ClBH_2$ and cobalt hydride species. (Scheme 1) [14]. The latter could yield cobalt carbonyl species in the presence of carbon

Table 1
Reaction of Alkenes with $Ph(Et)_2N{:}BH_3/CoCl_2/CO$ System[a]

Alkene	Dialkylketone [b]	Yield (%)[c]
$CH_3(CH_2)_9CH{=}CH_2$	 $CH_3(CH_2)_{11}\underset{\underset{O}{\|}}{C}(CH_2)_{11}CH_3$ (1)	70
$CH_3(CH_2)_7CH{=}CH_2$	 $CH_3(CH_2)_9\underset{\underset{O}{\|}}{C}(CH_2)_9CH_3$ (2)	69
$CH_3(CH_2)_5CH{=}CH_2$	 $CH_3(CH_2)_7\underset{\underset{O}{\|}}{C}(CH_2)_7CH_3$ (3)	67
$CH_3(CH_2)_3CH{=}CH_2$	 $CH_3(CH_2)_5\underset{\underset{O}{\|}}{C}(CH_2)_5CH_3$ (4)	66
$H_3COOC(CH_2)_8CH{=}CH_2$	 $H_3CO_2C(CH_2)_{10}\underset{\underset{O}{\|}}{C}(CH_2)_{10}CO_2CH_3$ (5)	60
	 (6)	53
	 (7)	50

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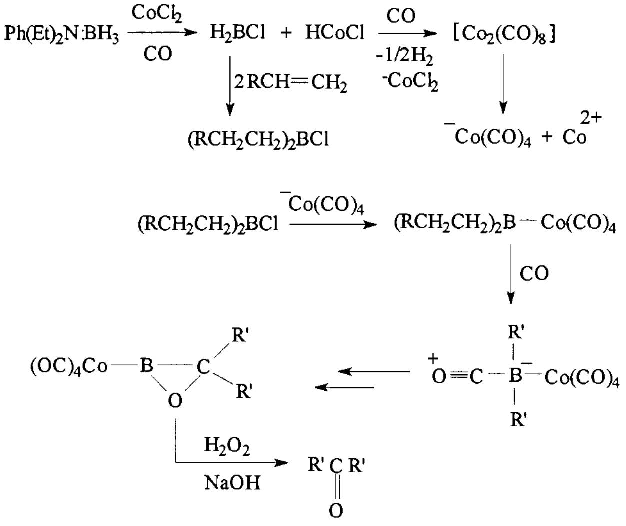
[a] All the reactions were carried out using 10 mmol of $Ph(Et)_2N{:}BH_3$ complex and 10 mmol of $CoCl_2$ with 20 mmol of alkene at room temperature and the oxidation of organoborane was carried out with $H_2O_2/NaOH$. In the case of methyl-10-undecenoate (entry No. 5, Table 1) the oxidation was carried out using H_2O_2/sodium acetate. [b] The dialkyl ketone and the alcohol were separated by column chromatography using ethyl acetate in hexane as eluents respectively. All products are identified by the spectral data (IR, ^1H, ^{13}C NMR) and in comparison with the reported data. [c] Yields are of isolated products and based on the amount of alkene used.



Scheme 1.

monoxide. The $ClBH_2$ species would be expected to give R_2BCl on reaction with an alkene [14]. However, the formation of $HBCl_2$ to some extent through further reaction of BH_2Cl cannot be ruled out. In this case, the alcohol would result, if the intermediate boron compound does not undergo carbonylation.

In a control experiment carried out using $Ph(Et)_2N{:}BH_3$ complex with 1-decene without using $CoCl_2$, the ketone was not formed after oxidation with $H_2O_2/NaOH$. Only, the hydroboration–oxidation product, 1-decanol was obtained in 84% yield.

