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Carbonylation of R_2BI in the presence of $NaCo(CO)_4$ and $Na_2Fe(CO)_4$: A simple synthesis of dialkyl ketones

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Abstract

Reaction of $NaCo(CO)_4$ with R_2BI under carbon monoxide at atmospheric pressure at room temperature readily gives the dialkyl ketones in good yields (61–85%) after H_2O_2/OH^- oxidation.

Introduction

Organometallic compounds containing one or more metal–metal bonds have been of interest in recent years [1,2]. Most of the investigations have focused on the preparation and physical properties of such compounds and their reactivities have not been investigated in detail. We report below that the intermediate formed by the reaction of $NaCo(CO)_4$ with R_2BI under carbon monoxide at atmospheric pressure at room temperature readily gives the dialkyl ketone in good yield after H_2O_2/OH^- oxidation.

Results and discussion

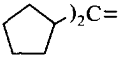
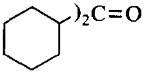
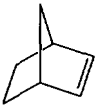
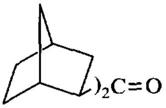
We have recently developed convenient methods for the synthesis of $NaCo(CO)_4$ [3], $Na_2Fe(CO)_4$ [4] and R_2BI [5]. It was of interest to investigate the reactions of species produced *in situ* by the interaction of $Co(CO)_4{}^-$, $Fe(CO)_4{}^{2-}$ and R_2BI (R = alkyl) reagent under carbon monoxide.

When R_2BI (10 mmol, R = n-octyl) in benzene (40 ml) was treated with $NaCo(CO)_4$ (10 mmol) in THF (60 ml) for 2 h, and the mixture then treated with CO for 4–5 h and subsequently stirred for 12–36 h at room temperature, di-n-octyl ketone was isolated in 72% yield after H_2O_2/OH^- oxidation. The transformation is a general one and several other R_2BI reagents were converted into R_2CO (Table 1).

It is known that reaction of the species R_3B (e.g. R = n-octyl) with carbon monoxide at 100–120 °C for 8 h in the presence of H_2O gives di-n-octyl ketone [6]. When R_2BI (R = n-octyl) prepared in benzene (40 ml) was, after addition of THF (60 ml), carbonylated for 4–5 h at room temperature in the absence of $Co(CO)_4{}^-$ followed by stirring for 36 h, octanol (75%) and di-n-octyl ketone (15%) were isolated after oxidation. These results show that the presence of $Co(CO)_4{}^-$ in the system certainly enhances the ease of carbonylation of R_2BI.

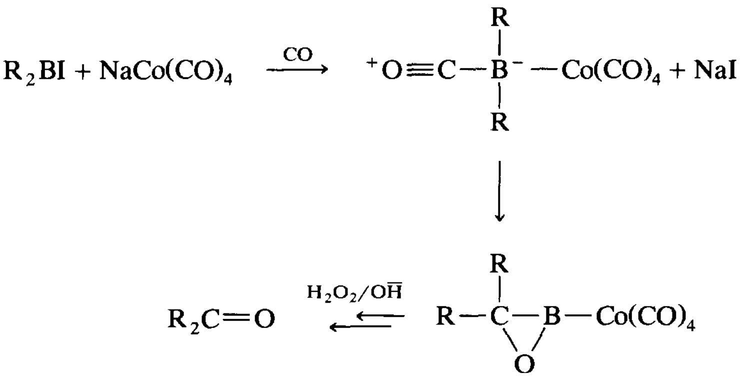
Table 1

Reaction of R_2BI with $NaCo(CO)_4$ under carbon monoxide

Alkene	Time (h)	Product [a]	Yield [b]
$C_4H_9CH=CH_2$	36	$C_4H_9CH_2-CH_2)_2C=O$ (1)	76 [c]
$C_6H_{13}CH=CH_2$	36	$C_6H_{17}CH_2-CH_2)_2C=O$ (2)	72 [c]
$C_8H_{17}CH=CH_2$	36	$C_8H_{17}CH_2-CH_2)_2C=O$ (3)	74 [c]
	12	 (4)	85
	24	 (5)	75
	24	 (6)	73
$H_3COOC(CH_2)_8CH=CH_2$	36	$H_3COOC(CH_2)_9CH_2)_2C=O$ (7)	61 [c]

[a] Products obtained after oxidation with H_2O_2/OH^-. Products were identified by analysis of spectral data (IR, ^{13}C and ^1H NMR) and comparison with reported data. Selected ^{13}C NMR data (δ, ppm): **1**: 210.8, 42.3, 31.2, 28.5, 23.4, 22.1, 13.5; **2**: 210.7, 42.5, 31.7, 29.3, 29.2, 29.1, 23.7, 22.5, 13.9; **3**: 211.4, 42.8, 31.9, 29.4, 29.2, 23.8, 22.6, 14.0; **4**: 215.0, 50.0, 28.6, 25.5; **5**: 216.4, 48.9, 28.4, 25.7, 25.5; **6**: 212.6, 212.3, 52.7, 52.3, 40.1, 39.5, 35.4, 34.2, 32.9, 32.1, 29.5, 29.2, 28.4; **7**: 211.5, 174.5, 51.3, 42.8, 34.1, 29.4, 29.2, 25.0, 24.9, 24.0. [b] Yields are of products isolated by column chromatography with hexane/ethylacetate (95/5) as an eluent. [c] 20–25% of alcohol (i.e. hydroboration–oxidation product) was also isolated.

