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Some Facile Syntheses of Optically Active 2-Substituted Indanones, Indanols, Tetralones, and Tetralols via Their Chromium Tricarbonyl Complexes

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Abstract: 1-Indanone- and 1-tetralonetricarbonylchromium were resolved into optically pure forms and their absolute configurations ascertained. These complexes can be used as precursors to chiral arene compounds difficult or impossible to prepare by other routes. Thus, examples of the syntheses of 2-methyl-1-indanone and 2-methyl-1-tetralone, *cis*- and *trans*-2-methyl-1-indanols, and 2-methyl-1-tetralols are shown. All these reactions are stereospecific.

In the last few years, the use of organometallic complexes in the synthesis of novel organic compounds has become common.[1] However, the utilization in this manner of arene tricarbonylchromium derivatives has not been studied systematically. Nevertheless, these compounds offer considerable synthetic possibilities because of their particular chemical and stereochemical properties.

Recently, the quantitative liberation of arene ligands from tricarbonyl arene chromium derivatives has been accomplished simply by exposure of their ether solutions to sunlight.[2] The modification, on complexation, of steric and electronic factors and of the symmetry of the substrate ligand can thus be used to advantage in the synthesis of benzene derivatives difficult or impossible to prepare by other methods. In this communication, we report the resolution into enantiomers of 1-indanone- and 1-tetralonetricarbonylchromium and their use in the synthesis of new chiral molecules.

The $Cr(CO)_3$ group not only confers a third dimension on the aromatic precursor but also induces stereospecific exo nucleophilic attack on the alicyclic ring, thus creating new chiral centers. Quantitative liberation of the optically active organic ligand may then be easily accomplished at ambient temperature in air.

Resolution and Absolute Configuration of 1-Indanone- and 1-Tetralonetricarbonylchromium. Optically pure 1-indanone- and 1-tetralonetricarbonylchromium were obtained by oxidation of the corresponding 1-*endo*-indanoltricarbonylchromium and 1-*endo*-tetraloltricarbonylchromium with MnO_2 (yields around 70%). These secondary alcohols are themselves prepared in an optically active state by fractional crystallization of the cinchonidine salts of their acid succinates in acetonitrile. The maximal optical rotation values are given in Table I.

The optical purity and absolute configuration of these derivatives can easily be ascertained by displacement of the $Cr(CO)_3$ group from the active alcohols **1** and **5**.[4] Thus, from **1** ($[\alpha]^{22}D$ −60.7°), **3** is obtained (mp 72°; $[\alpha]^{22}D$ +34° (*c* 1.895)), having the *S* absolute configuration,[6] while **5** ($[\alpha]^{22}D$ −20°) yields **7** ($[\alpha]^{22}D$ −26.8° (*c* 6.04, benzene)) also having the *R* absolute configuration.[7] The ketones **4** ($[\alpha]^{22}D$ −334°,) and **8** ($[\alpha]^{22}D$ +870°) are thus optically pure and have the absolute configurations shown in Chart I. The same transformation sequence was made on both enantiomers.

From the chart, it is apparent the central chirality of **3** and **7** and the planar chirality[8] of **4** and **8** are interrelated, for the endo nature of alcohols **1** and **5** is now well established.[9,10] Thus, the two sorts of chirality, i.e., planar and central coexisting in **1** and **5**, are not independent of one another.

Preparation of Optically Active 2-Methyl-1-indanone and 2-Methyl-1-tetralone. This use of the $Cr(CO)_3$ moiety has been applied to other syntheses. The first example is the preparation of optically active 2-methyl-1-indanone and 2-methyl-1-tetralone. The obtention of optically active ketones remains tedious, and the difficulty increases when the asymmetric center α to the carbonyl group possesses a hydrogen atom,[11] thus adding risks of racemization. Scheme I shows how the use of tricarbonylchromium derivatives overcomes this difficulty.

The first reaction sequence illustrates the conversion of 1-indanonetricarbonylchromium (**4**) ($[\alpha]^{22}D$ −334°) to (2*R*)-2-methyl-1-indanone (**12**) ($[\alpha]^{22}D$ −42° (*c* 1.72, dioxane)) via 2-*exo*-methyl-1-indanonetricarbonylchromium (**10**) (mp 153-154°; $[\alpha]^{22}D$ −300° (*c* 0.92)). The second sequence shows the identical route used for the tetralone derivative **8** ($[\alpha]^{22}D$ +870°) giving **20** (mp 88°; $[\alpha]^{22}D$ +675° (*c* 1.06)), which then yields **22** ($[\alpha]^{22}D$ −51.2° (*c* 2,5-dioxane)), having the *S* absolute configuration.

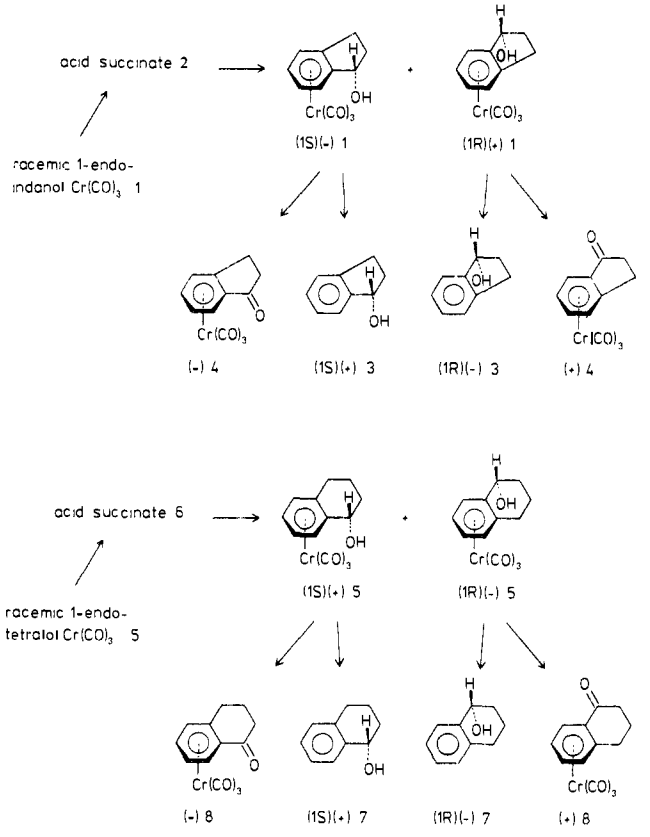
These monomethylation reactions occur stereospecifically in an exo fashion. Products **10** and **20** have been com-

