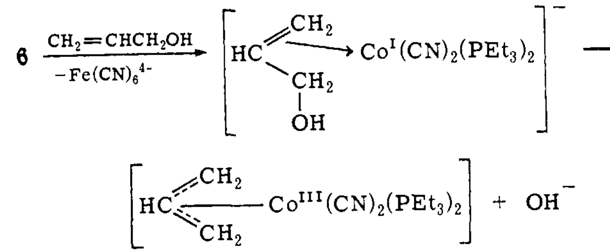
the reaction sequence



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(5)

4. The trapping of **6** by CO results in the regeneration of **1** and thus provides the basis for a *catalytic cycle, i.e.*, **1** → **3** (**5**) → **6** → **1**, in which the oxidation of CO by $Fe(CN)_6^{3-}$ proceeds readily under the catalytic influence of **1**, *i.e.*

$$CO + 2Fe(CN)_6^{3-} + 4OH^- \xrightarrow{1} CO_3^{2-} + 2Fe(CN)_6^{4-} + 2H_2O \quad (6)$$

This was confirmed in an experiment in which the (incremental) addition of 9.4×10^{-3} *M* $Fe(CN)_6^{3-}$ to a CO-saturated solution (pH 12) containing a catalytic amount (3.0×10^{-4} *M*) of **1** resulted in the formation of 4.6×10^{-3} *M* CO_3^{2-} (determined gravimetrically as $BaCO_3$).

The reaction scheme that we have described possesses several features in common with certain other systems, notably (1) the reactions of water or alcohols with other carbonyl complexes such as $[IrCl_2(PR_3)_2(CO)_2]^+$ and $[PtCl(PR_3)_2(CO)]^+$ to yield the corresponding stable hydroxycarbonyl and alkoxycarbonyl derivatives, *i.e.*, $[IrCl_2(PR_3)_2(CO)(COOH)]$[10] and $[PtCl(PR_3)_2(COOR)]$,[11,12] and (2) the reductions of various other metal complexes, notably of Rh(III),[13] by CO, many of which probably proceed through related mechanisms involving the loss of CO_2 from intermediates of the type MCOOH which were first proposed for the oxidation of CO by Hg(II)[14] and Ag(I).[15] Of particular interest in this context are some recent studies on the reduction of vitamin B_{12a} and certain related cobalt(III) complexes by CO, the mechanisms of which have been the subjects of considerable uncertainty and controversy.[1-4] It is not unlikely that at least some of these reactions, including the reported aquocobalamin-catalyzed oxidation of CO by O_2,[1] proceed through mechanistic schemes similar to that which we have described.

Acknowledgment. Support of this research through grants from the National Science Foundation (GP 26600) and the National Institute of Arthritis and Metabolic Diseases (AM 13339) is gratefully acknowledged. L. Y. G. also thanks the University of Malaya for a leave of absence.

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13 Hz, CHH′), 3.72 (2 H, d, J = 7 Hz, CHH′), 5.4 (1 H, m, CH). The π-allyl region of the nmr spectrum resembles that of other π-allyl complexes.[9]

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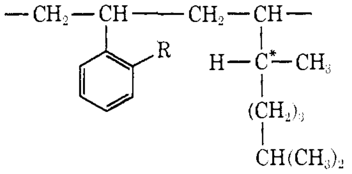
Received May 26, 1972

Circular Dichroism between 230 and 185 nm of the Aromatic Chromophore in High Molecular Weight Hydrocarbons[1]

Sir:

The main disadvantage in investigating chiroptical properties of the aromatic chromophore in low molecular weight alkyl aryl hydrocarbons is, in general, the very low ellipticity of its π → π* electronic transitions with respect to the absorption. As a consequence, the investigation[2,3] has been until now limited to the ^1L_b transition[4] and in one case only[5] the first extremum of the Cotton effect, related to the ^1L_a transition, has been reached.

In a previous paper, it was reported[6] that the absorption band between 275 and 245 nm of coisotactic copolymers of (*R*)-3,7-dimethyl-1-octene (I) with styrene (II) is optically active and its ellipticity is much larger than in low molecular weight models, when less than 20–25% units of II are present.[6,7] Considering that contour and vibrational spacing were similar in the copolymer and in the models, the larger ellipticity of the former was attributed to the smaller conformational mobility[8] of the aromatic rings in the dissymmetric environment of the one screw sense helical macromolecules.



