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OPTICALLY ACTIVE MONOSUBSTITUTED CYMANTRENE DERIVATIVES. RELATIONSHIP OF CHIROPTICAL CHARACTERISTICS WITH ABSOLUTE CONFIGURATION OF THE COMPOUNDS

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Summary

The results of the study of the chiroptical properties (CD, ORD and [α]), of fourteen optically active monosubstituted cymantrene derivatives with a chiral center directly attached to the Cp ring are summarized for the first time. It has been found that the (*R*)-enantiomers of these compounds exhibit a negative Cotton effect for the "metallocenyl" transition in CD spectra within the range 310–360 nm independent on the nature of the substituent and the solvent.

Optically active compounds of the cymantrene series monosubstituted at the Cp ring with a chiral center in the substituent were little known prior to our study [1,2]. Because of this, the problem of the relationship of absolute configuration of this type of compounds with their chiroptical characteristics and, hence, the possibility of using ORD and CD spectra for establishing the configurations of monosubstituted cymantrenes has remained unsolved.

In this paper the results of studies on the chiroptical properties of optically active monosubstituted cymantrene derivatives, I–XIV, are summarized for the first time and an attempt is made to establish the relationship between the characteristics of CD, ORD spectra and the $[\alpha]_{578}$ values and absolute configuration of these compounds.

The synthesis and properties of optically active compounds, I, VI–VIII are described by us in another paper [2]. Enantiomers of compounds II–V and IX–XIV that have been obtained for the first time are described in this paper (Scheme 1). Their structure was supported by elemental analysis and PMR spectra (see Experimental). The presence of a chiral center in the side chain in I–XIV makes hydrogen atoms of the Cp ring diastereotopic in pairs [3]. Therefore, in the PMR spectra of compounds IV, IX and XIII two multiplets for α-protons are observed, while in X, XI and XII all four protons of the Cp ring directly attached to the chiral center possess different chemical shifts. In IV and V hydrogen atoms of the methylene group are also diastereotopic and show up in the spectrum as an AB-system.

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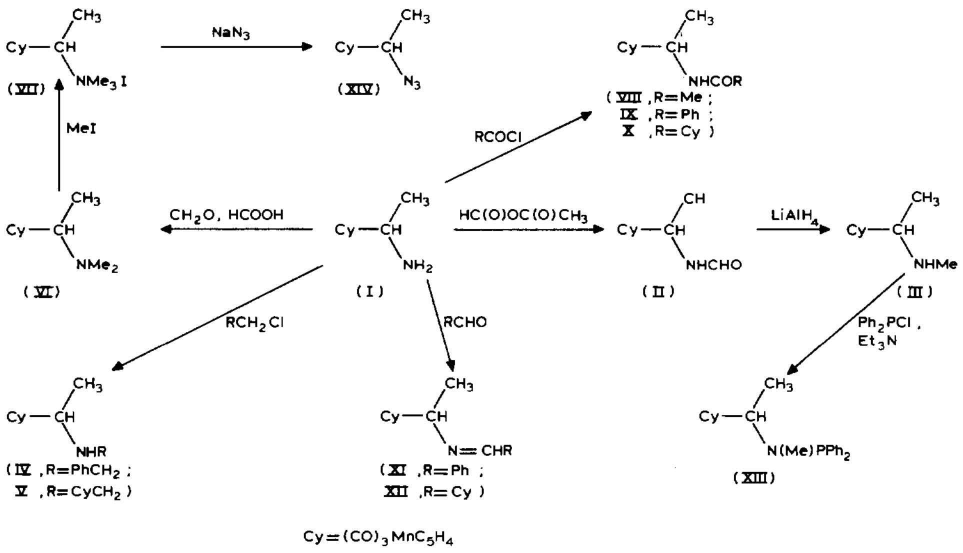

SCHEME 1

This paper describes the properties of the enantiomers II–XIV synthesized from (−)-(*R*)-I, though we have worked with compounds II–XIV prepared from both enantiomers of I. As can be seen in Scheme 1, the synthesis of II–XIII does not comprise stages of cleavage of bonds at the asymmetric carbon atom. Consequently, absolute configurations of the initial amine (−)-(*R*)-I and of the derivatives II–XIII produced from it are identical. Only in the case of the conversion of the ammonium salt (+)-(*R*)-VII into azide (−)-XIV could one expect a changed configuration of the chiral center. We, however, have found that this process proceeds with 87% retention of the configuration *.