Table I[a]

1-Indanone-tricarbonylchromium (4)	1-*endo*-Indanol-tricarbonylchromium (1)	Cinchonidine salts
mp 143°	mp 110°	
$[\alpha]^{22}D$ −334°	$[\alpha]^{22}D$ −60.7°	$[\alpha]^{22}D$ −172°
$[\alpha]^{22}D$ +332°	$[\alpha]^{22}D$ +60.9°	$[\alpha]^{22}D$ +63°
1-Tetralone-tricarbonylchromium (8)[3]	**1-*endo*-Tetralol-tricarbonylchromium (5)**	**Cinchonidine salts**
mp 118°	mp 140°	
$[\alpha]^{22}D$ +870°	$[\alpha]^{22}D$ −20°	$[\alpha]^{22}D$ +41°
$[\alpha]^{22}D$ −864°	$[\alpha]^{22}D$ +20°	$[\alpha]^{22}D$ −186°

[a] $[\alpha]^{22}D$ were measured in $CHCl_3$ solution.

Chart I. Resolution and Absolute Configuration of 1-Indanone- and 1-Tetralonetricarbonylchromium



pared with authentic racemic samples of known exo configuration.[12,13] The absolute configurations of products **12** and **22** are related to those of the starting ketone complexes.

Although the reaction medium is basic, none of the endo isomer, resulting from equilibrium through the enolic form,[14] is isolated using methyl iodide in excess as reagent in the reactions of **4** to produce **10** and **8** to **20.** However, its transient existence is proved by the isolation, in addition to **10** or **20,** of 2,2-dimethyl-1-indanonetricarbonylchromium (**9**) (mp 142°; $[\alpha]^{22}D$ −441° (*c* 0.955)) or 2,2-dimethyl-1-tetralonetricarbonylchromium (**19**)[15] (mp 158°; $[\alpha]^{22}D$ +756° (*c* 1.23)). The total yield for this reaction is around 80% based on isolated products. The reaction is followed by thin layer chromatography and stopped before completion.

Although these tricarbonylchromium compounds possess a remarkable enantiomeric stability, we have verified that no racemization occurred in the course of the reaction sequence shown in Charts II and III.[16] The optical purity of these derivatives can thus be taken as 100%.[17]

Scheme I

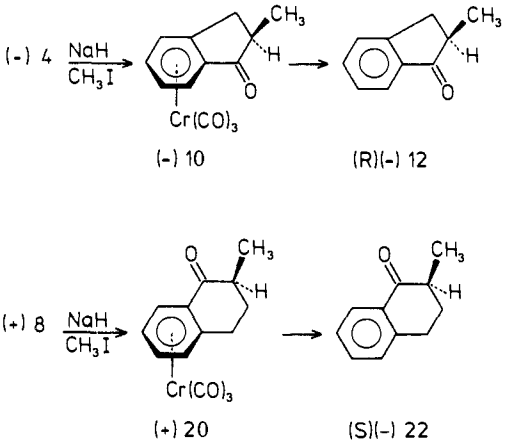
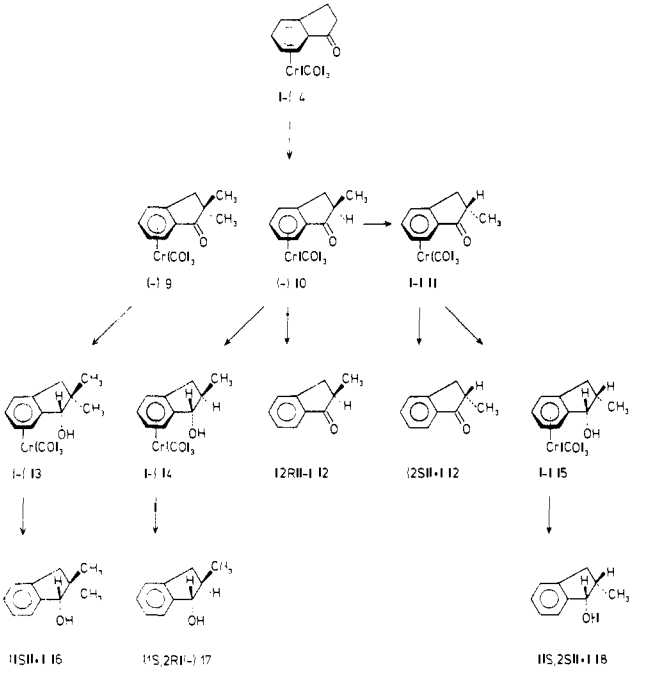


