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Optically Active Alkylcobalt Carbonyls

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Asymmetric syntheses by means of transition metal complexes are in the focus of increasing interest [1]. Although most work has been done on hydrogenation, asymmetric hydroformylation [2, 3] represents an outstanding challenge since it leads to centers of asymmetry in many more cases than hydrogenation of the corresponding olefins. In spite of these possibilities the problem has scarcely been explored. Thus far, rhodium-based catalysts have provided the highest enantiomeric excesses. For example, diastereoselective [4] syntheses which were nearly quantitative [3, 5] and enantioselective [4] catalysis achieving 30–40% [6] optical yields have been reported. On the other hand, cobalt-based systems have produced much lower e.e. values [7]. Because of the less efficient but more general nature of the enantioselective reaction a comparison of models for these two approaches attracted our interest.

It can be reasonably concluded [2, 3] that the structure of intermediate alkylmetal carbonyls should be of decisive importance for the development of new centers of asymmetry. The recently observed stability of $ROOCCH_2Co(CO)_3L$ (R = alkyl, benzyl; L = CO, EPh_3; E = P, As, Sb) type alkylcobalt derivatives [8] prompted us to try to introduce centers of chirality into these compounds.

Results and Discussion

We synthesized $ROOCCH_2Co(CO)_3L$ compounds with R = Et, L = PPh_2Men^*, (Men^* = (1R,3R,4S)-(–)-menthol) (I); R = Men*, L = CO(II); R = Men*, L = PPh_3(III) and R = Men*, L = PPh_2Men^*(IV) and obtained their CD spectra along with those of the starting PPh_2Men^* and $BrCH_2COOMen^*$ (Fig. 1).

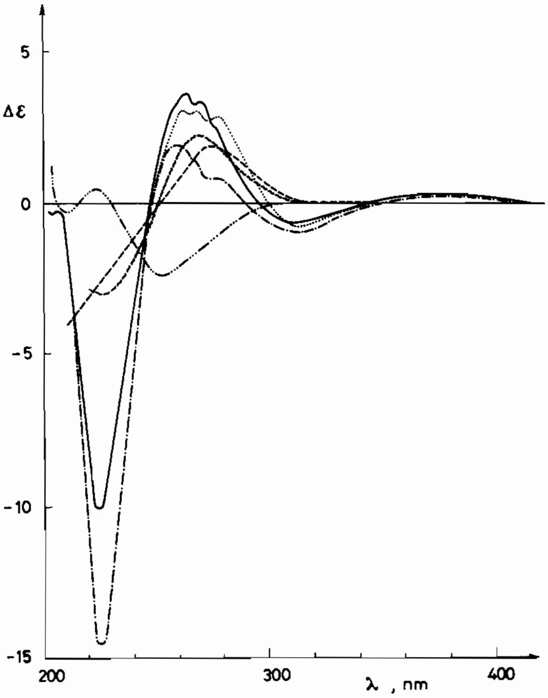

Fig. 1. CD spectra of the alkylcobalt compounds (I) ((–·–), (II) (~~~), (III) (– – –), (IV) (——), PPh_2Men^* (–…–) and the sum of the spectra of (I) and (III) (………). (The 320 nm maximum of (II) and the 220 nm maximum of $BrCH_2$-$COOMen^*$ are only of $\Delta\epsilon = 0.06$.)

Within the above series, compounds with chiral R served as models for enantioselective, while those with chiral L for diastereoselective syntheses. This has the advantages that (i) hydrogen shifts [7c] cannot occur in the alkyl group and (ii) the α-carbon of the carbalkoxymethyl group is achiral and thus the induction – if it exists – should be a net representation of the interaction between the center(s) of chirality and the metal carbonyl moiety.

The organometallic compounds showed much higher optical activity than the starting chiral substances. The shapes of the CD spectra of the organometallic esters are similar.

The maxima in the 250–280 nm range can be attributed to chiral n → π* transitions of the ester carbonyl group [9], while the bands at higher wavelengths belong to transitions involving electrons of the metal carbonyl moiety. The effective mechanism of the perturbation of the carbonyl band by the phosphine as well as the development of the lower energy bands probably involves the formation of chiral rotamers*. Most probably the energy

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*Compared with the rotamers detected by X-ray diffraction in the solid state for $PhCH_2OOCCH_2Co(CO)_3PPh_3$ [8].

barriers between the corresponding electron transitions are low; consequently, the individual rotamers are of low population and the CD bands of relatively low intensity.

It is of interest that not only are the shapes of the CD curves of compounds (I), (II) and (III) similar, but that, if the spectra of (I) and (III) are summarized, almost exactly the spectrum of (IV) can be obtained. This not only shows that the effects of chiral R or chiral L are of similar character, but also that they are of additive nature.

These results indicate that with both active ligand and active substrate, the cobalt carbonyl part of alkylcobalt carbonyls can be chirally perturbed. Furthermore, the mechanism of introduction seems to be similar suggesting the possibility of achieving much better optical yields with enantioselective catalysis.

Experimental

All operations were made with the usual inert technique. Starting compounds were of commercial origin with the exception of $Co_2(CO)_8$ (prepared according to [10]), $BrCH_2COOMen^*$ (prepared according to [11], $\alpha_D = -74.85°$ (neat)) and PPh_2Men^* (prepared according to [12], $[\alpha]_D^{20} = -87.4°$ (C 1.57, CH_2Cl_2)).

IR and CD spectra were obtained with IR-75 (Carl Zeiss, Jena) and DICHOGRAPH 3 (Jobin-Yvon) spectrometers respectively.

$Men^*OOCCH_2Co(CO)_4$ (II)

A $Na[Co(CO)_4]$ solution in 40 cm^3 Et_2O was prepared from 0.341 g (1 mmol) $Co_2(CO)_8$ and 40 g 1.5% Na/Hg and cooled to 0 °C. Then 0.54 g (1.9 mmol) $BrCH_2COOMen^*$ dissolved in 5 cm^3 Et_2O was added at once under stirring to the reaction mixture. NaBr starts to precipitate almost instantaneously and the colour of the solution turns to reddish brown. After 10–20 min all ν(C–O) bands other than those attributed [8, 13] to (II) disappear. The product is a brown oily substance which resisted attempts at crystallization. ν(C–O) bands (n-hexane, DCl calibration): 2111.0(m), 2045.5(s), 2036.0(vs), 2027.0(vs), 1712.0(w).

Substituted compounds (I), (III) and (IV)

These compounds were prepared from $EtOOCCH_2Co(CO)_4$ [8] or (II) in etheral solution with 1 molar excess phosphine. Upon addition of the phosphine at room temperature vigorous CO evolution was observed; 6–8 h stirring was needed to complete the reaction. The products (I) and (IV) were reddish-brown oily substances while (III) was obtained, by cooling to −78 °C and adding an equal volume of cold n-pentane, as a greenish-yellow, moderately air sensitive powder. Two or three recrystallizations transformed the powder to analytically pure crystals, ν(C–O) (n-hexane, DCl calibration): (I) 2054.0(w), 1989.0(s), 1977.0(s), 1710.5(m); (III) 2049.0(w), 1985.0(s), 1975.0(s), 1705.5(w); (IV) 2053.0(w), 1988.0(s), 1975.0(s), 1702.0(m).

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