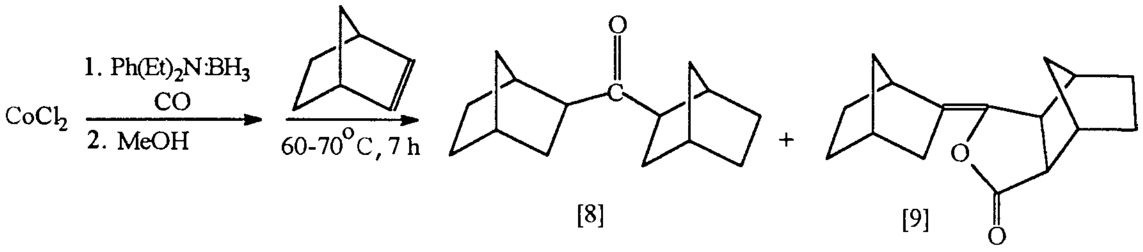
Recently, it has been reported from this laboratory that the BH_3–THF can be readily generated in situ by mixing $NaBH_4$ and I_2 in THF [15]. We have carried out an experiment using the BH_3–THF generated in this way for further reaction with $CoCl_2$. In this case, the corresponding dialkyl ketone (entry 1, Table 1) was isolated in 40% yield. Hence, the BH_3–THF can be used in the place of $Ph(Et)_2N{:}BH_3$ complex for this transformation. However, the yields are better in the latter case (Table 1). It has been reported that the dicobalt octacarbonyl reacts with BH_3–THF at $-15°C$ to give $H_2BCo(CO)_4(THF)$ [16]. However, the $H_2BCo(CO)_4$, prepared in this way, has been reported to decompose at 25°C with the evolution of H_2 in THF to give polymeric products, resulting in a deep reddish brown solution. In the present case, a deep green coloured reaction mixture results when the $Ph(Et)_2N{:}BH_3$ in benzene is added to the blue coloured anhydrous $CoCl_2$ in THF under carbon monoxide. The IR spectrum recorded, after stirring the reaction mixture for 2 h, exhibited a strong absorption band at 1890 cm^{-1} indicating the presence of cobalt carbonyl species. This absorption band was also observed after stirring the mixture for 6 h with alkene in the presence of CO. This is similar to the reaction of R_2BI with $NaCo(CO)_4$ where the dialkyl ketones were obtained after oxidation [17].

The present transformation may be visualised by a sequence of reactions involving initial hydroboration of alkene with H_2BCl complex followed by cobalt assisted carbonylation, subsequent migration of alkyl groups from boron to carbon of the CO moiety (Scheme 1).

This mechanistic sequence is similar to that suggested for the reaction of R_2BI with $NaCo(CO)_4$ and according to the mechanism proposed for the reaction of CO with R_3B [13,17]. The interesting point is the involvement of $^{-}Co(CO)_4$ species. Seyferth and Spohn [18,19] noted previously that the $Co_2(CO)_8$ cleaved by THF to give $^{-}Co(CO)_4$ and Co^{2+}. The strong absorption in the IR spectrum of the reaction mixture at 1890 cm^{-1} does indicate the formation of cobalt carbonyl species in this transformation. So, we have decided to investigate the reactivities of the cobalt carbonyl species generated in this way by masking the reactivities of the borane species.

2.2. Reactions of the cobalt carbonyl reagent formed

We have carried out a series of experiments with olefins after adding methanol to the reagent system to convert the hydroborating ‘BH’ species to ‘$BOCH_3$’ (Eq. (2)). Whereas simple olefins such as 1-decene and cyclopentene did not react under the reaction conditions, norbornene did undergo carbonylation. After workup, the dinorbornylketone **8** and the enol-lactone **9** were obtained in 15% and 70% yields, respectively. We have also established that the species generated using BH_3 amine complex and methanol under similar conditions does not hydroborate olefins. Clearly, the observed reactivity of norbornene should result from the hydridocobalt carbonyl species formed in situ in the reaction mixture. It is well-known such species, which are formally acidic in nature, are stable in protic medium.

