STOICHIOMETRIC HYDROGENATIONS USING TETRACARBONYL-COBALTATE(−I)

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(Received October 15th, 1979)

Summary

Methanolic solutions of tetracarbonylcobaltate(−I) in the presence of an acid
are simple and useful reducing agents for the selective hydrogenation of conjug-
ated carbon-carbon double bonds. The reaction has the following stoichiometry:

$$3 \; \diagdown C = C \diagup + 2 \left[Co(CO)_4 \right]^- + 6\,H^+ \longrightarrow 3 \; \diagdown CH - CH \diagup + 2\,Co^{2+} + 8\,CO$$
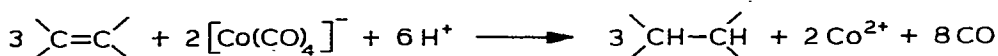
Introduction

Cobalt carbonyl hydride and its tertiary phosphine substituted derivatives can
act as hydrogenating agents in stoichiometric and catalytic reactions. Hydrogena-
tion of olefins, diolefins, alkynes, aldehydes, polycyclic aromatic compounds
and hydrogenolysis of alcohols and carboxylic acid anhydrides have been
described [1].

Mild conditions (1 bar of carbon monoxide and 25°C) are required for stoi-
chiometric hydrogenations using solutions of $CoH(CO)_4$ in hydrocarbons or
diethyl ether. The stoichiometry of the reaction in the above solvents is:

$$\diagdown C = C \diagup + 2\,CoH(CO)_4 \longrightarrow HC - CH \diagup + Co_2(CO)_8 \qquad (1)$$
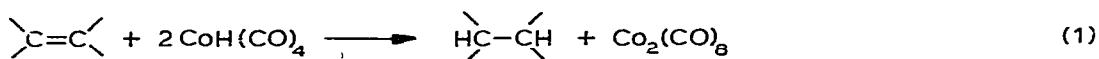
yielding 0.5 mole of hydrogenated product for one mole of $CoH(CO)_4$.

We now describe a modification of this procedure which allows a more effi-
cient and simple use of cobalt carbonyl hydride.

Results and discussion

In the presence of water, methanol, ethanol or other protic polar solvents we
observed a substantially different stoichiometry from that indicated in reaction
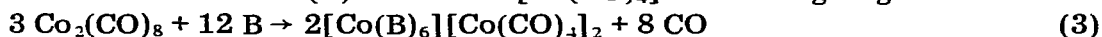
1, which leads to 1.5 moles of hydrogenated product for each mole of CoH-$(CO)_4$. In the presence of an acid the reaction has the form:

$$3 \; \text{C=C} \; + \; 2\,CoH(CO)_4 \; + \; 4\,H^+ \; \longrightarrow \; 3 \; \text{CH-CH} \; + \; 2\,Co^{2+} \; + \; 8\,CO \tag{2}$$
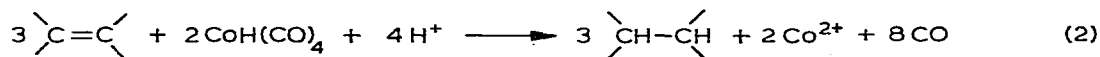
Thus by change of solvent three times as much of the unsaturated compound can be reduced with a given amount of $CoH(CO)_4$.

In polar solvents $CoH(CO)_4$ dissociates into H^+ and $[Co(CO)_4]^-$. The methanolic solution of $CoH(CO)_4$ shows only one broad infrared absorption band at $1904 \; cm^{-1}$, which is characteristic for the tetracarbonylcobaltate(—I) anions [2]. It is therefore obviously not necessary to use $CoH(CO)_4$, which is difficult to handle since it decomposes easily even at room temperature [3], since a solution of $[Co(CO)_4]^-$ combined with an acid will give the same reactions.

