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ASYMMETRIC INDUCTION IN BENCHROTRENE DERIVATIVES: DIARYLIMINES

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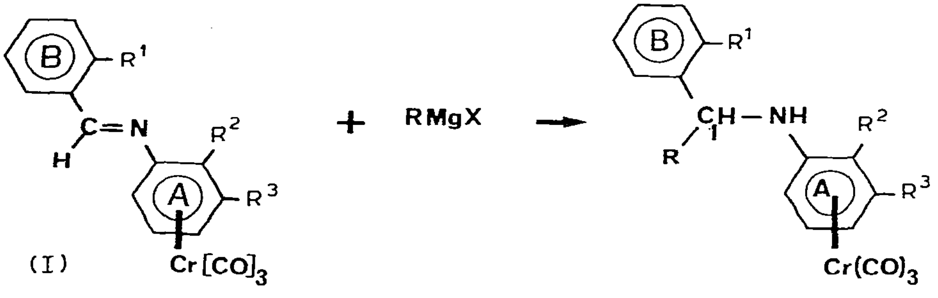
Summary

A high degree of asymmetric induction can be obtained in reactions of Grignard reagents with chiral chromium tricarbonyl complexes of diarylimines.

Introduction

We describe below the results of a study of the reactions of some Grignard reagents with chiral chromium tricarbonyl complexes of diarylimines (I).



(I)

	a	b	c	d	e	f	g
R^1	H	Me	Me	Me	OMe	Cl	Me
R^2	Me	Me	Et	Ph	Me	Me	H
R^3	H	H	H	H	H	H	Me

(II $R = CH_3$;
III $R = C_6H_5CH_2$)

A high degree of asymmetric induction would be expected for the reactions of complexes of type IVa by analogy with the results obtained with the carbonyl

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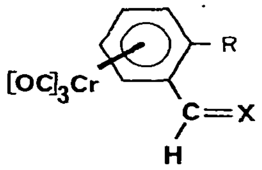
compounds IVb [1—6], but it was less certain that asymmetric induction woulc be possible for reactions of complexes I, and we have carried out some experiments relative to this point.



(IVa : X = NC_6H_5 ;
IVb : X = O)

Results and discussion

The results are shown in Table 1. Although the stereochemical assignments o the major and minor diastereomeric products (IIa—IIg, IIIa—IIIg) have not beer completely established, it is unlikely that the stereochemistry of the preferred diastereomer would change on going from methyl-Grignard to benzyl-Grignard (or with increase in the size of the substituent R^2), as such a change has never been reported for reactions of the Felkin type [7] which involve addition of achiral Grignards to chiral substrates.

From the results given (Table 1), it can be seen that: (1) Very high asymmeti induction can be obtained. (2) The extent of asymmetric induction depends strongly on the position of the substituent on ring A; *ortho*-substitution leads to higher asymmetric induction than *meta*-substitution. (3) A larger entering group leads to higher asymmetric induction. (4) *Ortho*-substitution on ring B does not much change the degree of asymmetric induction.

TABLE 1

YIELD OF REACTIONS OF COMPOUNDS Ia—Ig WITH RMgX

	RMgX	Reaction conditions [a]		Chemical yield (%)	Diastereomer (%) [b]	Asymmetric induction (%)
		t (°C)	time (h)			
Ia [c]	CH_3MgI	5	48	90	67/33	34
Ib	CH_3MgI	5	36	94	67/33	34
	$PhCH_2MgCl$	—70	36	92	100/0	100
Ic	CH_3MgI,	5	48	90	68/32	36
	$PhCH_2MgCl$	—70	12	95	100/0	100
Id	CH_3MgI	5	48	67	66/34	32
Ie	$PhCH_2MgCl$	—70	24	92	100/0	100
If	$PhCH_2MgCl$	—70	24	89	100/0	100
Ig	CH_3MgI,	5	26	86	55/45	10
	$PhCH_2MgCl$	—70	16	92	57/43	14

[a] Temperature maintained during addition of Grignard reagent (after addition t was allowed to rise to 20°C) and reaction time before work-up. [b] NMR precision ±2%. [c] The complexes are prepared from the complexed substituted aniline and the corresponding carbonyl compound (reflux in benzene/catal. PTS). NMR characteristics are given in ref. 10.