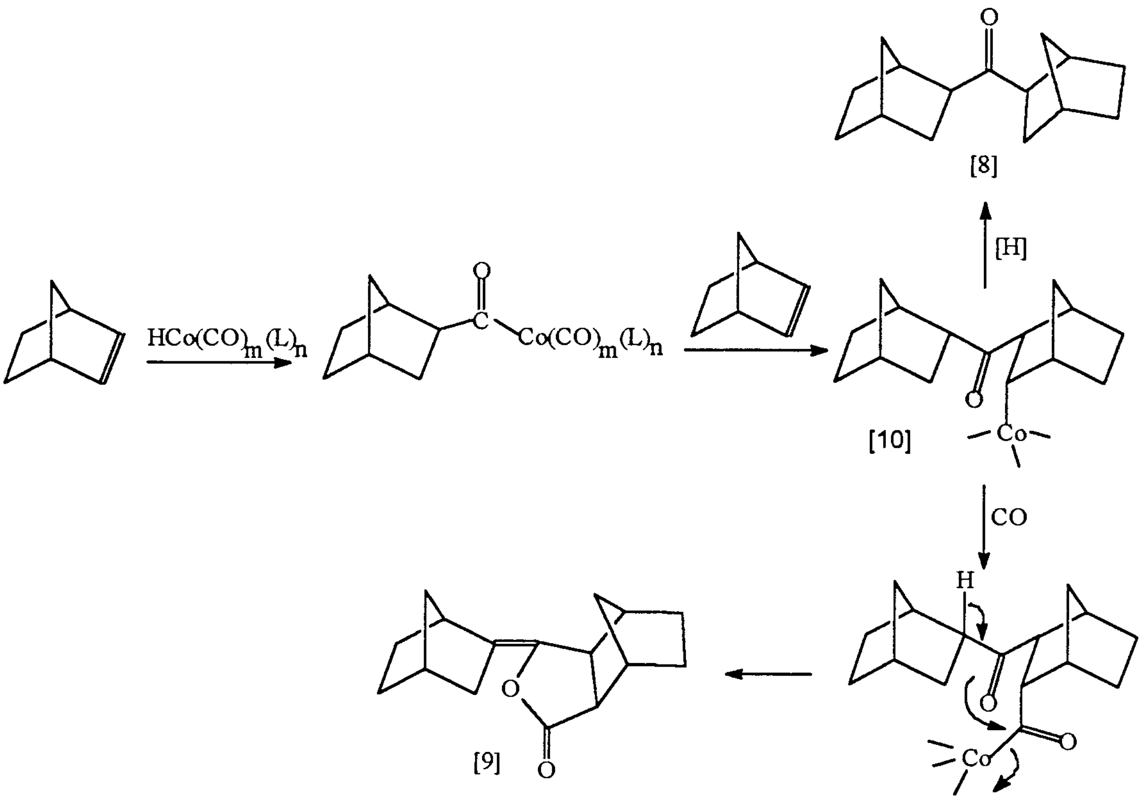


(2)

Previously, it has been observed in this laboratory that the reagent generated by the reduction of $CoCl_2$ with $NaBH_4$ and CH_3OH in THF under CO, on reaction with norbornene gave the dinorbornylketone (**8**) and a novel enol-lactone **9** (Eq. (2)) [20]. The ^{13}C NMR spectrum of enol-lactone **9** indicated the presence of an isomeric mixture (two closely spaced signals for several carbon atoms). This enol-lactone **9** earlier has been reported in the reaction of norbornene with a palladium (0) complex in the presence of CO [21]. Structural assignment of the enol-lactone **9** is based on the spectral data (IR, ^{1}H, ^{13}C NMR and mass) and agrees with the reported data [21].

