HYDROGEN TRANSFER FROM ORGANIC COMPOUNDS DURING THE PROCESS OF OLEFIN CARBONYLATION
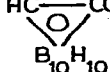
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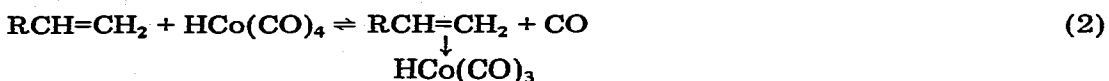
Summary

Vinyl-, allyl- and isopropenyl-*o*-carboranes are only hydrated to the respective alkyl-*o*-carboranes under conditions of hydroformylation, i.e. initial H_2 pressure, 20—60 atm; total initial H_2 + CO pressure, 60—150 atm; catalyst, $Co_2(CO)_8$ or $Rh_4(CO)_{12}$; temperature, 100—160°C; solvent, saturated alcohols, diethyl ether, THF or toluene. The same reaction proceeds when carbonylating these alkenyl-*o*-carboranes in a CO atmosphere (initial CO pressure of 60—300 atm in saturated alcohols) hydrogen being transferred from the alcohols. A study of this reaction in deuterated alcohols established that the hydroxyl group is the hydrogen donor. In deuteromethanol (CH_3OD) a product of isopropenyl-*o*-carborane deuteration, HC———$CCDCH_3CH_2D$, was obtained. In CH_3CD_2OH only a product of hydration, propyl-*o*-carborane is formed.
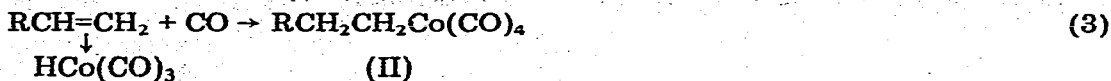
Introduction

Metal carbonyls, particularly $Co_2(CO)_8$ and $Rh_4(CO)_{12}$, are known to catalyze hydrogenation of unsaturated hydrocarbons and hydroformylation of olefins, the latter reaction being frequently accompanied by hydrogenation [1]. The mechanism of olefin hydroformylation catalyzed by metal carbonyls has been comprehensively studied. Under the action of hydrogen, 30—60 atm $Co_2(CO)_8$ is converted into an active catalyst system, $HCo(CO)_4$, which forms complex I with the substrate (reactions 1 and 2). Under high pressure, complex I undergoes

$$Co_2(CO)_8 + H_2 \rightleftharpoons 2\ HCo(CO)_4 \tag{1}$$

$$RCH=CH_2 + HCo(CO)_4 \rightleftharpoons RCH=CH_2 + CO \tag{2}$$
$$\downarrow$$
$$HCo(CO)_3$$

(I)

a π—σ rearrangement into alkyltetracarbonylcobalt (II) (reaction 3). Complex II is then carbonylated to acyltetracarbonylcobalt which is reduced to the end pro-

$$RCH\!=\!CH_2 + CO \rightarrow RCH_2CH_2Co(CO)_4 \tag{3}$$
$$\downarrow$$
$$HCo(CO)_3 \qquad (II)$$

duct, an aldehyde. At the same time a side reaction, reduction of alkyltetracarbonylcobalt to the end product of hydrogenation, may occur [1,2].

As we have established previously, vinyl- and isopropenyl-o-carboranes, under conditions of hydroformylation, are only hydrogenated to ethyl- and isopropyl-o-carboranes [3]. It should be noted that alkenyl-o-carboranes are hydrogenated in an atmosphere containing only hydrogen, presumably because $HCo(CO)_4$ decomposes at step 2 in the absence of CO and the π—σ-rearrangement does not take place (step 3). Thus, alkenyl-o-carboranes form complexes I and II with $HCo(CO)_4$ and are then reduced to alkyl-o-carboranes, but are not carbonylated. Such behavior is probably due to the strong electron—acceptor effect of the carboranyl group [3].

Alkenyl-o-carboranes are similarly hydrogenated in the presence of cobalt and rhodium salts, since they are readily converted into the respective carbonyls under the conditions of the process.