Tables 1 and 2 shows values of specific rotation and characteristics of CD and UV spectra for (*R*)-enantiomers of I–XIV. Shown in Figs. 1–4 are the UV, ORD and CD curves for some of them. In the UV spectra of the compounds a wide long-wave absorption band (λ_{max} 330–340 nm) is observed apparently related to the $d \rightarrow d^{\star}$ transition of the cymantrenyl chromophore, as well as an intensive absorption within the range of shorter waves (below 300 nm) caused by electron transitions of other types.

It can be seen from Table 1 that the values of $[\alpha]_{578}$ for various compounds differ both in their magnitude and sign. Therefore, no direct relationship exists between the absolute configuration of a compound and the value of $[\alpha]$. It is likely that ORD spectra may be used for the purpose of establishing absolute configuration of monosubstituted cymantrene derivatives. However, the pattern of ORD curves for the studied compounds frequently appears to be too complicated for their unambiguous interpretation [2] (Fig. 1).

The circular dichroism spectra of compounds discussed in this paper (Fig. 2–4 and Table 1) present a different picture. In CD spectra of enantiomers I–XIV two

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* Detailed discussion of this result will be given later.

TABLE 1

PARAMETERS OF CD AND UV SPECTRA AND VALUES OF $[\alpha]_{578}$ FOR (*R*)-ENANTIOMERS OF $(CO)_3MnC_5H_4CH(Me)X$

Compounds		Solvent	CD		UV		$[\alpha]°$ (c)
No.	X		$[\theta]°$	λ_{max}	log ϵ	λ_{max}	
I	NH_2	EtOH	−190	335	3.05	330	−10.4(2)
II	NHCHO	EtOH	−1822	335	2.91	336	+50.1(2)
III	NHMe	EtOH	−787	340	2.90	336	+20.1(2.6)
IV [a]	$NHCH_2Ph$	EtOH	−972	335	3.05	331	−15.2(0.93)
V [a]	$NHCH_2C_5H_4Mn(CO)_3$	EtOH	−1135	335	3.35	331	−21.7(0.97)
VI	NMe_2	EtOH	−1584	344	3.13	331	+17.2(2)
VII	$^+NMe_3$	MeCN	−1105	344	3.05	332	+22.6(2) [b]
		$MeOCH_2CH_2OH$	−1736	342	3.09	333	+26.9(2)
VIII	NHCOMe	EtOH	−1705	333	3.21	330	+24.5(1)
IX [a]	NHCOPh	MeOH	−2562	333	3.05	332	−61.2(0.42) [b]
X [a]	$NHCOC_5H_4Mn(CO)_3$	MeOH	−3452	336	3.36	333	−52.2(0.41) [b]
XI [a]	N=CHPh	EtOH	−1933	323	3.05	329	−137.3(0.08) [c]
XII [a]	$N{=}CHC_5H_4Mn(CO)_3$	EtOH	−3604	350	3.44	333	−106.7(0.05) [c]
XIII	$N(Me)PPh_2$	EtOH	−2405	343	3.10	333	−74.6(1.5)
XIV [d]	N_3	C_6H_6	−655	340	3.50	328	−21.6(2)

[a] Obtained from (−)-(*R*)-I with $[\alpha]_{578}$ −9.5° (c 2, ethanol). [b] For solution in ethanol. [c] For solutions in n-hexane. [d] Enantiomeric purity 87.4%.

regions of optically active transitions can be noted within the 250–600 nm range *. The 300–400 nm range of the spectrum is a characteristic range of absorption for a metallocenyl chromophore, the contribution of other chromophores present in molecules of I–XIV to this range can be apparently neglected. The short-wave spectrum range ($\lambda < 300$ nm) is caused by electron transitions of both the metallocenyl fragment and other chromophores. In this connection, the pattern of a CD spectrum within the 300–250 nm range depends essentially on the nature of the substituent bonded to the Cp ring. In contrast, the pattern of a CD spectrum in the 310–360 nm range remains always the same when the passing from one compound to another. The (*R*)-enantiomers of compounds I–XIV have a negative Cotton effect for the metallocenyl transition, while the nature of a compound manifests itself only in location of the maximum of this transition and its intensity.

