

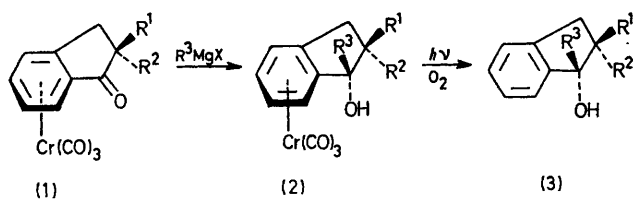
Stereospecific Attack of Grignard Reagents on Optically Active (Indan-1-one)- and (1-Tetralone)-tricarboxyl chromium Derivatives. Use in the Synthesis of Free Optically Pure Tertiary Alcohols

By ANDRÉ MEYER and GÉRARD JAOUEN*

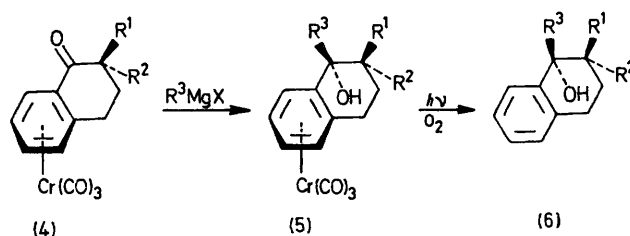
(Laboratoire de Chimie des Organométalliques, Université de Rennes, 35031 Rennes cedex, France)

Summary The use of chiral tricarbonyl chromium complexes in the preparation of optically active tertiary alcohol derivatives of indan-1-ol and 1-tetralol is described.

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 racemisation.¹ We show here how tricarbonylchromium complexes may be used in solving this problem.



To our knowledge, no optically active tertiary alcohol based on the indan-1-ol or 1-tetralol skeleton has been reported.² These compounds may be easily prepared taking into account the following points. (Indan-1-one)-



and (1-tetralone)-tricarbonylchromium have been resolved.³ These compounds readily undergo substitution at the carbon α to the ketonic group to produce mono- and di-alkyl derivatives. The absolute configuration and optical purity (100%) of these complexes have been determined by chemical correlation.³ Attack of Grignard reagents on these substances is stereospecific in the 'exo' position even when the alicyclic ring is alkyl substituted. The 'endo' alcohol derivative is obtained. Ready, quantitative decomplexation with sunlight in air⁴ destroys the induced planar chirality, and the optically active aromatic ligand may be recovered. A total asymmetric synthesis may thus be accomplished.⁵ Tables 1 and 2 illustrate this approach.

TABLE 1

R ¹	R ²	R ³	Ketone (1)			(2)			(3)		
			$[\alpha]_D^{22}$	<i>c</i>	M.p.	$[\alpha]_D^{22}$	<i>c</i>	M.p.	$[\alpha]_D^{22}$	<i>c</i>	
H	H	Me	} -334°	1.165	143°	{	-90°	1.705	81°	+21°	3.52
H	H	Ph					-209°	1.75	117°	-48°5' ^a	1.56
Me	H	Me					-115°	1.353	106°	-7°	1.69
H	Me	Me	-450°	1.26	137°	-60°	1.353	79°	+38°5' ^b	2.75	
H	Me	Me	-441°	0.955	147°	-66°	1.38	102°	+22°	3.27	

^a M.p. 71°. ^b M.p. 30°.

TABLE 2

R ¹	R ²	R ³	Ketone (4)			(5)			(6)		
			$[\alpha]_D^{22}$	<i>c</i>	M.p.	$[\alpha]_D^{22}$	<i>c</i>	M.p.	$[\alpha]_D^{22}$	<i>c</i>	
H	H	Me	} +870°	0.99	118°	{	+22°7'	1.625	100°	-29°5' ^a	3.8
H	H	Ph					+208°	1.615	118°	-32°	4.2
Me	H	Me					-5°	1.44	137°	-82°	3.8
H	Me	Me	+849°	1.14	157°	+136°	1.805	101°	+17°	3.28	
Me	Me	Me	+756°	1.23	158°	+37°5'	2.0	151°	-48°	3.87	

^a M.p. 69°

Optical rotations were measured in CHCl₃ using a Perkin-Elmer 241 MC polarimeter. The absolute configurations are those shown in the Tables. The optical purity may be assumed to be that of the starting ketones, *i.e.* 100%.

Besides the variety of compounds which are accessible in this way, the method is also simple in that only a single resolution of the (indan-1-one)- and (1-tetralone)-tri-

carbonylchromium complexes is required. In addition, this method is not limited to cyclic ketones, and even for several open-chain derivatives we have obtained asymmetric inductions in excess of 95%.

We thank Dr. J. A. S. Howell for helpful discussions.

(Received, 17th July 1974; Com. 879.)

¹ A. W. Ingersoll in 'Organic Reactions,' vol. 2, ed., R. Adams, Wiley, New York, 1944, ch. 9; S. H. Wilen in 'Topics in Stereochemistry,' vol. 6, Wiley-Interscience, 1971, p. 107 *et seq*; P. H. Boyle, *Quart. Rev.*, 1971, 323.

² S. H. Wilen, 'Tables of Resolving Agents and Optical Resolutions,' ed. E. L. Eliel, University of Notre Dame Press, 1972.

³ G. Jaouen and A. Meyer, to be published.

⁴ G. Jaouen and R. Dabard, *Tetrahedron Letters*, 1971, 1015.

⁵ J. D. Morrison and H. S. Mosher, 'Asymmetric Organic Reactions,' Prentice-Hall, Englewood Cliffs, New Jersey, 1971, pp. 4 *et seq*.