Whilst the mechanism of formation and the role of $HCo(CO)_4$ in hydroformylation reactions is more or less clear, the same cannot be said about carbonylation of olefins and acetylenes to carboxylic acids that proceed under the same conditions but in the absence of free hydrogen, H_2. $HCo(CO)_4$ is presumably also active in these processes, but the mechanism of its formation and the source of hydrogen have not yet been investigated. Usually carbonylation of olefins and acetylenes, catalyzed by metal carbonyls, is carried out in the presence of HX promoters, for example, dry hydrogen chloride [4]. It is quite possible that the role of promoters involves generation of $HCo(CO)_4$. However, carbonylation with $Co_2(CO)_8$, in alcohol and H_2O solutions, also proceeds in the absence of promoters [5], the hydrogen source being alcohol or water. Therefore, intermolecular hydrogen transfer from alcohol or water to the substrate may occur during carbonylation of olefins and acetylenes. $HCo(CO)_4$ is generated at the first step and carbonylation then follows the same scheme as hydroformylation (steps 2, 3 and 4).

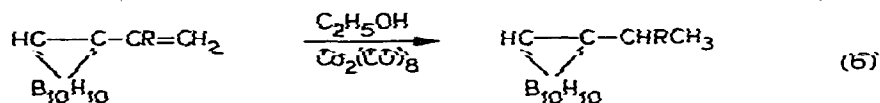$$RCH_2CH_2Co(CO)_4 + CO \rightleftharpoons RCH_2CH_2COCo(CO)_4 \tag{4}$$

Formation of the end product and regeneration of the catalyst involves decomposition of the complex under the action of alcohol or water (reaction 5).

$$RCH_2CH_2CO\!-\!Co(CO)_4 + R'OH \rightarrow RCH_2CH_2CO\!-\!OR' + HCo(CO)_4 \tag{5}$$
$$(R' = H, CH_3, C_2H_5, \text{ etc.})$$
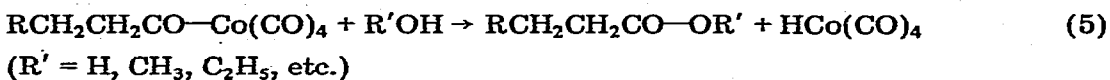
The greatest interest centres around the step of $HCo(CO)_4$ generation, as it is unclear whether the methylene or hyroxyl group is the source of hydrogen in alcohols. Intermolecular hydrogen transfer from organic compounds in the presence of transition metal complexes has been sufficiently well studied and it is considered that a hydride transition from the methylene group takes place [6].

Results and discussion

Attempts to carbonylate vinyl- and isopropenyl-o-carboranes under standard conditions, i.e. CO pressure, 60—300 atm; 100—190°C; catalyst, $Co_2(CO)_8$ or $Rh_4(CO)_{12}$; solvent, CH_3OH, C_2H_5OH or i-C_3H_7OH; as in the case of hydroformylation, lead only to hydrogenation to ethyl- and isopropyl-o-carboranes (eq. 6).

$$HC\text{---}C\text{-}CR=CH_2 \quad \xrightarrow[\text{Co}_2(\text{CO})_8]{C_2H_5OH} \quad HC\text{---}C\text{-}CHRCH_3 \qquad (6)$$
$$B_{10}H_{10} \qquad\qquad\qquad\qquad B_{10}H_{10}$$