I-II copolymer, R = H
I-III copolymer, R = CH_3

Taking into account the larger dissymmetry factor of the copolymers, we have now investigated the 230–185-nm spectral region, where the ^1L_a and ^1B transitions[4] of the benzene chromophore are located.

Figure 1 reports the CD spectrum (Roussell Jouan Dichrograph II) in the region of a coisotactic random copolymer[6,7] of I with II containing 20 mol % of the latter. At least four optically active bands can be observed: a rather weak positive band ($[\theta]_{max}$ per

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[1] III. Optically Active Hydrocarbon Polymers with Aromatic Side Chains. For paper II see F. Ciardelli, O. Pieroni, C. Carlini, and C. Menicagli, *J. Polym. Sci., Part A-1*, **10**, 809 (1972).

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Table I. Circular Dichroism between 230 and 185 nm of Coisotactic Random Copolymers of (*R*)-3,7-Dimethyl-1-octene[a] (I) with *o*-Methylstyrene (III)

Composition,[b] units from I/ units from III	Circular dichroism[c]: 230–205-nm region λ_{max}, nm	$[\theta]_{max}$,[d] $\times 10^{-3}$	λ_{max}, nm	$[\theta]_{max}$,[d] $\times 10^{-3}$	205–185-nm region λ_{max}, nm	$[\theta]_{max}$,[d] $\times 10^{-3}$	λ_{max}, nm	$[\theta]_{max}$,[d] $\times 10^{-3}$
80/20	224.5	+1.9	213	−19	200	−96	191	+74
54/46	225.5	+0.7	214.5	−19	200	−85	192.5	+71

[a] Optical purity 95–96%. [b] Determined by nmr. [c] In *n*-heptane at 27°. [d] Based on one unit from III.[9]

phenyl ring[9] +500) at 223.5 nm, a stronger negative band ($[\theta]_{max}$ −6900) between 220 and 205 nm, and two much stronger bands, the former negative ($[\theta]_{max}$ −63,000) at 195 nm and the latter positive ($[\theta]_{max}$ +36,000) at 187.5 nm. An analogous copolymer of I with *o*-methylstyrene (III), having the same composition I/III = 80/20 mol, shows a very similar CD spectrum (Figure 1). In fact four optically active bands can be observed between 230 and 190 nm, the sign and intensity of which follow in the same order as for the I–II copolymer. The red shift of about 5 nm of all bands could be caused by the hyperconjugative effect of the methyl substitution.[10] The increase of the content of III from 20 to 46 mol % leads to only a slight decrease of the ellipticity in the CD below 220 nm (Table I), whereas the $[\theta]_{max}$ at ~225 nm decreases from +1900 to +700 and that at 266 nm from +460 to +360. This last result is in keeping with data on copolymers of styrene with (*S*)-4-methyl-1-hexene.[7]

The CD data in the 205–185-nm region show that the ^{1}B transition of the phenyl ring is optically active and split into a negative and a positive band. This splitting, considering ellipticity and frequency separation of the two bands, has the characteristic exciton form.[11] Even if the splitting of the band related to the ^{1}B electronic transition of the benzene chromophore might be due to the low-site symmetry,[12] it seems at present that exciton interaction is the dominant mechanism.

The ^1L_a transition appears to be optically active also, but the difference between the areas of the two opposite sign bands in the 230–205-nm region is very large. Moreover, the positive band at 225 nm is markedly affected by the *o*-methylstyrene content, whereas the negative one between 220 and 205 nm is not (Table I). However, the occurrence of exciton splitting cannot be entirely excluded for the ^1L_a transition and further work is needed to clarify this point.