The CD and UV spectra shown in Table 1 and Fig. 2 were recorded for solutions of compounds I–XIII in alcohols. Since a solvent can substantially affect the pattern of spectra and signs of Cotton effects, we studied the effect of the solvent nature on CD and UV spectra of some compounds discussed here (Table 2 and Figs. 3 and 4). In the case of the amines IV–VI the character of a solvent affect only an intensity of a Cotton effect of a cymantrenyl chromophore in the range of 310–360 nm. In this case an increase of the absolute $[\Theta]$ value with increasing polarity of the medium is observed. For secondary amides the transition from a non-polar (benzene) to a polar solvent (MeOH or CH_3COOH) results merely in changed intensity and in a small hypsochromic shift of the maximum absorption of a metallocenyl chromophore. At

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* Strong UV absorption in the short-wave range of the spectrum does not enable recording CD spectra below 250–270 nm.

TABLE 2

DEPENDENCE OF THE CHARACTERISTICS OF CD AND UV SPECTRA ON THE NATURE OF THE (*R*)-ENANTIOMERS OF $(CO)_3MnC_5H_4CH(Me)X$

Compound		CD		UV		Solvent
No	X	$[\theta]^\circ$	λ_{max}	log ϵ	λ_{max}	
IV	$NHCH_2C_6H_5$	−273	340	3.02	332	hexane
		−681	337	3.05	329	MeCN
		−972	335	3.05	331	EtOH
		−1633	340	3.02	330	0.1 *N* HCl
		−1668	341	3.01	333	CH_3COOH
V	$NHCH_2C_5H_4Mn(CO)_3$	−534	337	3.31	334	hexane
		−975	333	3.35	330	MeCN
		−1135	335	3.35	331	EtOH
		−1959	341	3.36	332	CH_3COOH
VI	NMe_2	−1840	348	3.04	331	hexane
		−1584	344	3.13	331	EtOH
		−2000	345			0.1 *N* HCl
IX	$NHCOC_6H_5$	−912	343	3.025	331	benzene
		−2562	333	3.045	332	MeOH
		−2273	335	2.97	330	CH_3COOH
X	$NHCOC_5H_4Mn(CO)_3$	−1172	355	3.36	334	benzene
		−3452	336	3.36	333	MeOH
		−2846	340	3.38	332	CH_3COOH
XI	$N{=}CHC_6H_5$	+146	367	3.06	333	hexane
		−667	319	3.27	289 sh	
		+1333	289	3.46	278 sh	
		−1933	323	3.05	327	EtOH
				3.40	288	
				3.53	278	
		−970	345	3.04	333	CH_3COOH
				3.30	290	
				3.35	281	
XII	$N{=}CHC_5H_4Mn(CO)_3$	−4876	359	3.34	337	hexane
		+1994	286	3.43	286	
		−3604	350	3.34	333	EtOH
		−1084	343	3.43	337	CH_3COOH
				3.35	289	

the same time, in the 270–310 nm range these compounds exhibit a reversed course of the CD curve with a similar change of the solvent nature.

More essential changes in CD and UV spectra, depending on the solvent nature, are observed in the case of azomethines (Table 2, Fig. 4). Characteristics of CD spectra of solutions of (−)-(*R*)-XI and (−)-(*R*)-XII in acetic acid are substantially the same. Replacement of acetic acid with ethanol results in a considerable increase of the Cotton effect in the 300–350 nm range in the CD spectrum of (−)-(*R*)-XII and in a certain shift in location of its maximum towards the long-wave region of the spectrum. An increased intensity of the Cotton effect of the cymantrenyl chromophore is also observed in the case of (−)-(*R*)-XI. However, at the same time a hypsochromic shift of its maximum by 22 nm also takes place. As a result, the general form of CD curves for solutions of these compounds in ethanol becomes different. The difference in the form of CD spectra of (*R*)-enantiomers of XI and

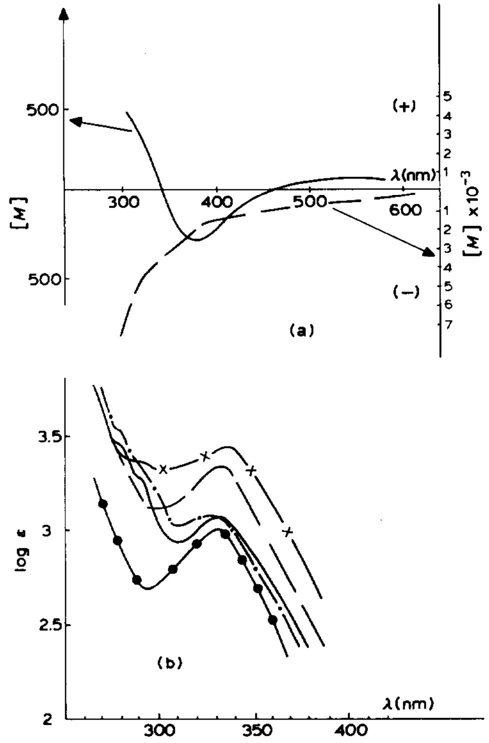

Fig. 1. (a) ORD spectra of (*R*)-enantiomers of (+)-VI in EtOH (———) and (−)-XI in EtOH (— — —); (b) UV spectra of IV in hexane (—●—), X in MeOH (— — —), XI in EtOH (— · —) and hexane (———), XII in CH_3COOH (— × —).