$(R = H, CH_3)$

Such behaviour may be attributed, as in the case of hydroformylation, to the strong electron-withdrawing effect of the o-carboranyl group. Even introduction of a methylene bridge between the vinyl group and the o-carboranyl moiety does not affect the reaction route, 1-methyl-2-allyl-o-carborane is also only hydrogenated under the same conditions.
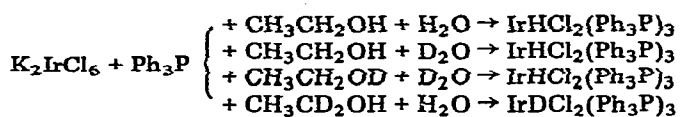
Alkenyl-o-carboranes are hydrogenated under these conditions as a result of intermolecular hydrogen transfer from an alcohol molecule to the substrate. Alcohols, in their turn, are converted to ketones or ethers, for instance, acetone is formed in the case of isopropanol. Cobalt and rhodium carbonyls are the catalysts of hydrogen transfer and act as transmitters of hydrogen. As expected, $Rh_4(CO)_{12}$ is substantially more active than the cobalt carbonyl. Hydrogenation of alkenyl-o-carboranes proceeds under milder conditions with $Rh_4(CO)_{12}$, working CO pressure, 30—60 atm; and 10 times as much $Co_2(CO)_8$ is required to the produce the same effect.

Although reactions of hydrogen transfer from organic to substrate molecules in the presence of transition metal complexes have been widely studied, representing a new branch of homogeneous hydrogenation [6], studies concerning hydrogen transfer in carbonylation processes are very rare. It has been shown [7] that carbonylation of cyclohexane in CH_3OH and i-C_3H_7OH, along with carbonylation products, $C_6H_{11}COOR$ and $C_6H_{11}COCH_3$, yields $C_6H_{11}CHO$ and $C_6H_{11}CH_2OH$ as the result of intermolecular hydrogen transfer from alcohols, which are converted into dimethyl ether and acetone, respectively.

In this respect it is interesting to investigate hydrogen transfer in the process of olefin carbonylation using alkenyl-o-carboranes, which are only hydrogenated under these conditions and, thus facilitate analysis of results.

For most reactions of hydrogen transfer in the presence of transition metal complexes, hydride hydrogen transfer from organic compounds, hydride donors, has been established [6,8]. It has been shown for $IrHCl_2(Ph_3P)_3$ that only hydride transfer from the α-carbon atom of the alcohol occurs (Scheme 1). As can be

SCHEME 1

$$K_2IrCl_6 + Ph_3P \begin{cases} + CH_3CH_2OH + H_2O \rightarrow IrHCl_2(Ph_3P)_3 \\ + CH_3CH_2OH + D_2O \rightarrow IrHCl_2(Ph_3P)_3 \\ + CH_3CH_2OD + D_2O \rightarrow IrHCl_2(Ph_3P)_3 \\ + CH_3CD_2OH + H_2O \rightarrow IrDCl_2(Ph_3P)_3 \end{cases}$$
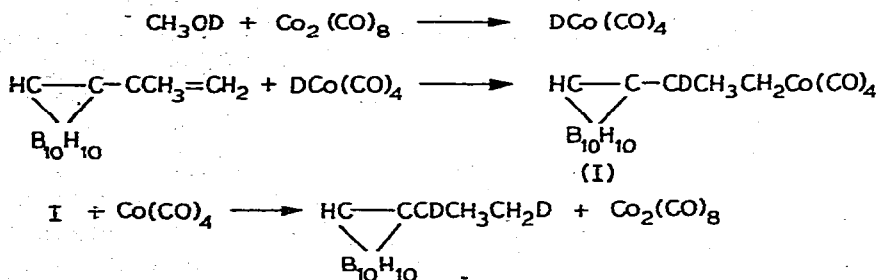
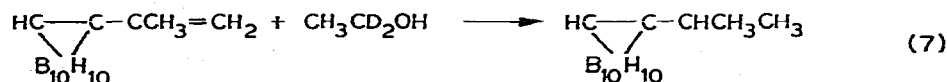seen from the scheme, neither water nor the hydroxyl donate hydrogen to iridium compounds [8].