Chart II. Optically Active 1-Indanonetricarbonylchromium and Related Derivatives

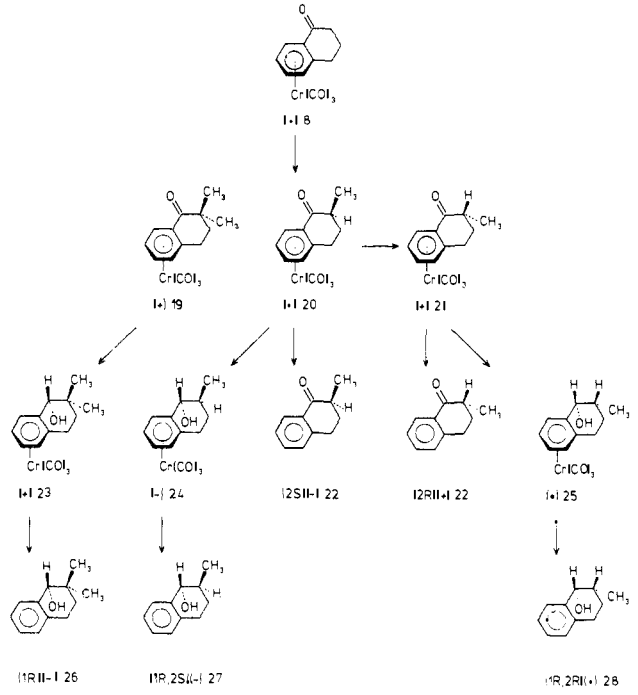


Stereospecific Attack of Potassium Borohydride. Synthesis of Free Optically Pure Secondary Alcohols. The preparation of optically active *exo*- and *endo*-2-methyl-1-indanone- and 2-methyl-1-tetralonetricarbonylchromium provides a simple route to the two pairs of pure cis and trans alcohols, possessing a nonambiguous stereochemistry.[18] It is well known that the reduction of benchrotrenic cyclic ketones by potassium borohydride is stereospecific (Table II). The alcohol obtained is always the endo derivative.[19] This synthetic application is shown in Charts II and III.

We have verified that no epimerization of the ketones occurs during the reduction by KBH_4. This has been recently observed when the reduction is performed in the absence of water.[20] Thus, the products from Charts II and III can be considered as optically pure, and the absolute configurations are those shown in the charts. The yields are in the region of 95%.

Stereospecific Attack of Grignard Reagents. Synthesis of Free Optically Pure Tertiary Alcohols. The use of chiral tricarbonylchromium complexes in the preparation of optically active tertiary alcohol derivatives of 1-indanol and 1-tetralol is described in the next examples.

Chart III. Optically Active 1-Tetralonetricarbonylchromium and Related Compounds

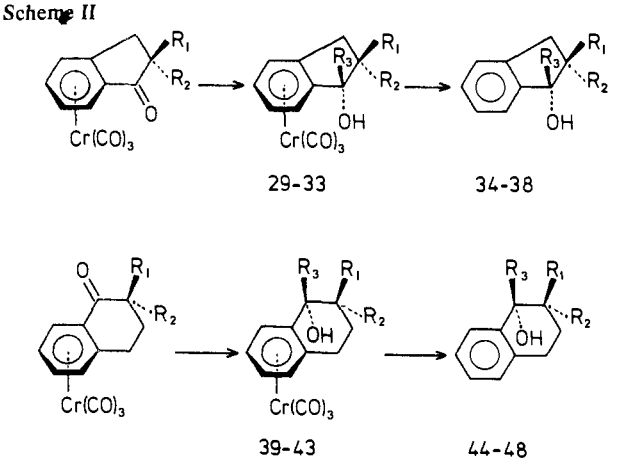


A general procedure for the resolution of tertiary alcohols into optical enantiomers has not yet been developed. The difficulty in the use of acid phthalates for this type of resolution lies in the tendency of the substrates to undergo dehydration and racemization.[21] Tricarbonylchromium complexes may also be used in solving this problem for specific cases.

To our knowledge, no optically active tertiary alcohol based on the 1-indanol or 1-tetralol skeleton has been reported.[22] These compounds may be easily prepared taking into account the stereospecific attack in the exo position of Grignard reagents on ketonic precursors even when the alicyclic ring is alkyl substituted. The endo alcohol derivative is obtained.

Ready, quantitative decomplexation with sunlight in air destroys the induced planar chirality, and the optically active aromatic ligand may be recovered. A total asymmetric synthesis may thus be accomplished.[23] Scheme II illustrates this approach.

Scheme II



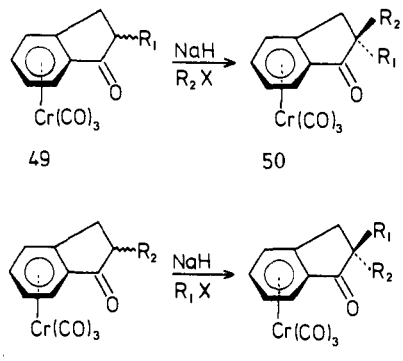
The absolute configurations of compounds given in Table III are those shown in Scheme II. The optical purity may be assumed to be that of the starting ketones, i.e., 100%.

Table II. Stereospecific Attack of Potassium Borohydride Synthesis of Free Optically Pure Secondary Alcohols

Compd	$[\alpha]^{22}D$, deg	c ($CHCl_3$)	Mp, °C
13	−53	1.27	168
14	−85	1.845	111
15	−32	1.77	136
16	+29	1.31	
17	−10	1.27	112
18	+30	3.33	45
23	+16	1.86	145
24	−20	1.80	98
25	+99	1.06	87
26	−23.5	3.37	
27	−89	1.80	54
28	+63	2.74	

Additional Examples of the Total Control of the Stereochemistry on α Carbon to a Ketonic Group. The following examples show the total control of the stereochemistry by the $Cr(CO)_3$ group during the formation of a new asymmetric center α to a ketonic carbonyl. The reaction sequence is shown in Scheme III.

Scheme III[a]

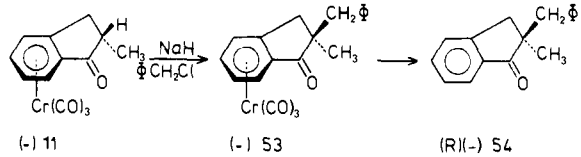


[a] Racemic forms, **50** [$R_1 = CH_3$; $R_2 = CH(CH_3)_2$; $\delta_{CH_3 endo}$ 1.41 ppm ($CDCl_3$)] and **52** [$R_1 = CH_3$; $R_2 = CH(CH_3)_2$; mp 125°; $\delta_{CH_3 exo}$ 1.15 ppm ($CDCl_3$)].[24]

For compounds **50** and **52**, it is not necessary to use the pure isomer, and an exo-endo mixture may be used instead. The second attack occurs stereospecifically in an exo manner only on the endo isomer present in the basic reaction medium by equilibration through the enolic form. Thus, complexes **50** and **52** are obtained (yield around 80%) simply by a change in the order of introduction of the substituents. Then, for example, from the same optically active ketone, it is possible to obtain various enantiomer molecules.