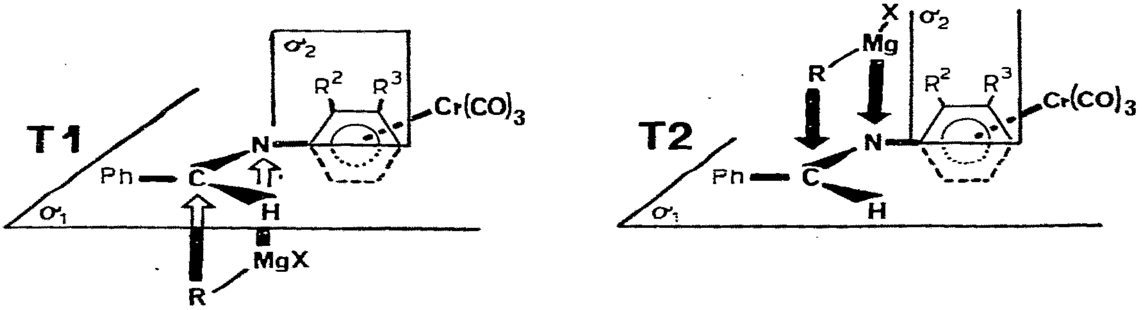
TABLE 2

250 MHz ^{1}H NMR SPECTRA OF COMPOUNDS OF TYPE II AND III (diastereomers mixtures) [a,c]

	IIa	IIb [b]	IIc	IId	IIg	IIIb	IIIc	IIIe	IIIf	IIIg
$R^1 = CH_3$		2,51/*2,53*s	2,43/*2,45*s	2,40/*2,44*s	2,51/*2,53*s	*2,36*s	*2,35*s			
$R^1 = CH_3O$								*3,91*s		
$R^2 = CH_3$	2,08/*2,15*s	2,29/*2,32*s				2,01s		*2,01*s	*2,00*s	
$R^2 = CH_3CH_2$			1,27/*1,32*t 2,52m							
$R^2 = C_6H_5$				7,17m			*0,98*t 2,30m			
$R^3 = CH_3$					2,13/2,28s					
$R = CH_3$	*1,52*/1,54d	1,52/*1,56*d	1,46/*1,50*d	*1,28*/1,30d	1,50/*1,52*d					
$R = Ph{-}CH_2$	*3,02* $^2J_{AB}$–14 Hz	*2,55* $^2J_{AB}$–15 Hz	*3,05* $^2J_{AB}$–14 Hz	*2,88* $^2J_{AB}$–15 Hz	*3,02*					
C(1)–H	4,32m	5,30m	4,52m	4,52m	4,67m	*4,56*m	*4,55*m	*4,62*m	*4,62*m	4,57m
Cycle A	*4,52* 4,33 } d	*4,74* 4,80 } d	*4,56* 4,76 } d	*4,34* 4,59 } d	4,34 4,91 } d	*4,42*d	*4,34*d	*4,62*d	*4,38*d	4,18d
	4,72 4,80 } t	*5,06* 5,12 } t	*4,96* 5,03 } t	*4,72* 4,76 } t	4,45 *4,98* } s	*4,78*t	*4,72*t	*4,78*t	*4,78*t	4,32 *4,72* s
	5,24 5,29 } t	*5,62* 5,64 } t	*5,48* 5,54 } t	5,40 *5,52* } t	4,80d	5,22t	*5,20*t	*5,18*t	*5,14*t	4,64d
	5,52 5,38 } d	*5,94* 5,78 } d	*5,78* 5,72 } d	5,58 *5,60* } d	5,54 *5,70* } t	*5,31*d	*5,26*d	*5,28*d	*5,22*d	5,28 *5,44* t
NH	3,78d	4,21(br)	3,84s	2,91/4,05d	3,93d	*3,88*d	*2,92*(br)	*4,22*d	*3,94*d	3,95/*4,00*d

[a] $CDCl_3$/TMS, after filtration on 0,2 μm millipore to remove traces of chromium oxide. [b] Acetone-d_6/TMS. [c] Numbers in italics indicate the major diastereomer. [d] Assignment is impossible: 2,15, 2,14, 2,12, 2,00.

SCHEME 1



These observations suggest a transition-state model (Scheme 1) in which (a) the $Cr(CO)_3$ moiety is situated almost in the plane of chirality [8] σ_1 (because of $n - \pi$ interaction [9]) and plays a rather secondary role, and (b) the approach of the reactant is nearly orthogonal to the plane σ_1 of the azomethine group and so to ring B (which is very little twisted out of this plane because of $\pi - \pi$ interaction [9]). The asymmetric induction is thus directly governed by the interaction between the entering RMgX and the substituent on ring A.

The least strained transition-state is obviously T_1 when ring A is *ortho*-substituted, and, though to a lesser extent, when ring A is *meta*-substituted. Substitution on ring B should have little influence on the relative stabilities of T_1 and T_2. This is in accord with our observations.

The small change in the degree of asymmetric induction on going from methyl to ethyl substituents (Ib vs. Ic) is to be expected on the basis of the conformation of these groups. For $R^2 = C_6H_5$, Dreiding models show that even this group can adopt a conformation which is not sterically demanding.

The preferred absolute configuration of the asymmetric carbon formed is under investigation, as it is important to know whether the model also allows the correct prediction of the nature of the asymmetric induction: that is, is the absolute configuration of the newly created asymmetric carbon *R* if that of the starting chromium tricarbonyl complex of the substituted aniline is *1S* [11]?

Experimental

Grignard reactions were conducted under argon, with THF as solvent, and worked up as usual when the initial red colour turned completely to pale yellow. The organic layer was then evaporated to dryness (under argon) and the yellow crystals immediately studied by 250 MHz ^1H NMR (Table 2) to avoid any change of the ratio of diastereomers.

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