However, according to our results, under conditions of olefin carbonylation, in the presence of $Co_2(CO)_8$, the hydroxyl group is the source of hydrogen. While carrying out carbonylation of i-propenyl-o-carborane in CH_3OD solution (initial CO pressure 180 atm, 160°C, 10 h, 0.03 M $Co_2(CO)_8$) we observed deut-

SCHEME 2

$$CH_3OD + Co_2(CO)_8 \longrightarrow DCo(CO)_4$$

$$HC\!\!-\!\!\!-\!\!C\!\!-\!\!CCH_3\!\!=\!\!CH_2 + DCo(CO)_4 \longrightarrow HC\!\!-\!\!\!-\!\!C\!\!-\!\!CDCH_3CH_2Co(CO)_4$$
$$B_{10}H_{10} \qquad\qquad B_{10}H_{10}$$
$$(I)$$

$$I + Co(CO)_4 \longrightarrow HC\!\!-\!\!\!-\!\!CCDCH_3CH_2D + Co_2(CO)_8$$
$$B_{10}H_{10}$$

eration (Scheme 2). The fact that I is not carbonylated to acyltetracarbonylcobalt is apparently connected with the instability of the complex and the readiness with which it is reduced to alkyl-o-carborane.

Carboxylation of i-propenyl-o-carborane in CH_3CD_2OH also confirms the proposed scheme of hydrogen transfer, since it yields, under the same conditions, only the product of hydrogenation, i-propyl-o-carborane (eq. 7). Deuteration products were absent in the reaction mixture.

$$HC\!\!-\!\!\!-\!\!C\!\!-\!\!CCH_3\!\!=\!\!CH_2 + CH_3CD_2OH \longrightarrow HC\!\!-\!\!\!-\!\!C\!\!-\!\!CHCH_3CH_3 \qquad (7)$$
$$B_{10}H_{10} \qquad\qquad B_{10}H_{10}$$

Studies of i-propenyl-o-carborane carbonylation in solvents that donate hydride ions showed that hydrogenation of the substrate does not occur. Thus, we investigated branched hydrocarbons, diethyl ether, THF, dioxane and toluene, and in all these solvents the initial compound remains unchanged.

Apparently the mechanism of $HCo(CO)_4$ formation in the rather rigid conditions of olefin carbonylation differs from the mechanism of hydride hydrogen transfer from compounds with high hydride mobility. It may be assumed that formation of $HCo(CO)_4$ proceeds through coordination of alcohol oxygen with cobalt atom in $Co_2(CO)_8$, redistribution of electron density in the complex, transition of the hydride to the other cobalt atom and to isolation of the forming $HCo(CO)_4$.

Experimental

Reactions were carried out in an electrically heated steel autoclave (0.5 l) equipped with a mixer. The purity of the starting compounds and products was monitored by GLC on a "Tsvet-4" chromatograph at 150–200°C using a column ($d = 4$ mm, $l = 2$ m) packed with Celite 545 treated with 20% silicon E-301. IR spectra were recorded with a No. 547–5001 Perkin–Elmer instrument. PMR spectra were obtained on a R-12 Perkin–Elmer instrument and ^{2}D NMR spectra on HX-90 Bruker.

Hydrogenation of isopropenyl-o-carborane

A solution of 9.2 g of i-propenyl-*o*-carborane (0.05 mol) in 100 ml of absolute ethanol and 0.1 g of $Co_2(CO)_8$ (catalyst concentration 0.003 M) was placed in the autoclave. Hydrogen was introduced to a pressure of 80 atm and then CO to a total H_2 + CO pressure of 150 atm. The mixture was then mixed for 10 h at 100—160°C. After cooling and unloading the autoclave the solvent was evaporated and the residue was distilled in vacuo at 91—92°C/1 mmHg (lit. [9] b.p. 90°C/1 mmHg) giving 6—9 g (64—96%) depending on conditions of the process, to give a transparant colorless liquid, n_d^{20} 1.5278 [9].

A solution of 9.2 g (0.05 mol) of i-propenyl-*o*-carborane in 100 ml of absolute ethanol and 0.1 g of $Co_2(CO)_8$ (0.003 M) was placed in the autoclave and a CO pressure of 120—150 atm was created. The mixture was stirred for 10 h at 160—190°C. After distillation in vacuo 92—94°C/1 mmHg 9.1 g (98%) of a transparent colorless liquid was obtained, n_d^{20} 1.5284.