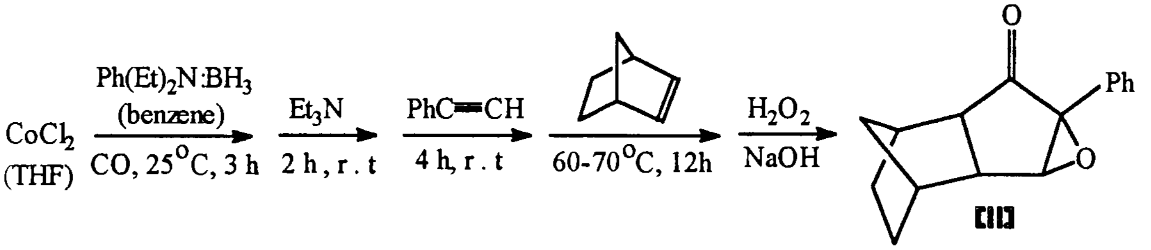
Most probably, these products could have formed through the reaction of hydridocobalt species, generated in situ, with norbornene followed by migratory insertion of another norbornene through intermediate **10**. The dinorbornyl ketone **8** could result from the protonolysis/reduction of the intermediate **10** (Scheme 2). The formation of enol-lactone **9** could result from the cyclisation of the intermediate.

In the above experiment (Eq. (2)) methanol was added to convert the hydroborating B–H species to $B{-}OCH_3$ to mask the reactivity of the borane species. However, this led to the formation of the H–Co species. It was thought that the cobalt carbonyl species of the type $Co_2(CO)_8$ would result if Et_3N is used to trap the hydroborating species as unreactive $Et_3N{:}BH_3$. The formation of $Co_2(CO)_8$ can be readily examined by performing the reaction in the



Scheme 2.

presence of an alkyne to obtain the (alkyne) $Co_2(CO)_6$ complex. In turn, it is also possible to examine the presence of this complex by performing the Pauson–Khand reaction with norbornene [22]. To examine this possibility, an experiment was performed using triethylamine and phenyl acetylene (Eq. 3). The crude product obtained was oxidised with $H_2O_2/NaOH$ to remove any organoborane that might have formed and to destroy the $BH_3{:}N(Et)_3$. Interestingly, the epoxy–ketone **11** was obtained in 30% yield (Eq. (4)).



(4)

Presumably, the epoxide is formed through Michael type addition reaction of the Pauson–Khand cyclopentenone with the HOO^- present in the medium [23,24]. The epoxide ring formed may be expected to be exo to the existing bicyclooctyl skeleton. The epoxy-ketone was also prepared through the reaction of HOO^- with an authentic sample of the corresponding cyclopentenone under similar reaction conditions [22]. Obtention of the epoxy-ketone derived from the Pauson–Khand cyclopentenone indicates the generation of $Co_2(CO)_8$ or equivalent species in situ in the above experiment using triethylamine.

In summary, a simple, convenient method has been developed using the $BH_3{:}N(Et)_2Ph/CoCl_2/CO$ reagent combination for the hydroboration and carbonylation of alkenes to obtain the corresponding dialkyl ketones after oxidation. It was further observed that the hydridocobalt species can be generated by the addition of methanol to this reagent combination as illustrated in the formation of dinorbornyl ketone and novel enol-lactone **9** with norbornene. Also, the dicobalt octacarbonyl or its equivalent species has been generated in the presence of triethylamine, as demonstrated by the formation of epoxy-ketone **11** derived from the Pauson–Khand cyclopentenone using phenylacetylene and norbornene. Obtention of the epoxy-ketone from four fragments, i.e., phenylacetylene, norbornene, carbon monoxide and H_2O_2 in a single pot operation is interesting from the synthetic point of view.