XII becomes even more noticeable when passing from solutions in ethanol to hexane. While the change of ethanol for hexane only slightly affect the CD spectrum of (−)-(*R*)-XII, a similar change of the solvent in the case of (−)-(*R*)-XI results not

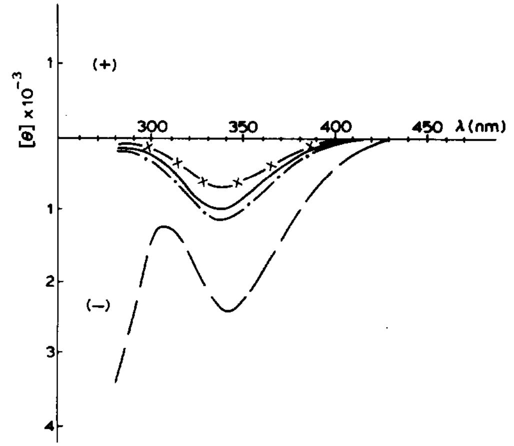

Fig. 2. CD spectra of (−)-(*R*)-IV (———), (−)-(*R*)-V (—●—), (−)(*R*)-XIII (— — —) and (−)-(*R*)-XIV (— × —).

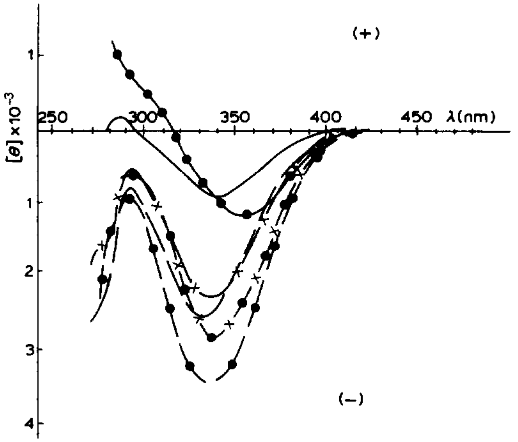

Fig. 3. CD spectra of (R)-enantiomers of IX in benzene (———), MeOH (— — —), CH_3COOH (— × —) and X in benzene (——●——), MeOH (● ●), CH_3COOH (● × ●).

only in a sharp drop of intensity of the Cotton effect at λ_{max} 319 nm, but also in the appearance of a positive absorption in the 350–400 nm range. Furthermore, the course of the CD curve at $\lambda < 300$ nm is also changed. It is likely that the CD spectrum of azomethines XI and XII in the range 280–400 nm results from overlapping of the positive Cotton effect of the transition of an unknown nature

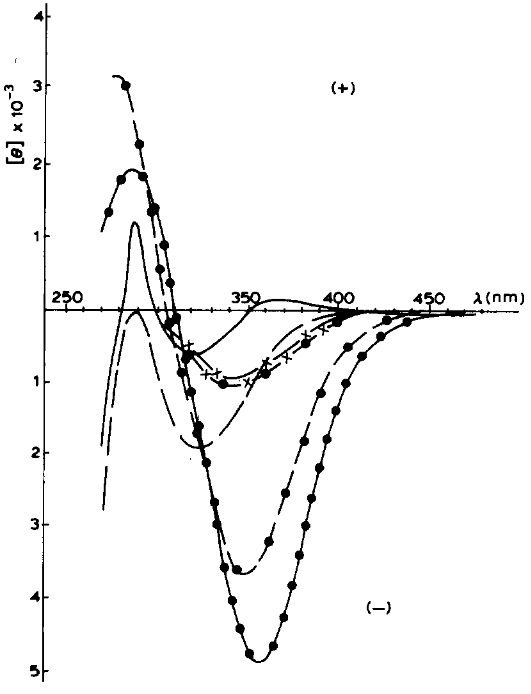

Fig. 4. CD spectra of (R)-XI in hexane (———), EtOH (— — —), CH_3COOH (— × —) and (R)-XII in hexane (——●——), EtOH (● ●), CH_3COOH (● × ●).