A solution of 9.2 g (0.05 mol) of i-propenyl-*o*-carborane in 100 ml of absolute ethanol, 0.025 g of $Rh_4(CO)_{12}$ (catalyst concentration 0.0003 M was placed in the autoclave and CO was introduced to a pressure of 20—30 atm. The mixture was stirred for 3 h at 100°C. Distillation in vacuo 93°C/1 mmHg yielded 9.1 g (98%) of a transparent colorless liquid, n_d^{20} 1.5280.

A solution of 9.2 g (0.05 mol) of i-propenyl-*o*-carborane, 0.1 g of $Co_2(CO)_8$ in 25 ml of CH_3CD_2OH was placed in the autoclave. The mixture was stirred for 10 h at 180°C under a CO pressure of 180 atm. Distillation in vacuo 92—94°C/ 1 mmHg afforded 9 g (96%) of a transparent colorless liquid, n_d^{20} 1.5281, i-propyl-*o*-carborane [9].

IR spectrum of i-propyl-*o*-carborane, liquid film (ν, cm^{-1}): 3100, 3080, 2990, 2940, 2890, 2870, 2600 s, 1470, 1450, 1385, 1340, 1285, 1210, 1130 s, 1060 s, 1010 s, 920 w, 770 s, 725 s, 705 s.

Hydrogenation of vinyl-o-carborane

8.5 g (0.05 mol) of vinyl-*o*-carborane, 0.1 g of $Co_2(CO)_8$ (0.003 M) in 100 ml of absolute ethanol were placed in the autoclave. The mixture was stirred for 10 h at 180°C under a CO pressure of 180 atm. Distillation in vacuo 80°C/1 mmHg yielded 8.1 g (94%) of ethyl-*o*-carborane, a white crystalline substance, m.p. 53°C [9].

Hydrogenation of 1-methyl-2-allyl-o-carborane

A solution of 9.9 g (0.05 mol) of 1-methyl-2-allyl-o-carborane and 0.1 g of $Co_2(CO)_8$ (0.003 M) in 100 ml of absolute ethanol was placed in the autoclave. The mixture was stirred for 10 h at 180°C under CO pressure of 180 atm. Evaporation of solvent and recrystallization from hexane yielded 8.5 g (85%) of a white crystalline substance, m.p. 75°C (Found: C, 35.41; 35.53; H, 9.51, 9.45. $C_6H_{20}B_{10}$ calcd.: C, 36.06; H, 10.00%.)

IR spectrum of 1-methyl-2-propyl-*o*-carborane, KBr pellets (ν, cm^{-1}): 3100, 2980, 2960, 2895, 2600 s, 1460, 1450, 1390, 1320w, 1300w, 1240, 1180, 1030, 970, 940, 735s, 700w.

Deuteration of isopropenyl-o-carborane

A solution of 9.2 g (0.05 mol) of i-propenyl-*o*-carborane and 0.1 g of $Co_2(CO)_8$

in 25 ml of CH_3OD was placed in the autoclave. The mixture was stirred for 10 h at 180°C under a CO pressure of 180 atm. After evaporating CH_3OD the residue was distilled under vacuum giving 8.9 g (93%) of a transparent colorless liquid A, b.p. 95°C/1 mmHg

$$HC\underset{B_{10}H_{10}}{\overset{O}{\diagdown\diagup}}C-CDCH_3CH_2D$$

(A)
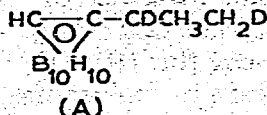
IR spectrum of liquid film (ν, cm^{-1}): 3100, 3090w, 2990, 2975, 2600s (B—H), 1465, 1440, 1400w, 1390, 1386w, 1340w, 1290, 1210, 1130, 1120, 1080, 1010, 930w, 740, 630, 500, 540.

NMR spectra of PMR spectrum (δ, ppm, external standard tetramethylsilane): 1.15 s (CH_3), 1.20 s ($-CH_2D$) and 3.62 s CH carborane. ^{2}D NMR spectrum (δ, ppm, external standard D_2O): two signals 4.8 (CH_2D) and 7.5 (CD).

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