3. Experimental

3.1. General

All glassware were pre-dried at 140°C in an air oven for 4 h, assembled in hot and cooled under a stream of dry nitrogen. All the operations/transformations of organoborane reagent transferred using standard syringe, septum techniques as recommended for handling air sensitive organoboranes [21]. All dry solvents and liquid reagents distilled using appropriate drying agents just before use. Sodiumborohydride (97%) supplied by LOBA-Chemie, India and Fluka, Switzerland were utilised and kept under N_2 in a desiccator. Anhydrous $CoCl_2$ was prepared from its hydrated salt supplied by Fluka, Switzerland, LOBA Chemie and E. Merck, India. The hydrated metal salt was kept in the air oven for 5–6 h further, dried at 150°C for 4 h under vacuum and was kept under nitrogen in a desiccator. The alkenes utilised were commercial samples supplied by Fluka, Switzerland. 1-alkynes were prepared following a literature procedure [22]. IR spectra were recorded on Perkin–Elmer IR spectrometer Model 1310 and JASCO FT 5300 with polystyrene as reference. ^1H and ^{13}C NMR spectra were recorded on a JEOL-FX-100 and Bruker AC-200 spectrometers with chloroform-d as a solvent and TMS as reference ($\delta = 0$ ppm). Column chromatography was carried out using Acme's silica gel (100–200 mesh) using hexane/ethyl acetate as eluent. Carbon monoxide was generated by dropwise addition of formic acid 98% to conc. H_2SO_4 96% at 80–90°C using an apparatus recommended for utilisation in the carbonylation of organoboranes [21].

3.2. General procedure for the reaction of $Ph(Et)_2N{:}BH_3/CoCl_2/CO$ with 1-decene

The $Ph(Et)_2N{:}BH_3$ (10 mmol) complex in benzene (30 ml) was prepared according to literature procedure [11]. This was added to a suspension of anhydrous $CoCl_2$ (10 mmol, 1.29 g) in THF (50 ml) at 25°C while bubbling carbon monoxide, through a double ended needle under N_2 atmosphere. The reaction mixture was stirred for 2 h under carbon monoxide atmosphere. Alkene (1-decene, 20 mmol, 2.8 g) was added and carbon monoxide bubbling was continued for 5–6 h. The contents were further stirred for 36 h at 25°C. The resulting mixture was poured into water (20 ml). The organic phase was separated and the aqueous phase was saturated with NaCl extracted with ether (2×30 ml). The combined organic extracts were washed with brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The residue was dissolved in THF (30 ml) and oxidised with $H_2O_2/NaOH$. After oxidation, the organic phase was separated and the aqueous phase was saturated with NaCl solution and extracted with ether (2×30 ml). The combined organic extracts were washed with 3 N HCl (2×30 ml), water (20 ml), brine (30 ml), dried over anhydrous $MgSO_4$ and concentrated. The crude product was subjected to chromatography on a silica gel column. Di-*n*-decylketone (69%, 2.13 g) and *n*-decanol (25%, 0.79 g) were isolated using ethyl acetate (3% and 5%) in hexane as eluents respectively. The compound was identified by IR, ^1H, ^{13}C NMR and by comparison with the literature data. The same procedure was followed for other substrates and the spectral data of the products were in 1:1 correspondence with the reported data [17].

3.3. Reaction of the species generated from $Ph(Et)_2N{:}BH_3/CoCl_2/CO/$methanol with norbornene

The $Ph(Et)_2N{:}BH_3$ (10 mmol) kendy complex in benzene (30 ml) was prepared according to literature procedure [11]. This was added to a suspension of anhydrous $CoCl_2$ (10 mmol, 1.29 g) in THF (50 ml) at 25°C while bubbling carbon monoxide through a double-ended needle under N_2 atmosphere. The reaction mixture was stirred for 2 h under carbon monoxide atmosphere. Dry methanol (30 mmol) was added and the reaction mixture was stirred for 1 h under carbon monoxide atmosphere. Norbornene (10 mmol, 0.94 g) was added and the contents were further stirred for 7 h at 70–80°C. The resulting mixture was poured into water (30 ml). The organic phase was separated and the aqueous phase was saturated with NaCl solution and extracted with ether (2×30 ml). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated. The crude product was subjected to column chromatography on silica gel. The dinorbornyl ketone (**8**) was isolated in 15% (0.17 g) yield using ethyl acetate (5%) in hexane as eluent. Ethyl acetate (10%) in hexane eluted 70% (0.85 g) yield of enol-lactone **9**. The spectral data of the products **8** and product **9** show 1:1 correspondence with the data previously reported [17,21]. Dinorbornyl ketone **8**: M.P. 53°C (Ref. [25] M.P. 53–54°C); IR (neat) 1700 cm^{-1}; ^1H NMR δ 0.9–1.9 (m), 2.1–2.6 (m); ^{13}C NMR δ 28.4, 29.2, 29.5, 32.1, 32.9, 34.2, 35.4, 39.5, 40.1, 52.3, 52.7, 212.3, 212.6 (CO). Enol-lactone **9**: IR (neat) 1720, 1780 cm^{-1};^1H NMR δ 0.9–1.6 (m), 1.9–2.7 (m);^{13}C NMR δ 26.9, 27.0, 27.4, 27.5, 27.7, 27.9, 28.8, 28.9, 33.7, 36.0, 39.0, 39.7, 39.8, 39.4, 40.3, 42.7, 44.6, 44.8, 48.4, 48.5, 119.9, 120.0, 141.8, 142.2, 176.8; Mass (m/z) 244 (M^+).