with $\lambda_{max} \sim 290$ nm (see UV spectrum in Fig. 1) and the negative Cotton effect of the $d \rightarrow d^{\star}$ transition of the cymantrenyl chromophore with λ_{max} 330 nm. However, the replacement of ethanol by hexane exerts a greater effect on the position of the absorption band maximum in the 280–290 nm range and its intensity in the CD spectrum of (−)-(*R*)-XI than in the case of (I)-(*R*)-XII. Although the above data show that the solvent affects characteristics of CD spectra of enantiomers of compounds I–XIV, nevertheless, in all cases the sign of the Cotton effect of the cymantrenyl chromophore in the range of 310–360 nm remains negative for compounds with (*R*) absolute configuration.

Therefore, a direct relationship exists between the sign of the Cotton effect of the $d \rightarrow d^{\star}$ transition of the cymantrenyl chromophore and the absolute configuration of optically active monosubstituted cymantrene derivatives with the chirality center directly bonded to the Cp ring. Enantiomers of the (*R*)-series have a negative Cotton effect, while enantiomers of the (*S*)-series are positive. The chiral relationships found suggest the following explanation for the above-mentioned absence of a relationship between the sign of $[\alpha]_{578}$ and the configuration of compounds I–XIV. It follows from CD spectral data that the intensity of a metallocenyl transition in the long-wave range of ORD spectra is relatively small as compared to the powerful Cotton effects of other optically active transitions occurring at lesser wavelengths. As a result, the sign and value of $[\alpha]$ at $\lambda \sim 580$ nm is frequently defined by these very transitions rather than by the $d \rightarrow d^{\star}$ transition of the cymantrenyl chromophore which is the most long-wave one in UV spectra of cymantrene derivatives.

The cymantrene derivatives discussed in this paper pertain to different classes of organic compounds: primary, secondary and tertiary amines, quaternary ammonium salts, amides, azomethines, azides, aminophosphines. These compounds contain chromophores of a different nature which possess optically active transitions of their own. Nevertheless, the presence of such different chromophores in I–XIV does not provide essential influence on the character of CD spectra of these compounds in the 315–360 nm range. This enables us to assume that the established relationship of characteristics of CD spectra for cymantrene derivatives I–XIV with their absolute configuration will be valid for many optically active compounds of the $(CO)_3MnC_5H_4CX(Y)Z$ type, since, as a rule, the majority of chromophores absorb in UV spectra at shorter wavelengths than a cymantrenyl chromophore.

Experimental

The $[\alpha]_{578}$ values were measured on a "Polamat A" polarimeter. CD and ORD spectra were recorded on a "Jasco J-20" spectropolarimeter at room temperature. Electron spectra were obtained on a Specord UV-VIS spectrophotometer. PMR spectra were taken on Bruker WP-200SY and Hitachi-Perkin-Elmer R-20 (60 MHz) spectrometers. The synthesis and properties of (*R*)-enantiomers of I and VI–VIII are described in ref. 2. Compounds (+)-II, (+)-III, (−)-XIII and (−)-XIV were prepared from (−)-(*R*)-I with $[\alpha]_{578}$ −10.4° (*c*, 2, ethanol); for the preparation of (−)-IV, (−)-V, (−)-IX, (−)-X, (−)-XI and (−)-XII (−)-(*R*)-I was used with $[\alpha]_{578}$ −9.5° (*c* 2, ethanol).

(+)-(R)-[1-(N-Formylamino)ethyl]cymantrene, (R)-II

To a mixed anhydride of formic and acetic acids prepared from 6.8 g (0.067 mol) of Ac_2O and 2.8 g (0.06 mol) of HCOOH 10 g (0.04 mol) of (−)-(*R*)-I are added with stirring so that the temperature of the reaction mixture is not more than 40°C. Then the mixture is diluted with 20 ml of ether and stirred for an additional 4 h at 20°C. The reaction mixture is then poured into 100 ml of ether, washed and dried over Na_2SO_4. After removal of the solvent in vacuum 10.5 g (96%) of (*R*)-II are obtained; m.p. 52–53°C, $[\alpha]_{578}^{22}$ +50.1° (*c* 2, ethanol). Analysis: Found: C, 48.66; H, 3.64; N, 5.24. $C_{11}H_{10}NO_4Mn$ calcd.: C, 48.02; H, 3.66; N, 5.09%. PMR ($CDCl_3$, δ, ppm): 1.57 (d, 3H, ^3J 11.0 Hz, CH_3); 4.84 (m, 2H, C_5H_4); 5.02 (m, 2H, C_5H_4); 5.04 (m, 1H, C*H*CH_3); 6.60 (br s, 1H, NH); 8.42 (s, 1H, CHO).