Several methods are known for preparing solutions of $[Co(CO)_4]^-$, e.g. by reduction of $Co_2(CO)_8$ electrochemically or with alkali metals, or by reduction of Co^{2+} salts with CO. Most simply, solutions of $Co_2(CO)_8$ or $Co_4(CO)_{12}$ in the presence of a Lewis base (B) lead to the $[Co(CO)_4]^-$-containing reagent:

$$3 \; Co_2(CO)_8 + 12 \; B \to 2[Co(B)_6][Co(CO)_4]_2 + 8 \; CO \tag{3}$$

$$3 \; CO_4(CO)_{12} + 24 \; B \to 4[Co(B)_6][Co(CO)_4]_2 + 4 \; CO \tag{4}$$

If the Lewis base is present in excess a continuous cycle of reactions 1 and 3 account for the observed stoichiometry of reaction 2. This is most conveniently attained by using alcoholic solutions of $Co_2(CO)_8$ in the presence of H^+.
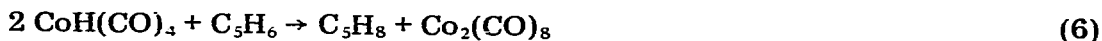
Results of stoichiometric hydrogenation experiments performed in this way are listed in Table 1.

The stoichiometric hydrogenation with tetracarbonylcobaltate(—I) solutions proved to be highly selective, not only in the case of diolefins such as cyclopentadiene but also in the regioselective reduction of 6-methylene tetracycline derivatives. In this latter case the α-epimer was preferentially formed, with the same high selectivity as in the catalytic hydrogenation using $RhCl(Ph_3P)_3$ as catalyst [4] or in the stoichiometric hydrogenation using phosphine substituted cobalt carbonyls [5].

In the case of styrene the hydrogenation of the carbon—carbon double bond was accompanied by a little hydroformylation. The hydroformylated products become predominant when the carbon—carbon double bond is not conjugated, as in the case of 1-heptene:

$$3 \; C_7H_{14} + 2[Co(CO)_4]^- + 6 \; H^+ \to 3 \; C_7H_{15}CHO + 2 \; Co^{2+} + 5 \; CO \tag{5}$$
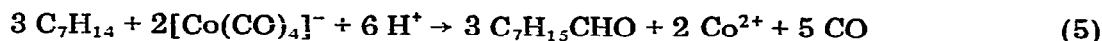
The selectivity of the $Co_2(CO)_8/MeOH/H^+$ hydrogenating reagent was most strikingly revealed by use of cyclopentadiene (cf. Table 1). Using $CoH(CO)_4$ in hydrocarbons for the hydrogenation of this olefin the reaction did not have the expected simple stoichiometry according to equation 6:

$$2 \; CoH(CO)_4 + C_5H_6 \to C_5H_8 + Co_2(CO)_8 \tag{6}$$

instead $(\eta^3\text{-}C_5H_7)Co(CO)_3$ and $(\eta^5\text{-}C_5H_5)Co(CO)_2$ are formed as byproducts:

$$Co_2(CO)_8 + 2 \; C_5H_6 \to C_5H_7Co(CO)_3 + C_5H_5Co(CO)_2 + 3 \; CO \tag{7}$$
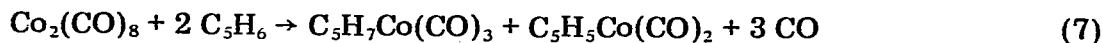
and a slow subsequent reaction between $(\eta^3\text{-}C_5H_7)Co(CO)_3$ and C_5H_6 leads to

TABLE 1

STOICHIOMETRIC HYDROGENATION OF VARIOUS SUBSTRATES USING SOLUTIONS OF TETRACARBONYLCOBALTATE(—I) AT 25°C AND CO ATMOSPHERE IN THE PRESENCE OF 3.6 MOL HCl/MOL [Co(CO)$_4$]$^-$. REACTION TIME: 5 HOURS