This approach, starting with optically active ketone (−)-**11**, is illustrated in Scheme IV. Pure 2-*exo*-benzyl compound **53** [mp 150°; $[\alpha]^{22}D$ −270° (*c* 0.985, $CHCl_3$)] was isolated,[25] giving rise, by decomplexation, to (*R*)-2-benzyl-2-methyl-1-indanone (**54**) ($[\alpha]^{22}D$ −115° (*c* 2.73)) which may be assumed also to be optically pure.

Scheme IV



Besides the variety of compounds which are accessible in this way, the method is also simple in that only a single resolution of the 1-indanone- and 1-tetralonetricarbonylchromium complexes is required. There are undoubtedly many further cases which may benefit by application of these syn-

Table III. Stereospecific Attack of Grignard Reagents on Active 1-Indanone- and 1-Tetralonetricarbonylchromium Derivatives. Related Optically Pure Tertiary Alcohols

R_1	R_2	R_3	Compd	Starting ketone	$[\alpha]^{22}D$, deg	c ($CHCl_3$)	Mp, °C	Compd	$[\alpha]^{22}D$, deg	c ($CHCl_3$)	Mp, °C
H	H	Me	29	(−)-4	−90	1.705	81	34	+21	3.52	
H	H	Ph	30	(−)-4	−209	1.75	117	35	−48.5	1.56	71
Me	H	Me	31	(−)-10	−115	1.385	106	36	−7	1.69	
H	Me	Me	32	(−)-11	−60	1.853	79	37	+38.5	2.75	30
Me	Me	Me	33	(−)-9	−66	1.38	102	38	+22	3.27	
H	H	Me	39	(+)-**8**	+22.7	1.625	100	44	−29.5	3.8	69
H	H	Ph	40	(+)-8	+208	1.615	118	45	−32	4.20	
Me	H	Me	41	(+)-20	−5	1.44	137	46	−82	3.8	
H	Me	Me	42	(+)-21	+136	1.805	101	47	+17	3.28	
Me	Me	Me	43	(+)-19	+37.5	2.0	151	48	−48	3.87	

[a] It was also possible to prepare optically active tertiary alcohols by using organolithium compounds instead of Grignard reagents. Thus, the addition of (+)-1-tetralonetricarbonylchromium (8) to a solution of vinyllithium in tetrahydrofuran gave rise to (*R*)-1-*exo*-vinyl-1-*endo*-tetralol-tricarbonylchromium (yield 65%): mp 64°, $[\alpha]^{22}D$ +130° (*c* 1.22, $CHCl_3$) (racemic form, mp 86°). [b] By decomplexation of this vinyl alcohol, the free (*R*)-1-vinyl-1-tetralol was liberated, $[\alpha]^{22}D$ −64° (*c* 3.5, $CHCl_3$). Consequently, optically pure ethylenic tertiary alcohols can be easily obtained.

thetic techniques, perhaps of interest in the chemistry of natural products. We are currently undertaking further studies in this area.

Experimental Section[26]

1-*endo*-Indanoltricarbonylchromium (1) was prepared by heating a solution of 1-indanol and $Cr(CO)_6$ in a mixture of dibutyl ether-heptane to reflux under nitrogen: mp 105° (lit.[9] 105°); ir (CCl_4) 3626, 3593 cm^{-1} (O-H stretch).

1-*endo*-Indanoltricarbonylchromium Acid Succinate (2). The acid succinate of **1** was formed by reaction of 15 g of succinic anhydride with 7 g of **1** in 150 ml of freshly distilled pyridine. The mixture was maintained in the dark at room temperature for 2 weeks and the reaction followed by TLC. The solution was poured into water, acidified with hydrochloric acid, and extracted with ether. The organic extract was washed with 10% hydrochloric acid and water. The solution was extracted with 10% sodium bicarbonate until the extract was colorless. The aqueous phases were acidified with hydrochloric acid, and the crude succinate was filtered and dried (7.4 g), mp 123° (from ether-pentane).

Anal. Calcd for $C_{16}H_{14}CrO_7$: C, 51.90; H, 3.81. Found: C, 52.02; H, 3.98.

Resolution of 1-*endo*-Indanoltricarbonylchromium Acid Succinate. A solution of 7.4 g of the acid succinate **2** in 60 ml of hot acetonitrile was added to a solution of 6.1 g of cinchonidine in 60 ml of hot acetonitrile. The yellow salt, which was collected on allowing to stand overnight at room temperature, was filtered, washed with cold acetonitrile, and dried to afford 8.8 g, $[\alpha]^{22}D$ −136° (*c* 2.005, $CHCl_3$). Two other recrystallizations of this salt give 5.9 g of material of constant rotation, $[\alpha]^{22}D$ −172° (*c* 1.815, $CHCl_3$).

The salt was treated with 10% hydrochloric acid and the acid succinate extracted with ether. The extracts were washed with dilute acid and water. Then the succinate was cleaved with 10% sodium hydroxide. The organic layer was washed with water, dried (K_2CO_3), and concentrated by rotatory evaporation under reduced pressure. The residue was recrystallized from ether-petroleum ether to give 1.15 g of yellow prismatic crystals of (−)-1-*endo*-indanoltricarbonylchromium (**1**): mp 110°; $[\alpha]^{22}D$ −60.7°; $[\alpha]^{578}$ −63.6°; $[\alpha]^{546}$ −73° (*c* 2.14, $CHCl_3$).

In the mother liquor from the resolution, yellow needles were collected (2.6 g), $[\alpha]^{22}D$ +63° (*c* 2.105, $CHCl_3$), and decomposed in the same way to afford, after two recrystallizations, the dextrorotatory 1-*endo*-indanoltricarbonylchromium (+)-(**1**), mp 110°, $[\alpha]^{22}D$ +60.9° (*c* 2.07, $CHCl_3$).

