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Preliminary communication

DOUBLE ASYMMETRIC INDUCTION IN BENCHROTRENE DERIVATIVES

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Summary

Attachment of a $Cr(CO)_3$ moiety to one of the aromatic rings in rigid diaryl ketones of very low prochirality followed by addition of a chiral and optically pure reagent leads to satisfactory asymmetric induction ~40%. Asymmetric induction is smaller in the case of acyclic systems.

Attachment of a $Cr(CO)_3$ group to one of the two aromatic rings in type I or II diaryl ketones should be a way to differentiate between the rings clearly and temporarily, allowing not only measurable asymmetric induction from classical asymmetric synthesis but also the possibility of choosing the enantiomer to be synthesised, according to which ring is complexed. However, the presence of a $Cr(CO)_3$ group on one ring introduces a molecular dissymmetry, and thus there is a double induction system, and four transition states have to be considered during addition of a chiral (and optically pure) reagent R* (say III) on a chiral, but racemic, substrate: K^+, K^- (say tricarbonylchromium complexes of ketones I or II). The chiral carbon created C_1 is R or S.

Figure 1 represents the general situation. But, because of the strong effect of $Cr(CO)_3$ on the stereoselectivity of addition on the carbon α to the complexed ring [2, 3] the actual situation is represented by Fig. 2, and transition states 3 and 4 play little or no part. The asymmetric induction is determined by $\Delta G^{\neq}_1$.

Racemic complexes $CA\underline{1}_H = CB\underline{1}_H$ (X = H), $CB\underline{1}_{CH_3}$ (X = *para*-methyl) and $C\underline{2}$ have been submitted to condensation with the optically pure chiral compound III [1] to give the complexes of the β-hydroxy esters IV (X = H and X = *para*-methyl) and V as diastereoisomer mixtures.

Only two diastereoisomers (resulting from *trans* addition with respect to $CrCO_3$) can be detected in the ^{13}C and proton NMR spectra. This is consistent with Fig. 2 and previous results. The percentage ratios of diastereoisomer mixtures IV (X = H), V and VII have been determined, with a ± 2% error, from the ^{13}C NMR

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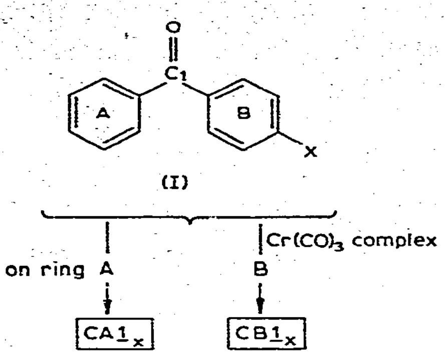

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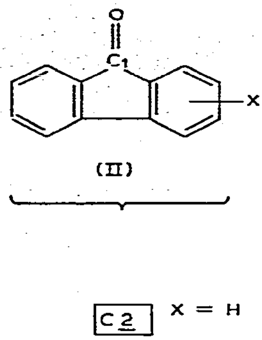

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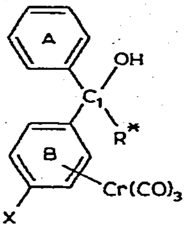

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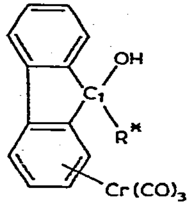

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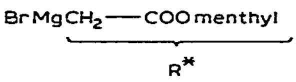

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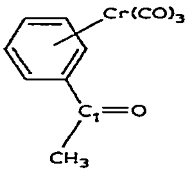

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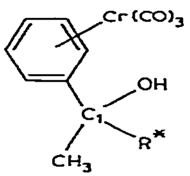

(VII)

spectra. Compounds IV ($X = CH_3$) have been converted, after removal of the $Cr(CO)_3$ to the methyl ester (the yield of each step has been close to 100%) and the enantiomeric purity has been determined by proton NMR in presence of chiral shift reagent: $Eu(TFC)_3$. Although $\Delta G_1^{\neq}$ values (Table 1) are not very accurate the general trend is significant. It appears that symmetric induction is reasonably high for the rigid fluorenone complex (~40%, e.e., $\Delta G_1^{\neq}$ ~0.5 kcal/mol) but quite low for non-rigid diaryl ketone complexes (~10% e.e., $\Delta G_1^{\neq}$ ~ 0.14 kcal/mol).