(+)-(R)-[1-(N-Methylamino)ethyl]cymantrene, (R)-III

To a suspension of 2.8 g (0.07 mol) of $LiAlH_4$ in 100 ml of absolute THF a solution of 10.5 g (0.04 mol) of (+)-(*R*)-II in 100 ml of absolute THF is added with stirring under argon. The temperature of the reaction mixture is maintained at not more than 40°C. Then the reaction mixture is stirred at this temperature for 3 h, cooled and treated with water. The resulting precipitate is separated from the solution and washed with ether. The filtrates are combined, the aqueous layer is acidified with 2*N* HCl and extracted with ether followed by treatment of the acidic solution with 2*N* KOH and extraction of the amine with ether. The extract is washed with water and dried over Na_2SO_4. Vacuum distillation yields 3.3 g (31%) of (*R*)-III; b.p. 86–87°C/4 × 10^{-2} mmHg, n_D^{20} 1.5786, $[\alpha]_{578}^{25}$ +20.1° (*c* 2.6, ethanol). Analysis; Found: C, 50.62; H, 4.76; N, 5.76. $C_{11}H_{12}NO_3Mn$ calcd.: C, 50.59; H, 4.63; N, 5.36%. PMR ($CDCl_3$, δ, ppm): 0.9 (br s, 1H, NH), 1.25 (d, 3H, ^3J 10 Hz, CH_3). 2.4 (s, 3H, NCH_3), 3.35 (qd, 1H, ^3J 12.5 Hz, CH); C_5H_4: 4.65 (m, 2H), 4.85 (m, 2H).

(−)-(R)-[1-(N-Benzylamino)ethyl]cymantrene, (R)-IV

A mixture of 1.2 g (0.005 m) of (−)-I with 0.51 g (0.004 mol) of benzyl chloride in 1 ml of ethanol diluted with 2 ml of water is refluxed for 6 h in the presence of 0.21 g (0.002 mol) of anhydrous Na_2CO_3. Then the reaction mixture is cooled, added with stirring to 20 ml of 1.5 *N* HCl and the precipitate formed is filtered off. The filter cake is washed with 1.5 *N* HCl to remove the excess of free amine * and the salt is treated with 2*N* KOH. The free amine is extracted with ether, the extract washed with water and dried with $MgSO_4$. Then the solution is evaporated and the residue is chromatographed on silica gel (100/160 μ, acetone). In this manner 0.74 g (55%) of (*R*)-IV is isolated as an oil with $[\alpha]_{578}^{22}$ −15.2° (*c* 0.93, ethanol). Analysis: Found: C, 60.88; H, 5.06; Mn, 15.79. $C_{17}H_{16}NO_3Mn$ calcd.: C, 60.54; H, 4.78, Mn, 16.29%. PMR ($CDCl_3$, ppm): 1.37 (d, 3H, ^3J(HH) 6.5 Hz, CH_3), 1.51 (br s, 1H, NH), 3.52 (quad, 1H, ^3J(HH) 6.5 Hz, C*H*CH_3), CH_AH_B: 3.86 (d, 1H, ^2J(HH) 13 Hz) and 3.82 (d, 1H, ^2J(HH) 13 Hz), C_5H_4: 4.60 (m, 2H), 4.82 (m, 1H) and 4.87 (m, 1H), 7.38 (m, 5H, C_6H_5).

(−)-(R)-(1-[N-(Cymantrenylmethyl)amino]ethyl)cymantrene, (−)-(R)-V

A mixture of 1.2 g (0.005 mol) of (−)-I with 0.2 g of anhydrous Na_2CO_3 and 0.63 g (0.0025 mol) of chloromethylcymantrene, $CyCH_2Cl$ prepared by passing dry HCl through a solution of $CyCH_2OH$ [4] in CH_2Cl_2 at 10°C, is heated at 60–80°C for

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* Hydrochlorides of secondary amines (−)-(*R*)-IV and (−)-(*R*)-V are sparingly soluble in diluted HCl.