In order to explain the exciton splitting of the ^{1}B electronic transition, the coupling must be assumed to be between the excitation moments of the interacting aromatic residues, which are in fixed mutual stereochemical positions.[11,13] The latter can be realized if even short isotactic blocks of styrene or *o*-methylstyrene units are in a helical conformation with a predominant screw sense. The larger ellipticity and its small dependence on composition in the *o*-methylstyrene-(*R*)-3,7-dimethyl-1-octene copolymers are probably connected with the fact that both homopolymers from I[14] and from III[15] have, in the crystalline state, helical conformations with four units per turn; this type of helix should be at least partially maintained in solution, the favored screw sense being the right-handed one as for isotactic poly-(*R*)-3,7-dimethyl-1-octene.[16]

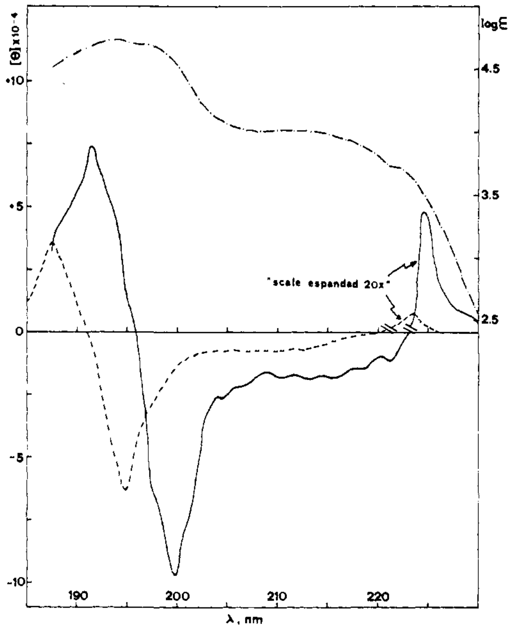

Figure 1. CD and uv spectra of copolymers of (*R*)-3,7-dimethyl-1 octene (I) with styrene (II) and *o*-methylstyrene (III) in *n*-heptane a 27°: (- - -) CD spectrum of I–II copolymer, 80/20 mol (noise level ≤10% until 195 nm and ~20% below 195 nm; slit width in the maximum absorption region, ~1.5 mm); (—) CD spectrum of I–III copolymer, 80/20 mol (noise level, ≤5% until 200 nm and ~10% below 200 nm; slit width, 0.6–0.7 mm in the maximum absorption region); (–·–) uv spectrum of I–III copolymer, 80/20 mol. The values of [θ] and log ε are based on one aromatic residue.

The preliminary results, reported in the present communication, allow us to draw the following conclusions. (1) The benzene chromophore in the side chains of coisotactic copolymers of styrene with optically active α-olefins shows, in the region of the ^{1}B transition, two CD bands of equal area and opposite sign which are to be connected to the helical conformation of the macromolecules. The order of the signs of these two bands is related to the predominant screw sense of the helix. (2) Care must be taken in interpreting CD data of polypeptides and proteins having

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(9) $[\theta] = \Delta\epsilon \times 3300$, where $\Delta\epsilon = d \times 10^{-5}/cl$; d = recorded deflection in mm, l = spectral light path of the cell in cm, and c = (g of copolymer × wt % of unit II (or III))/(mol wt of unit II (or III) × l.).

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aromatic side chains[17] as the splitting observed between 205 and 185 nm occurs in the same spectral region as that of the peptide chromophore in an α helix,[18] the ellipticity of the CD bands being of the same order of magnitude.

Acknowledgment. The authors wish to express their particular thanks to Mr. C. Bertucci for his skillful assistance in obtaining the uv and CD spectra. The financial support by the Consiglio Nazionale delle Ricerche (C.N.R.), Rome, Italy, is gratefully acknowledged.

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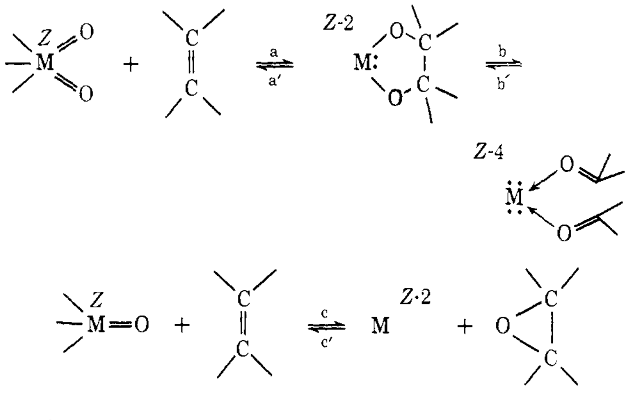
Received March 14, 1972