Substrate	Solvent [a]	mol substrate / mol [Co(CO)$_4$]$^-$	Products [b]
Benzylidene acetone	methanol	1.31	4-Ph-2-butanone: 88% benzylidene acetone: 7% unidentified: 5%
Ethyl cinnamate	ethanol	0.67	ethyl-3-Ph-propionate: 8% ethyl cinnamate: 92%
Dimethyl maleate	methanol	1.08	dimethyl succinate: 82% dimethyl fumarate: 9% dimethyl maleate: 9%
Dimethyl maleate	methanol	0.68	dimethyl succinate: 96% dimethyl fumarate: 4% dimethyl maleate: traces
Diethyl fumarate	ethanol	1.48	diethyl succinate: 83% diethyl fumarate: 17%
Diethyl fumarate	ethanol	0.73	diethyl succinate: 99% diethyl fumarate: traces
1,3-cyclopentadiene	methanol	1.25	cyclopentene: 100%
Styrene	methanol	1.29	ethylbenzene: 26% styrene: 58% phenylpropanal-dimethyl-acetal isomers: 12% unidentified: 4%
Styrene	methanol	0.66	ethyl benzene: 46% styrene: 34% phenylpropanal-dimethyl-acetal isomers: 15% unidentified: 5%
Heptene-1	methanol	1.50	octanals [c]: 68%
6-Demethyl-6-desoxy-6-methylene-5-hydr-oxytetracycline. HCl	methanol	1.22	α-6-desoxy-5-hydroxytetracycline [d]: 90% β-6-desoxy-5-hydroxytetracycline [d]: <2%

[a] 5 ml/mmol substrate +5 ml/mmol [Co(CO)$_4$]$^-$. [b] based on GLC analyses. [c] reaction time 40 hours; products isolated as 2,4-dinitro-phenylhydrazones. [d] reaction time 10 hours at 50°C and 3 hours at 60°C; products isolated as sulfosalicylate adducts.

further formation of cyclopentene:

$$C_5H_7Co(CO)_3 + C_5H_6 \rightarrow C_5H_5Co(CO)_2 + C_5H_8 + CO \qquad (8)$$
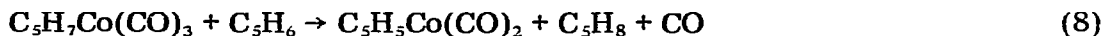
Experimental

All operations involving cobalt carbonyls were performed under a carbon monoxide atmosphere. Solvents were dried over sodium and saturated with CO. CoH(CO)$_4$ was prepared by the method of Sternberg et al., [6]. Solutions of tetracarbonylcobaltate(—I) were prepared by dissolving CoH(CO)$_4$ or Co$_2$(CO)$_8$ in methanol (or ethanol) and from Co$_2$(CO)$_8$ with Li in abs. THF [7].

Stoichiometric hydrogenation of benzylidene acetone in methanol (general procedure)

To a solution of 286 mg (1.96 mmol) of benzylidene acetone in 10 ml of methanol containing 175 mg (4.8 mmol) of HCl a solution of 342 mg (1.0 mmol) of $Co_2(CO)_8$ in 6.5 ml of methanol was added dropwise with stirring during 3 hours. Vigorous evolution of CO was observed. To complete the reaction, stirring was continued for 2 hours. After dilution with 50 ml of water, the product was extracted with 3 × 2 ml of chloroform, the combined extracts were neutralized with aqueous $NaHCO_3$ and dried over anhydrous Na_2SO_4; the chloroform was removed to yield 279 mg of a yellow oil. Analysis by GLC (3 m, 5% PEG on Chromosorb P, at 150°C) gave 4-phenyl-2-butanone: 88%, benzylidene acetone: 7%, unidentified compounds: 5%.

Stoichiometric hydrogenation of cyclopentadiene in the presence of methanol

342 mg (1.0 mmol) of $Co_2(CO)_8$ were dissolved in 7 ml cold anhydrous THF. This solution was added at 5°C to 15 mg (2.1 mmol) Li and stirred for 2 hours. The resulting clear solution was added dropwise at room temperature during 3 hours to 9 ml methanol containing 198 mg (3.0 mmol) of cyclopentadiene and 263 mg (7.2 mmol) of HCl. After stirring for an hour the CO evolution ceased and the reaction was complete. The mixture was diluted with 50 ml water and extracted with 3 × 5 ml pentane. GLC analysis showed 100% conversion in to cyclopentane.