It is known that Ph_2BCl reacts with $Co(CO)_4^-$ to give $Ph_2BCo(CO)_4$ [7]. The IR spectrum of the solution recorded after stirring of a mixture of R_2BI (10 mmol in benzene 40 ml) and $Co(CO)_4^-$ (10 mmol in THF 60 ml) for 2 h at room temperature exhibits a strong absorption at 1890 cm^{-1} arising from $Co(CO)_4^-$ [3]. However, after 36 h stirring at room temperature the solution IR spectrum shows a strong absorption at 2010 cm^{-1}, arising from neutral cobalt carbonyl species. Since $NaCo(CO)_4$ is very stable [3] in THF under carbon monoxide, the neutral cobalt carbonyl could have been formed only after the interaction of R_2BI with $Co(CO)_4^-$. Furthermore the product obtained before oxidation with H_2O_2/OH^- does not show any ketonic carbonyl absorption in the IR spectrum. However, the exact structure of the intermediate after carbonylation is not known. The results may be accounted for in terms of the following tentative mechanism, similar to that proposed for the carbonylation of R_3B at 100–120 °C [8].



In order to see whether the reaction time could be reduced by carrying out the reaction at higher temperature, we stirred a mixture of R_2BI (R = n-octyl) in benzene (40 ml) with $Co(CO)_4^-$ (10 mmol) in THF (60 ml) for 2 h at room temperature and then refluxed it under carbon monoxide for 12 h. In this case, after work-up and oxidation the di-n-octyl ketone was isolated only in 10% yield in addition to octanol (75%) and octane (10%). This indicates that the intermediate formed by the reaction of R_2BI and $Co(CO)_4^-$ is unstable at high temperature and also that it undergoes facile carbonylation only at room temperature.

We also examined carbonylation of R_2BI in the presence of Collman's reagent, $Fe(CO)_4^{2-}$. A mixture of R_2BI (10 mmol, R = n-octyl) in benzene (40 ml) and $Fe(CO)_4^{2-}$ (10 mmol) in THF (40 ml) was stirred for 2 h at room temperature, then carbon monoxide was bubbled in for 4–5 h and the mixture subsequently stirred for 36 h at room temperature. Di-n-octyl ketone (30%) and l-octanol (65%) were isolated after work-up and oxidation (for R = decyl, di-n-decyl ketone (28%) and decanol (62%) were isolated).

The infrared spectrum taken after a mixture of R_2BI (10 mmol) in benzene (40 ml) and $Fe(CO)_4^{2-}$ (10 mmol) in THF (40 ml) had been stirred for 2 h at room temperature exhibited absorptions at 1830, 1900, 1960 cm^{-1}. The species formed may be $R_2B{-}Fe(CO)_4^-$ since the spectral data are comparable with those for $R{-}Fe(CO)_4^-$ [9]. The formation of dialkyl ketone in low yield may be due to the presence of negative charge in $R_2B{-}Fe(CO)_4^-$ which can reduce the electrophilic nature of boron by back donation. Hence, nucleophilic attack on boron by carbon monoxide may not take place readily.

We conclude that the new method serves as a simple alternative [6,10–12] for the conversion of alkenes into symmetrical ketones. It has the advantages that there is no alkyl group loss and that the reactions are carried out under mild conditions. The study also throws some light on the stability and reactivity of the species $R_2B{-}Co(CO)_4$ and $R_2B{-}Fe(CO)_4^-$ under carbon monoxide.

Experimental

THF was distilled over benzophenone–sodium immediately before use. Carbon monoxide was generated by adding HCOOH (98–100%) to concentrated H_2SO_4 as described for carbonylation of organoborane [13]. $NaCo(CO)_4$ (10 mmol) was prepared *in situ* by the reduction of $CoCl_2/CoBr_2$ (10 mmol) with sodium (33 mmol) under carbon monoxide [3]. $Na_2Fe(CO)_4$ (10 mmol) was prepared *in situ* by the reduction of $Fe(CO)_5$ (10 mmol) with sodium (22 mmol) and naphthalene (7 mmol) under carbon monoxide [4]. The R_2BI (10 mmol) compounds were prepared by stirring the appropriate alkene (20 mmol) with $IH_2B:N(Et)_2Ph$ (10 mmol) for 6 h at room temperature then 3 h at 50 °C, except for R_2BI with R = cyclohexyl, which was made by treatment of the corresponding R_2BH compound with I_2 [5].

General procedure for the reaction of R_2BI with $NaCo(CO)_4$

The R_2BI (10 mmol) prepared in benzene (40 ml) from $IBH_2:N(Et)_2Ph$ (10 mmol) and l-octene (20 mmol) was added to $NaCo(CO)_4$ (10 mmol) in THF (60 ml). The mixture was stirred for 2 h and carbon monoxide was bubbled in for 4 h at room temperature. The mixture was stirred for a further 12–36 h then poured into H_2O (40 ml) containing ceric ammonium nitrate (20 mmol) to destroy the metal carbonyl. The organic phase was separated and the aqueous phase extracted with ether (2 × 30 ml). The combined organic extracts were dried over $MgSO_4$ and evaporated.

The residue was dissolved in THF (40 ml) and oxidised with 3*N*-NaOH and H_2O_2 by a procedure previously described for the oxidation of organoboranes [13]. The organic phase was subsequently separated and the aqueous phase was saturated with NaCl and extracted with ether (2 × 30 ml). The combined organic extracts were washed with 3*N* HCl (2 × 30 ml), H_2O (20 ml), and brine (30 ml), then dried over $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column (with hexane/ethyl acetate as eluent) to give the ketone R_2CO, in the yield shown in Table 1.

A similar procedure was used for the reaction of R_2BI with $Na_2Fe(CO)_4$.

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