8–10 h. The (R)-V is isolated as described above to give 0.42 g (36%) of an oil with $[\alpha]_{578}^{22}$ −21.7° (c 0.97, ethanol). Analysis: Found: Mn, 23.21. $C_{19}H_{15}NO_6Mn_2$ calcd.: Mn 23.72%. PMR ($CDCl_3$, δ, ppm): 1.26 (br s, 1H, NH), 1.35 (d, 3H, ^3J(HH) 5.85 Hz, CH_3), 3.54 (quad, 1H, ^3J(HH) 6.8 Hz, C*H*CH_3), CH_AH_B: 3.51 (d, 1H, ^2J(HH) 13.7 Hz) and 3.43 (d, 1H, ^2J(HH) 13.7 Hz): protons of Cp rings: 4.68 (m, 4H), 4.80 (m, 2H) and 4.84 (m, 2H).

(−)-(R)-[1-(N-Benzoylamino)ethyl]cymantrene, (R)-IX

To a mixture of 0.63 g (0.0026 mol) of (−)-(R)-I and 0.5 g of $NaHCO_3$ in 5 ml of benzene 0.38 g (0.0027 mol) of PhCOCl in 4 ml of benzene is added dropwise with stirring. The reaction mixture is stirred at 20°C for 2.5 h and then diluted with water. The organic layer is washed with 2 N HCl then with water and dried over Na_2SO_4. The amide is isolated chromatographically on silica gel (100/160 μ, eluent ethanol) to give 0.6 g (63% of an oil which is crystallized on rubbing: m.p. 54–56°C, $[\alpha]_{578}^{23}$ −61.2° (c 0.42, ethanol). Analysis: Found: C, 58.86; H, 4.20; Mn, 14.98; N, 4.49. $C_{17}H_{14}NO_4Mn$ calcd.: C, 58.13; H, 4.02; Mn, 15.64; N, 3.99%. Unfortunately, the recovery procedure used does not make it possible to fully purify the (R)-IX from contaminant PhCOCl and PhCOOH. However, their content in the resulting sample of IX does not exceed 5% according to PMR data. PMR ($CDCl_3$, δ, ppm): 1.45 (d, 3H, ^3J(HH) 6.7 Hz, CH_3), Cp ring: 4.61 (m, 2H), 4.79 (m, 1H) and 4.89 (m, 1H); 5.16 (m, 1H, C*H*Me), 6.43 (br d, 1H, ^3J(HH) 8.1 Hz, NH), 7.78 (m, 2H) and 7.44 (m, 3H) C_6H_5.

(−)-(R)-(1-[N-(Cymantrenylcarbonyl)amino]ethyl)cymantrene, (R)-X

To a mixture of 0.37 g (0.0015 mol) of (−)-(R)-I and 0.36 g (0.0043 mol) of $NaHCO_3$ in 4 ml of anhydrous $CHCl_3$ at 20°C under argon 0.39 g (0.0015 mol) of $(CO)_3MnC_5H_4COCl$ [5] is added with stirring. The reaction mixture is boiled for 30 min, then stirred for an additional 1.5 h at 25°C. Afterwards, the mixture is diluted with water, the organic layer is separated, washed with 2N HCl, again with water and dried over Na_2SO_4. The chloroform is removed under reduced pressure and the residue is recrystallized from a mixture of hexane-alcohol to give 0.52 g (75%) of (R)-X, m.p. 164–165°C and $[\alpha]_{578}^{22}$ −52.2° (c 0.41, ethanol). Analysis: Found: C, 47.81; H, 2.69; Mn, 22.98; N, 2.86. $C_{19}H_{13}NO_7Mn_2$ calcd.: C, 47.82; H, 2.75; Mn, 23.03; N, 2.94%. PMR ($CDCl_3$, δ, ppm): 1.42 (d, 2H, ^3J(HH) 6.0 Hz, CH_3), protons of Cp rings: 4.65 (m, 1H), 4.69 (m, 1H), 4.80 (m, 3H), 4.87 (m, 1H), 5.32 (m, 2H); 5.10 (m, 1H, C*H*CH_3), 5.66 (d, 1H, ^3J(HH) 9.1 Hz, NH).