(*S*)-(+)-1-Indanol (3). Determination of the Absolute Configuration. A solution of 0.1 g of (−)-1-*endo*-indanoltricarbonylchromium in 50 ml of dry ether was exposed to sunlight. The precipitate was filtered and the organic solution concentrated by rotory evaporation in vacuo, leaving a crude product. Recrystallization from ether-petroleum ether yielded 0.057 g of long colorless needles, mp 72°, $[\alpha]^{22}D$ +34° (*c* 1.895, $CHCl_3$), having *S* configuration.[6]

Similarly (*R*)-(+)-1-*endo*-indanoltricarbonylchromium was decomplexed in (R)-(−)-indanol.

(−)-1-Indanonetricarbonylchromium (4). Three grams of manganese dioxide was added in small amounts to a solution of 1 g of (−)-1-*endo*-indanoltricarbonylchromium (**1**) in 120 ml of dry ether, and the mixture was stirred for 3 hr at room temperature. After MnO_2 was filtered, concentration in vacuo gave a residue which was separated by preparative TLC, utilizing benzene as eluting solvent. Separation afforded 0.65 g of alcohol (−)-(**1**) and 0.215 g of levorotatory ketone **4**: mp 143° (from ether-petroleum ether); $[\alpha]^{22}D$ −334° (*c* 1.165, $CHCl_3$); ir (CCl_4) 1722 cm^{-1} (C=O stretch).

Anal. Calcd for $C_{12}H_8CrO_4$: C, 53.74; H, 3.01. Found: C, 53.62; H, 3.11.

Similarly, (+)-1-*endo*-indanoltricarbonylchromium gave (+)-1-indanonetricarbonylchromium (**4**), mp 143°, $[\alpha]^{22}D$ +332° (*c* 0.995, $CHCl_3$).

1-*endo*-Tetraloltricarbonylchromium (5) was obtained by the same way as 1: mp 130° (from ether-petroleum ether).

Anal. Calcd for $C_{13}H_{12}CrO_4$: C, 54.93; H, 4.25. Found: C, 54.98; H, 4.36.

1-*endo*-Tetraloltricarbonylchromium Acid Succinate (6). Following the procedure described above for compound **2**, the acid succinate **6** was prepared with a good yield, mp 143° (from ether-petroleum ether).

Anal. Calcd for $C_{17}H_{16}CrO_7$: C, 53.13; H, 4.19. Found: C, 53.45; H, 4.11.

Resolution of 1-*endo*-Tetraloltricarbonylchromium Acid Succinate. A mixture of 14.8 g of the succinate **6** and 11.2 g of cinchonidine was dissolved in 500 ml of boiling acetonitrile. The yellow salt which had crystallized after 48 hr at room temperature was collected: 8 g; $[\alpha]^{22}D$ +29° (*c* 3.45, $CHCl_3$). After two recrystallizations in hot acetonitrile giving 6.6 g of salt, the specific rotation was constant, $[\alpha]^{22}D$ +41° (*c*, 2.24, $CHCl_3$). The crystalline salt was cleaved by the usual way and the resulting alcohol recrystallized from ether-petroleum ether to yield 2.7 g of yellow needles of (−)-1-*endo*-tetraloltricarbonylchromium (**5**): mp 140°; $[\alpha]^{22}D$ −20° (*c* 2.245, $CHCl_3$).

From the original mother liquor another amount of salt (5.8 g) was collected after 2 days, $[\alpha]^{22}D$ −116° (*c* 2.24, $CHCl_3$), recrystallized in boiling acetonitrile giving a specific rotation $[\alpha]^{22}D$ −186° (*c* 2.04, $CHCl_3$).

The dextrorotatory alcohol **5** was obtained as described above: mp 138° (needles from ether-petroleum ether); $[\alpha]^{22}D$ +17° (*c* 2.1, $CHCl_3$); optical purity 85%.

(*R*)-(−)-1-Tetralol (7) was obtained by quantitative displacement of the $Cr(CO)_3$ moiety from a solution of (−)-**5** in ether: $[\alpha]^{22}D$ −26.8° (*c* 6.04, C_6H_6). The absolute configuration of this alcohol (−)-7 was *R*.[27]

(+)-1-Tetralonetricarbonylchromium (8). A solution of 3.5 g of (−)-1-*endo*-tetraloltricarbonylchromium (**5**) in 200 ml of dry ether was stirred with 10 g of MnO_2 for 4 hr. The reaction was followed by TLC. Then chromatography through a silicic acid column, eluting with benzene, was performed. The first eluted com-

Table IV

Compd	R	Mp, °C	$[\alpha]^{22}D$, deg	c ($CHCl_3$)	Analyses	Calcd	Found
13	2,2-Dimethyl-1-*endo*-OH	168	−53	1.27	$C_{14}H_{14}CrO_4$	C, 56.37 H, 4.73	C, 56.36 H, 4.63
14	2-*exo*-Methyl-1-*endo*-OH	111	−85	1.845	$C_{13}H_{12}CrO_4$	C, 54.93 H, 4.25	C, 54.58 H, 4.30
15	2-*endo*-Methyl-1-*endo*-OH	136	−32	1.77	$C_{13}H_{12}CrO_4$	C, 54.93 H, 4.25	C, 54.99 H, 4.29

Table V

Compd	R		Mp, °C	$[\alpha]^{22}D$, deg	c ($CHCl_3$)
16	2,2-Dimethyl-(1*S*)-indanol			+29	1.31
17	(2*R*)-Methyl-(1*S*)-OH	Trans	112	−10	1.27
18	(2*S*)-Methyl-(1*S*)-OH	Cis	45	+30	3.33

pound was the ketone. Crystallization of the crude product from ether–petroleum ether yielded 0.6 g of big red crystals of active 1-tetralonetricarbonylchromium (**8**):[28] mp 119°; $[\alpha]^{22}D$ +870° (*c* 0.99, $CHCl_3$).