Lower Valent Tungsten Halides. A New Class of Reagents for Deoxygenation of Organic Molecules

Sir:

The transfer of oxygen from an oxotransition metal compound to an organic substrate has well-known synthetic applications such as oxygenations a, b, and c in Scheme I.[1] We have discovered a new class of reactions which involve, at least formally, the reverse processes a′, b′, and c′ (Scheme I). The reagents which effect these deoxygenations are lower valent tungsten halide derivatives. Scheme II outlines the tungsten reagents we have investigated.[2] Only K_2WCl_6 (VII) has been known previously;[3] the other reagents are new inorganic substances which we are in the process of characterizing. Although tungsten derivatives have been reported to play catalytic roles in olefin dismutation[4] and olefin epoxidation,[5] this is the first time tungsten reagents have been used stoichiometrically for organic transformations.

Scheme I. Oxygenation–Deoxygenation



Scheme II. Tungsten Reagents

$$WCl_6 + 2RLi \xrightarrow{THF} I$$

$$WCl_6 + 3RLi \xrightarrow{THF} II$$

$$WCl_6 + 4RLi \xrightarrow{THF} III$$

$$WCl_6 + 2Li \text{ dispersion} \xrightarrow{THF} IV$$

$$WCl_6 + 3LiI \xrightarrow[\textit{in vacuo}, \text{ no solvent}]{130°} V$$

$$WCl_6 + 2LiI \xrightarrow[\textit{in vacuo}, \text{ no solvent}]{130°} VI$$

$$WCl_6 + 2KI \xrightarrow[\textit{in vacuo}, \text{ no solvent}]{130°} VII^3$$

$$VII + 2LiCl \xrightarrow{THF} VIII$$

We recently described the stereoselective deoxygenation of vicinal dialkoxides to olefins (transformation a′, Scheme I) using the tetrahydrofuran insoluble reagent VII (K_2WCl_6)[6] and have since found that the soluble tungsten reagents I, II, V, and VI are also effective for this transformation. We now report the direct reductive coupling of aldehydes and ketones to olefins (formally transformation b′ + a′, Scheme I) and the stereoselective reduction of epoxides to olefins (transformation c′, Scheme I).

Rapid formation of stilbene is observed when benzaldehyde is added at room temperature to the green solution (reagent I, Scheme II) generated by addition of 2 mol of butyllithium to tungsten hexachloride (Pressure Chemical Co.) in tetrahydrofuran. There is only one precedent for this remarkable conversion; it is based on a phosphorus reagent, requires extreme conditions, and succeeds only with aromatic aldehydes.[7] Table I reveals that reagent I is also more effective for

Table I. Direct Deoxygenation of Aldehydes and Ketones to Olefins[a]

Carbonyl	Yield of olefin, %[b]	Mole of reagent I / mole of carbonyl
Benzaldehyde	76	3.8
Benzaldehyde	70	4.3
Benzaldehyde	20	1.8
p-Methoxybenzaldehyde	47	3.3
p-Methoxybenzaldehyde	38	4.1
p-Methoxybenzaldehyde	26	1.7
p-Chlorobenzaldehyde	57	3.3
m-Chlorobenzaldehyde	28	4.2
p-Cyanobenzaldehyde	20	3.9
Acetophenone	44[c]	1.9
Acetophenone	21	4.1
2-Butanone	10[d]	3.6

[a] Typically, 0.8 mmol of WCl_6 was added to 10 ml of THF cooled to −78°, followed by 1.6 mmol of butyllithium. The reaction mixture was allowed to warm to room temperature over 20 min and then the carbonyl compound (0.2 mmol) was added. After standing for 6 hr the reactions were quenched with 20% NaOH solution and extracted with ether. [b] The yields were determined by glc using internal standards. Unless noted otherwise the olefin geometry is trans. [c] The isomeric dimethylstilbenes were produced in the ratio of 60% trans and 40% cis. [d] A mixture of cis and trans isomers.

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[2] We have also prepared a number of similar reagents which reduce epoxides to olefins. These result from reaction in THF of $MoCl_5$, WCl_5, or WBr_5 with 1 equiv of butyllithium and reaction of $MoCl_5$, WBr_6, and WF_6 with 2 equiv of butyllithium. However, none of these reagents is as effective as those described in Scheme II.

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