3.4. Reaction of the $Ph(Et)_2N{:}BH_3/CoCl_2/CO/NEt_3$ reagent system with $PhC{\equiv}CH$ and norbornene followed by $H_2O_2/NaOH$ oxidation

The $Ph(Et)_2N{:}BH_3$ (20 mmol) complex in benzene (30 ml) was prepared according to literature procedure [11]. This was added to a suspension of anhydrous $CoCl_2$ (20 mmol, 2.6 g) in THF (50 ml) at 25°C while bubbling carbon monoxide through a double-ended needle under N_2 atmosphere. The reaction mixture was stirred for 3 h under carbon monoxide atmosphere. To this, dry triethylamine (20 mmol, 2.02 g) was added and the reaction mixture was stirred for 2 h under carbon monoxide atmosphere. Then $PhC{\equiv}CH$ (5 mmol, 0.5 g) was added and the contents were further stirred for 4 h at room temperature. Norbornene (10 mmol, 0.94 g) was added to the reaction mixture and the contents were stirred at 60–70°C for 7 h. The contents were brought to 25°C and the metal carbonyl was oxidised with CAN in methanol. Water (20 ml) is added and the organic phase was separated. The aqueous phase was saturated with sodium chloride and extracted with ether (2×30 ml). The combined organic extract was dried over anhydrous $MgSO_4$ and concentrated. The residue was dissolved in THF (30 ml) and treated with $H_2O_2/NaOH$ to oxidise organoborane species (if any) present in the crude product mixture. The organic phase was separated and the aqueous phase was saturated with sodium chloride and extracted with ether (2×30 ml). The combined organic extracts washed with 3 N HCl (2×30 ml), brine, dried over anhydrous $MgSO_4$ and concentrated. The crude product thus obtained was subjected to chromatography on a silica gel column and the epoxy-ketone **11** was isolated in 30% (0.36 g) yield using ethyl acetate (2%) in hexane as eluent. The product was identified by IR, ^1H, ^{13}C (DEPT experiments) NMR and mass spectral data. Compound **11**: IR (neat) 2874, 2382, 1738, 1628, 1500, 1448, 1278, 1240, 1153,1097, 1043, 883, 756, 696, 609 cm^{-1}; ^1H NMR δ 1.12–1.68 (m, 6H), 2.38–2.45 (m, 3H), 2.65 (s, 1H), 3.62 (s, 1H), 7.26–7.28 (m, 5H);^{13}C NMR δ 28.0, 29.0 and 34.5 ($-CH_2$), 38.0, 42.6, 45.2 and 53.4 ($-CH$), 65.8 (quaternary), 69.0 ($-CH$), 126.8, 128.3 and 128.5 ($-CH$), 131.0, (quaternary), 210.0 (CO); Mass (m/z) 240 (M^+ , 20%), 173 (30%), 105 (100%), 77(40%). 41 (30%).

Acknowledgements

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