The second eluted compound was the starting material (2.55 g). (−)-1-Tetralonetricarbonylchromium (**8**) was obtained by oxidation of (+)-tetraloltricarbonylchromium ($[\alpha]^{22}D$ +17°, optical purity 85%). Two recrystallizations from ether–petroleum ether and separation of some dark red racemic crystals gave the pure active ketone: mp 119°; $[\alpha]^{22}D$ −864° (*c* 1.55, $CHCl_3$).

Methylation of (−)-1-Indanonetricarbonylchromium. To a solution of 0.5 g of (−)-4 in 70 ml of benzene-*N*,*N*-dimethylformamide (9:1) was added 0.1 g of a 50% sodium hydride dispersion. The mixture was stirred for 10 min at room temperature, 2.5 g of methyl iodide was then added, and the resulting solution was stirred for 1.5 hr. The reaction was followed by TLC (ether–petroleum ether, 1:3). The reaction mixture was poured into dilute hydrochloric acid and extracted with ether. The extracts were dried, concentrated, and submitted to a chromatography on preparative plates (ether–petroleum ether 1:3, as eluent). Three bands were separated,[29] and each was ether extracted. The first eluted compound was 2,2-dimethyl-1-indanonetricarbonylchromium (**9**) (0.11 g): mp 142° (from ether–petroleum ether); $[\alpha]^{22}D$ −441° (*c* 0.955, $CHCl_3$); NMR ($CDCl_3$) δ_{CH_3endo} 1.37, δ_{CH_3exo} 1.21.

Anal. Calcd for $C_{14}H_{12}CrO_4$: C, 56.76; H, 4.08. Found: C, 56.91; H, 4.12.

Then 0.24 g of 2-*exo*-methyl-1-indanonetricarbonylchromium (**10**) was obtained: mp 153–154°; $[\alpha]^{22}D$ −300° (*c* 0.92, $CHCl_3$); NMR ($CDCl_3$) δ_{CH_3exo} 1.26; ir (CCl_4) 1724 cm^{-1} (C=O stretch).

Anal. Calcd for $C_{13}H_{10}CrO_4$: C, 55.67; H, 3.57. Found: C, 55.68; H, 3.82.

0.07 g of (−)-**4** was recovered, the specific rotation of (−)-**4** being constant.

2-*endo*-Methyl-1-indanonetricarbonylchromium (11). 2-*exo*-Methyl-1-indanonetricarbonylchromium (**10**) (0.2 g) was treated with a sodium methoxide solution (0.44 g of sodium in 40 ml of absolute methanol), and the solution was stirred for 1 hr. The solution was poured into 200 ml of 5% hydrochloric acid and extracted with ether. The extracts were dried and concentrated, and the residue was submitted to preparative TLC (ether–petroleum ether 1:3) to yield 0.094 g of isomer **11**: mp 137°; $[\alpha]^{22}D$ −450° (*c* 1.04, $CHCl_3$); NMR ($CDCl_3$) δ_{CH_3endo} 1.36; ir (CCl_4) 1723 cm^{-1} (C=O stretch).

Anal. Calcd for $C_{13}H_{10}CrO_4$: C, 55.67; H, 3.57. Found: C, 55.56; H, 3.57.

The starting ketone (−)-**11** (0.086 g) was recovered.

(*R*)-(−)-2-Methyl-1-indanone (12). Using the same procedure as above for decomplexation, from 2-*exo*-methyl-1-indanone)tricarbonylchromium (**10**) ($[\alpha]^{22}D$ −300°), the levorotatory ketone was obtained, $[\alpha]^{22}D$ −42° (*c* 1.72, dioxane).

2-Alkyl-1-*endo*-indanoltricarbonylchromiums 13, 14, and 15. To a red solution of 0.15 g of (−)-**9** in methanol–water (50:10) was added 0.3 g of potassium hydroboride. The mixture was allowed to stir for 1 hr giving a pale-yellow solution, poured into 5% hydrochloric acid, and extracted with ether; recrystallization (from ether–petroleum ether) of the crude product gave 2,2-dimethyl-1-*endo*-indanoltricarbonylchromium (**13**). Using similar conditions, ketones (−)-10 and (−)-**11** gave alcohols **14** and **15**. The characteristics are given in Table IV.

Active 2-Alkyl-1-indanols 16, 17, and 18. An ether solution of the alcohols **13, 14,** or **15** was exposed to sunlight for 1 hr. The precipitate was filtered and washed with ether. The organic solution was dried (K_2CO_3) and evaporated to dryness under reduced pressure. When solid, the residue was recrystallized (ether–pentane) (Table V).

Methylation of (+)-1-Tetralonetricarbonylchromium (8). (a) Using the same procedure as for (−)-1-indanonetricarbonylchromium, from 1.7 g of (+)-1-tetralonetricarbonylchromium (**8**), 0.35 g of 50% NaH dispersion, and 4.2 g of CH_3I, 0.54 g of the unreacted starting ketone was recovered and with the same specific rotation.[30] The first zone contained 0.295 g of 2,2-dimethyl-1-tetralonetricarbonylchromium (**19**): mp 158° (from ether–petroleum ether); $[\alpha]^{22}D$ +756° (*c* 1.23, $CHCl_3$); NMR ($CDCl_3$) δ_{CH_3endo} 1.26, δ_{CH_3exo} 1.17.

Anal. Calcd for $C_{15}H_{14}CrO_4$: C, 57.63; H, 4.52. Found: C, 58.06; H, 4.66.