It is now well accepted that transition states in acyclic systems can accommodate the less energetic conformations [4] which may (and usually do) lead to asymmetric induction smaller than in more restricted systems. An entropy term (internal rotation contribution related to the uncomplexed ring) could be responsible for the difference between the behaviour of complexed acyclic diaryl ketone I and complexed fluorenone: this feature is being studied by temperature

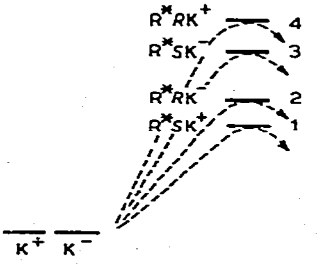

Fig. 1. General case: R* and K^+, K^- play a role (four transition states, assignment is arbitrary).

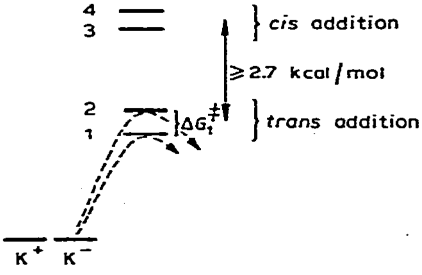

Fig. 2.

TABLE 1

Substrates	Chemical yield (%) [a]	Diastereoisomers			Asymmetric induction (%)	$\Delta G_1^{\neq}$ (kcal/mol)	$\Delta \mid \Delta G_1^{\neq} \mid$ [b] (kcal/mol)
		number	^{13}C	^{1}H			
II (C2)	~50	2	70/30 ± 2		40 ± 4	0.50 ± 0.05	0.50
I:($CA1_H = CB1_H$)	~90	2	55/45 ± 2		10 ± 4	0.14 ± 0.05	.0.14
I ($CB1_{CH_3}$)	~90	2		55/45 ± 2	10 ± 4	0.14 ± 0.05	≤0.14
II	~25 [e]	2	85/15 ± 2		70 ± 4	1.04 ± 0.1	0.24 ± 0.19 [c]

[a] With respect to starting complexes. [b] $\Delta \mid \Delta G_1^{\neq} \mid = \Delta G_1^{\neq}$ (complexed ketone) – $\Delta G_1^{\neq}$ (uncomplexed ketone). [c] $\Delta G_1^{\neq}$ uncomplexed ketone = 0.80 ± 0.09 kcal/mole [1]. [d] Chemical yield is lower because of enolisation of the ketone.

variation. Moreover, the same condensation with complex VI leads to a ~10% increase in the extent of asymmetric synthesis ($\Delta \mid \Delta G_1^{\neq} \mid \sim 0.24$ kcal/mol) compared to that obtained with the uncomplexed ketone (Fig. 3), which is consistent with the previous results.

Larger asymmetric induction could be expected on (i) lowering the reaction temperature; (ii) using a chiral (optically pure) entering group bearing larger chiral information. But the present method is already satisfactory for the synthesis of partially resolved type V alcohols (as well as the decomplexed alcohols if one ring is substituted).

The preparation of partially resolved chiral alcohols IV and V whose chirality arises from isotopic substitution (deuterium or carbon-13) will probably be the most interesting application of this method which, of course, can be extended to other substrates and other types of asymmetric synthesis.

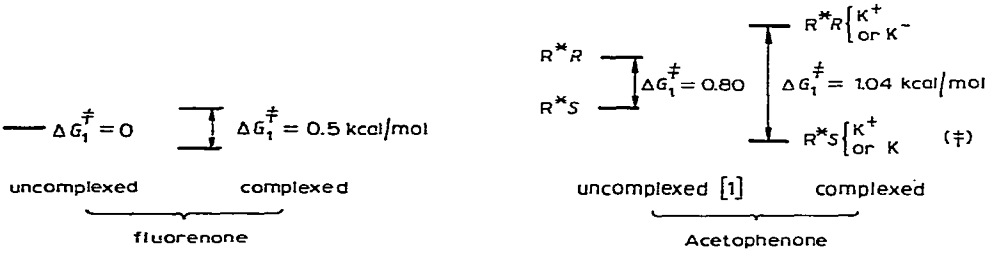

Fig. 3.

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[‡] Absolute configuration at C(1) is *S* in this preferential diastereoisomer, as determined by the sign of the rotatory power of the hydroxy acid [1].