(−)-(R)-[1-(N-Benzaliden/amino)ethyl]cymantrene, (R)-XI

To a solution of 1.02 g (0.004 mol) of (−)-(R)-I in 2 ml of absolute benzene at 24°C 0.4 ml of freshly distilled benzaldehyde is added with stirring. 5–10 min thereafter the reaction mixture gets heated and water is evolved which is combined by introducing into the flask 0.8 g of 4Å molecular sieves and stirring is continued for an additional 3–4 h. The reaction mixture is then filtered and the filtrate is evaporated in vacuum to give 1.3 g (97%) of an oil with $[\alpha]_{578}^{23}$ −137.3 (c 0.08, hexane). Analysis: Found: Mn, 15.90. $C_{17}H_{14}NO_3Mn$ calcd.: C, Mn, 16.39. PMR ($CDCl_3$, δ, ppm): 1.53 (d, 3H, ^3J(HH) 6.8 Hz, CH_3), 4.20 (m, 1H, CHMe), Cp ring: 4.62 (m, 2H), 4.79 (m, 1H) and 4.98 (m, 1H); Ph ring: 7.48 (m, 3H), 7.88 (m, 2H); 8.35 (s, 1H, CH=N).

(−)-(R)-[1-(N-Cymantrenylmethylidenamino)ethyl]cymantrene, (R)-XII

In a similar manner to that above, from 0.47 g (0.002 mol) of formylcymantrene [4] and 0.5 g (0.002 mol) of (−)-(*R*)-I in 4 ml of absolute benzene 0.85 g (92%) of (*R*)-XII is obtained; m.p. 96–98°C (from hexane), $[\alpha]_{578}^{21}$ −106.7° (*c* 0.05, hexane). Analysis: Found: C, 49.36; H, 3.13; Mn, 23.97. $C_{19}H_{13}NO_6Mn_2$ calcd.: C, 49.48; H, 2.84; Mn, 23.82%. PMR ($CDCl_3$, δ, ppm): 1.38 (d, 3H, ^3J(HH) 6.57 Hz, CH_3), 4.04 (quad., 1H, ^3J(HH) 6.54 Hz, CHMe), C_5H_4 4.59 (m, 1H), 4.65 (m, 1H) 4.73 (m, 1H) and 4.84 (m, 1H); $C_5H_4C{=}N$ 4.80 (m, 1H) 4.74 (m, 1H) and 5.28 (m, 2H); 7.90 (s, 1H, CH=N).

(−)-(R)-[N-Methyl-N-(1-cymantrenylethyl)amino]diphenylphosphine, (R)-XIII

Diphenylchlorophosphine (2.2 g, 0.01 mol) in 20 ml of benzene are added under argon to 2.6 g (0.01 mol) of (*R*)-III and 1.01 g of Et_3N in 50 ml of benzene with stirring and cooling with ice and the reaction mixture is maintained at a temperature of 10°C for 3 h. The precipitate is filtered off, the solvent is removed in vacuum to give 4.38 g (95%) of (*R*)-XIII (oil) with $[\alpha]_{578}^{24}$ −74.6° (*c* 1.5, ethanol). Analysis: Found: C, 61.95; H, 4.76; N, 3.24; P, 7.02; Mn, 12.45. $C_{23}H_{21}MnNO_3P$ calcd.: C, 61.89; H, 4.74; N, 3.14; P, 6.94; Mn, 12.31%. PMR ($CDCl_3$, δ, ppm): 1.51 (d, 3H, ^3J 12.5 Hz, CH_3), 2.42 (d, 3H, ^3J(PH) 5.0 Hz, NCH_3), 3.42 (m, 1H, CH); C_5H_4: 4.65 (m, 2H), 4.83 (m, 1H), 4.95 (m, 1H), 7.2–7.7 (m, 10H, C_6H_5).

(−)-(R)-(1-Azidoethyl)cymantrene, (R)-XIV

16.1 g (0.246 mol) of NaN_3 are dissolved upon heating in 300 ml of a 70% solution of diglyme in water. This solution is added to 9.6 g (0.023 m) of (*R*)-II and the reaction mixture is heated at 100°C under argon for 60 h. After cooling the mixture is diluted with 500 ml of water and extracted with ether. The extract is washed with water and dried over $MgSO_4$. Ether is removed and the residue is distilled in vacuum to give 3.74 g (59%) of (*R*)-XIV, b.p. 88–89°C/5×10^{-2} mmHg, n_D^{22} 1.5920, $[\alpha]_{578}^{25}$ −21.58° (*c* 2, ethanol). Analysis: Found: Mn, 19.93. $C_{10}H_8MnNO_3$ calcd.: Mn, 20.12%. PMR (CCl_4, δ, ppm): 1.17 (d, 3H, CH_3), 3.75 (quad, 1H, CH), Cp ring: 4.62 (m, 2H) and 4.82 (m, 2H).

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