The second eluate was pure 2-*exo*-methyl-1-tetralonetricarbonylchromium (**20**) (0.82 g), mp 88° (long red crystals from ether–petroleum ether), $[\alpha]^{22}D$ +675° (*c* 1.06, $CHCl_3$), showing identical NMR as racemic form, mp 74°. (b) Methylation of (+)-**8** was also performed by bubbling a stream of methyl bromide through the solution of (+)-**8** and NaH dispersion in benzene–DMF (9:1). The analysis showed a fourth eluate beside products **19, 20,** and **8**. This compound was identified with a known sample as 2-*endo*-methyl-1-tetralonetricarbonylchromium (**21**): mp 157° (red needles from ether–petroleum ether); $[\alpha]^{22}D$ +849° (*c* 1.14, $CHCl_3$).

Equilibration of 2-Methyl-1-tetralonetricarbonylchromiums 20 and 21. Under similar conditions as previously and after preparative TLC, 0.054 g of the starting material (+)-**20** and 0.216 g of the 2-*endo*-methyl-1-tetralone (**21**), $[\alpha]^{22}D$ +850°, were obtained from 0.3 g of the 2-exo isomer (+)-**20**.[31]

(*S*)-(−)-2-Methyl-1-tetralone (22). Following the procedure briefly described for decomplexation, (+)-2-*exo*-methyl-1-tetralonetricarbonylchromium [(*S*)-(−)-**22**] was obtained: $[\alpha]^{22}D$ −51.2° (*c* 2.5, dioxane).

The endo isomer (+)-**21** gave the enantiomer form, (*R*)-(+)-2-methyl-1-tetralone (**22**), $[\alpha]^{22}D$ +51.7° (*c* 2.4, dioxane).

2-Alkyl-1-*endo*-tetraloltricarbonylchromiums 23, 24, and 25. The ketones (+)-**19,** (+)-**20,** and (+)-**21** (0.12 g) were reduced to 1-substituted alcohols with potassium hydroboride in the usual way. The characteristics are given in Table VI. Elemental analyses were consistent with the proposed formulas.

Optically Active 2-Alkyl-1-tetralols 26, 27, and 28. An ether solution of the alcohols **23, 24,** and **25** was submitted to decomplexation. After filtration, the organic solution was dried (K_2CO_3) and evaporated (Table VII).

Preparation of Optically Pure Tertiary Alcohols. A solution of 0.12 g of optically active ketone in dry ether was added to an ether solution of methylmagnesium iodide (or phenylmagnesium bromide) in large excess. The mixture was stirred for 1 hr and the pale-yellow solution poured into 5% hydrochloric acid and extracted with ether. Ether layers were dried (K_2CO_3), concentrated, and purified by preparative TLC. The tertiary alcohols were recrystallized from ether–petroleum ether. Elemental analyses agreed well with the proposed formulas, and the characteristics are given in Table III.

Preparation of Optically Pure Aromatic Tertiary Alcohols. These alcohols were obtained by the general procedure described

Table VI

Compd		Mp, °C	$[\alpha]^{22}D$, deg	c ($CHCl_3$)
23	2,2-Dimethyl-1-*endo*-OH	145	+16	1.86
24	2-*exo*-Methyl-1-*endo*-OH	98	−20	1.8
25	2-*endo*-Methyl-1-*endo*-OH	87	+99	1.06

Table VII

Compd		Mp, °C	$[\alpha]^{22}D$, deg	c ($CHCl_3$)
26	2,2-Dimethyl-(1*R*)-OH		−23.5	3.37
27	(2*S*)-Methyl-(1*R*)-OH	54	−89	1.8
28	(2*R*)-Methyl-(1*R*)-OH		+63	2.74

for decomplexation. Some characteristics are reported in Table III.

Mixture of Racemic 2-*exo*-Methyl-1-indanonetricarbonylchromium and 2-*endo*-Methyl-1-indanonetricarbonylchromium 49. The mixture of these isomers was obtained either by methylation of racemic 1-indanonetricarbonylchromium (**4**) and equilibration of the exo isomer, or by cyclization of the 2-methyl-3-(phenyltricarbonylchromium)propanoic acid in polyphosphoric acid.

2-*exo*-Benzyl-2-*endo*-methyl-1-indanonetricarbonylchromium (53). To a solution of 0.5 g of the two isomers **49** in 40 ml of DMF was added 0.25 g of NaH dispersion (large excess), and the mixture was allowed to stir 15 min. Then 3 g of benzyl chloride was added, and the reaction was followed by TLC. A rapid reaction with only one new product was observed. The mixture was poured into 5% hydrochloric acid and extracted with ether. The organic extracts were washed several times with water, dried, and concentrated under reduced pressure. Purification by preparative TLC and recrystallization from ether–petroleum ether gave orange crystals of **53** (0.415 g): mp 144°; NMR ($CDCl_3$) δ_{CH_3endo} 1.43.

Anal. Calcd for $C_{20}H_{16}CrO_4$: C, 64.51; H, 4.33. Found: C, 64.79; H, 4.16.

2-*exo*-Isopropyl-2-*endo*-methyl-1-indanonetricarbonylchromium (50). Following the procedure described above, the mixture **49** is converted with NaH dispersion and isopropyl iodide into the α dissymetric disubstituted ketone **50**: NMR ($CDCl_3$) δ_{CH_3endo} 1.41.

2-*exo*-Isopropyl-1-indanonetricarbonylchromium (51) was prepared by cyclization of 2-isopropyl-3-(phenyltricarbonylchromium)propanoic acid in polyphosphoric acid and purification by preparative TLC, mp 116°.

Anal. Calcd for $C_{15}H_{14}CrO_4$: C, 57.63; H, 4.52. Found: C, 58.06; H, 4.66..

2-*exo*-Methyl-2-*endo*-isopropyl-1-indanonetricarbonylchromium (52). Following the same way, from 0.2 g of **51**, 0.15 g of NaH dispersion, and 1.5 g of CH_3I, 0.155 g of red crystals (from ether–pentane) was obtained: mp 125°; NMR ($CDCl_3$) δ_{CH_3exo} 1.15.

Anal. Calcd for $C_{16}H_{16}CrO_4$: C, 59.25; H, 4.97. Found: C, 59.20; H, 4.66.