Reaction of CoH(CO)₄ with cyclopentadiene in heptane

To 2.12 mmol of $CoH(CO)_4$ in 5.3 ml of heptane, 0.2 ml (2.44 mmol) of freshly prepared cyclopentadiene was added at room temperature. The mixture rapidly became brown. After shaking for 2 min the mixture was cooled to −80°C and the yellow crystalline $Co_2(CO)_8$ filtered off (360 mg, 1.05 mmol). GLC analysis of the filtrate (5% Dimethylsulfolane on Chromosorb P at 50°C, 2,3-dimethyl pentane internal standard) showed the formation of 1.02 mmol of cyclopentene.

When this experiment was repeated with 1.0 ml (12.2 mmol) of cyclopentadiene, after 3 days at room temperature no $Co_2(CO)_8$ could be isolated by cooling and 1.97 mmol of cyclopentene were formed. The infrared spectrum of the product showed the presence of $(\eta^3\text{-}C_5H_7)Co(CO)_3$ (2060 and 1998 cm^{-1}) and $(\eta^5\text{-}C_5H_5)Co(CO)_2$ (2035 and 1975 cm^{-1}). The two complexes could be separated by chromatography on a silica/gel column using hexane as eluent.

Stoichiometric hydrogenation of 6-demethyl-6-desoxy-6-methylene-5-hydroxy-tetracycline hydrochloride

The solution of 980 mg (2.86 mmol) of $Co_2(CO)_8$ in 15 ml methanol was added dropwise with stirring during 10 hours to a suspension of 1530 mg (3.2 mmol) of 6-demethyl-6-desoxy-6-methylene-5-hydroxy-tetracycline hydrochloride in 20 ml methanol containing 250 mg (6.85 mmol) HCl at 50°C. After additional stirring at 60°C for 3 hours, the evolution of CO ceased. The dark green mixture was cooled to room temperature. 1500 mg (6.88 mmol) of sulfosalicylic acid was added and the product diluted with 300 ml water. The resulting slurry was stirred for 10 minutes, then filtered and the light yellow crystalline solids were washed with water and dried in vacuo. The sulfosalicylic acid salts (1920 mg, 91.4%

yield) consist of 98% α-6-desoxy-5-hydroxtetracycline, 2% β-6-desoxy-5-hydroxy-tetracycline and less than 1% 6-demethyl-6-desoxy-6-methylene-5-hydroxytetra-cycline as indicated by quantitative TLC.

Stoichiometric hydroformylation of 1-heptene

The solution of 1025 mg (3.0 mmol) of $Co_2(CO)_8$ in 20 ml methanol was a added to 588 mg (6.0 mmol) of 1-heptene in 30 ml methanol containing 511 mg (14 mmol) of HCl at 25°C. The mixture was stirred for 40 hours until the slow CO evolution completely ceased. The heptanal product was isolated in the form of its 2,4-dinitrophenylhydrazone derivative (1260 mg, yield 68.3%, Mp.: 105°C).

References

1 A.J. Birch and D.H. Williamson, Org. Reactions, 24 (1976) 1.
2 Y. Iwashita, F. Tamura and H. Wakamatsu, Bull. Chem. Soc. Japan, 43 (1970) 1520.
3 F. Ungváry and L. Markó, J. Organometal. Chem., 20 (1969) 205.
4 R. Broggi and G. Cotti (Ankefarm S.p.A.), Ger. Offen. 2,308,227., Chem. Abstr. 79 (1973) 136908r.
5 C.J.V. Scanio (Pfizer Inc.), US 3 907 890, Chem. Abstr. 83 (1975) 206025j.
6 H.W. Sternberg, I. Wender, R.A. Friedel and M. Orchin, J. Amer. Chem. Soc., 75 (1953) 2717.
7 W.R. McClellan, H.H. Hoehn, H.N. Cripps, E.L. Muetterties and B.W. Howk, J. Amer. Chem. Soc., 83 (1961) 1601.