(−)-2-*exo*-Benzyl-2-*endo*-methyl-1-indanonetricarbonylchromium (53). Using the classical way, from 0.090 g of *endo*-(−)-**11** and after purification, 0.070 g was obtained: mp 150° (from ether–pentane); $[\alpha]^{22}D$ −270° (*c* 0.985, $CHCl_3$).

(*R*)-2-Benzyl-2-methyl-1-indanone (54). A solution of 0.045 g of (−)-**53** in dry ether was decomplexed. After working up, (−)-**54** was obtained, $[\alpha]^{22}D$ −115° (*c* 2.72, $CHCl_3$).

References and Notes

(1) For example see: (a) I. Wender and P. Pino, "Organic Syntheses via Metal Carbonyls," Interscience, New York, N.Y., 1968; (b) C. W. Bird, "Transition Metal Intermediates in Organic Synthesis", Academic Press, New York, N.Y., 1967; (c) M. I. Bruce compiled all the important review articles, *Adv. Organomet. Chem.*, **10**, 327 (1972); **11**, 463 (1973); (d) M. Rosenblum, *Acc. Chem. Res.*, 7, 122 (1974).

(2) G. Jaouen and R. Dabard, *Tetrahedron Lett.*, 1015 (1971).

(3) H. Falk, K. Schlögl, and W. Steyrer, *Monatsh. Chem.*, **97**, 1029 (1966), have reported the partial resolution of this ketone (optical purity, 2.5%).

(4) The mechanism of this reaction has not been elucidated. It may involve a rupture of the arene–chromium bond by peroxides formed in ether following uv irradiation; a mechanism involving oxidation of an excited state cannot be excluded for it seems that the effective wavelength for decomplexation is around 360 nm in the case of these alcohols.[5]

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(8) In this type of organometallic complexes, since the chirality follows from asymmetric substitution within one plane, which lies perpendicular to the molecular axis, in contrast to centro- and axial chiral compounds, the general expression planar chirality was suggested. K. Schlögl, *Top. Stereochem.*, **1**, 39 (1967).

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(12) G. Jaouen, *Tetrahedron Lett.*, 1753 (1973). Because of an accidental malfunction in the polarimeter, the optical rotations of two indanones were overestimated. In fact, the 2-*endo*-methyl-1-indanonetricarbonylchromium with an optical purity of 4% has $[\alpha]^{22}D$ +12°, and the 2,2-dimethyl-1-indanonetricarbonylchromium has a value of $[\alpha]^{22}D$ +18.5°.

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(14) For the methylindanone complex, the thermodynamic equilibrium endo/exo is 52/48 while, for the methyltetralone complex, it is 80/20.

(15) Nevertheless, bubbling slightly less than stoichiometry of gaseous CH_3Br through the solution, small amounts of 2-*endo*-methyl-1-tetralonetricarbonylchromium (**21**) [mp 157°; $[\alpha]^{22}D$ +849° (*c* 1.14)] can be isolated. This endo isomer **21** gives the enantiomer form of **22**: (2*R*)-2-methyl-1-tetralone ($[\alpha]^{22}D$ +51.7° (*c* 2.4 dioxane)).

(16) Some examples of intramolecular racemizations of planar chiral metallocenes have been reported, in one instance by nucleophilic substitutions reactions in arene tricarbonylchromium series: G. Jaouen and R. Dabard, *J. Organomet. Chem.*, **21**, P43 (1970).

(17) This has been confirmed by the values recently calculated for 2-methyl-1-tetralone: A. Schoofs, J. P. Guette, and A. Horeau, *C. R. Acad. Sci., Ser. C*, **274**, 1527 (1972). These authors also report the synthesis of the *cis*- and *trans*-2-methyltetralols.

(18) The *endo*-2-methyl-1-indanone- and 2-methyl-1-tetralonetricarbonylchromium complexes are obtained by equilibration of the exo isomers with sodium methoxide or polyphosphoric acid. There is no racemization during the reactions.

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(20) V. Hach, E. C. Fryberg, and E. McDonald, *Tetrahedron Lett.*, 2629 (1971).

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(23) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions", Prentice-Hall, Englewood Cliffs, N.J., 1971, p 4.

(24) Structures **50** and **52** are easily verified using NMR. It is well known that an alkyl group cis to a $Cr(CO)_3$ group is deshielded.[19]

(25) Racemic form of **53**, mp 144°; δ_{CH_3endo} = 1.43 ppm, $CDCl_3$.

(26) All melting points were determined on a Kofler Bank. Nuclear magnetic resonance spectra were recorded on a Varian A-60-A instrument. Chemical shifts are given as δ units, tetramethylsilane being used as internal standard. Specific rotations were obtained on a Perkin-Elmer 241 MC polarimeter, using a 1-dm cell and *c* being expressed in grams per liter of solution.

(27) We have checked that decomplexation of active 1-*endo*-tetraloltricarbonylchromium ($[\alpha]^{22}D$ +17°) gave dextrorotatory 1-tetralol (**7**) ($[\alpha^{22}D$ +23° (*c* 3.1, C_6H_6)), having *S* absolute configuration.

(28) No racemization occurred during this oxidation. To a solution of 0.050 g of (+)-**8** in a mixture of methanol–water (3:1), 0.1 g of KBH_4 was added. The solution was stirred for 1 hr at room temperature, poured into dilute hydrochloric acid, and extracted with ether. Concentration in vacuo and crystallization gave 0.045 g of (−)-1-*endo*-tetraloltricarbonylchromium ($[\alpha]^{22}D$ −20°).

(29) The separation of products **9** and **10** is not easy, the retention times being not very different.

(30) No racemization occurred in this medium. We have verified that stirring for 4 hr a mixture of (+)-**8** ($[\alpha]^{22}D$ +854° (*c* 1.04)) and NaH in benzene–DMF (9:1), the starting ketone after extraction showed: $[\alpha]^{22}D$ +860° (*c* 1.06, $CHCl_3$).

(31) This equilibration through the enolic form occurred also without racemization.