

## Chiral Metal Complexes.

8\*. Chiroptical and  $^1\text{H}$  NMR Studies on Diastereoisomeric Ternary Complexes of Co(III) with 1,10-Phenanthroline and *R,R*-Tartaric Acid or *S*-Malic Acid

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The complexes  $\Delta, \Lambda$ -[Co(1,10-phenanthroline)<sub>2</sub>-(oxyacidate)]·ClO<sub>4</sub>·3½H<sub>2</sub>O, where oxyacidate is *S*-(-)-malate(2-) and *R,R*-(+)-tartrate(2-) have been synthesised, the diastereoisomers separated, and characterized. High resolution  $^1\text{H}$  NMR spectroscopy indicates that intramolecular hydrogen bonding may be responsible for the stabilities of the various diastereoisomers both in aqueous solution and in the solid state. The ratios of diastereoisomers obtained do not reflect thermodynamic equilibrium, and solubility phenomena may give rise to the patterns of isomeric distribution found here, and by other workers.

## Introduction

During the course of our studies on chiral discriminations in complexes of the type  $\Delta, \Lambda$ -[M-(diimine)<sub>2</sub>L]<sup>n+</sup>, where M is a transition metal, diimine is phen, bipy<sup>†</sup> or their congeners and L is an optically active bidentate [1], we have had occasion to re-examine the species  $\Delta, \Lambda$ -[Co(phen)<sub>2</sub>(tartH<sub>2</sub>)]ClO<sub>4</sub>·xH<sub>2</sub>O and  $\Delta, \Lambda$ -[Co(phen)<sub>2</sub>(malH)]ClO<sub>4</sub>·yH<sub>2</sub>O. It was reported originally [2], that  $\Delta, \Lambda$ -[Co(phen)<sub>2</sub>-CO<sub>3</sub>]<sup>+</sup> reacted with *R,R*-(+)-tartH<sub>4</sub> in aqueous solution to yield  $\Lambda$ -[Co(phen)<sub>2</sub>(*R,R*-(+)-tartH<sub>2</sub>)]<sup>+</sup> stereospecifically and that the analogous reaction with *R*-(+)-malH<sub>3</sub> yielded, also stereospecifically,  $\Lambda$ -[Co(phen)<sub>2</sub>(*R*-(+)-malH)]<sup>+</sup>. Subsequently it was shown [3, 4] that in fact both  $\Delta$ - and  $\Lambda$ -diastereoisomers were present in the supposedly optically

pure products. While little chiral discrimination was apparent between the diastereoisomers containing optically active malic acid, the  $\Lambda$ -diastereoisomer of *R,R*-(+)-tartrate was obtained in a higher proportion to the  $\Delta$ -isomer. This was, for us, a surprising result in that steric interactions observed in related Ru(II) complexes containing optically active  $\alpha$ -amino acids suggested that the  $\Delta$ -diastereoisomer should probably be preferred if equilibrium were able to be established [5]. In addition, isomeric distributions are observed to be kinetically controlled [1] in related reactions to form  $\Delta, \Lambda$ -[Co(phen)<sub>2</sub>(aa)]<sup>n+</sup>, where aa is an optically active  $\alpha$ -amino acid. Because of these findings, and the observation [2] that the tartrate and malate complexes are photosensitive both in solution and in the solid state, we were prompted to reinvestigate these oxyacid species. We present the results of our studies below.

## Experimental

$\Delta, \Lambda$ -[Co(phen)<sub>2</sub>(*R,R*-(+)-tartH<sub>2</sub>)]ClO<sub>4</sub>·3½H<sub>2</sub>O was synthesised by the method of Haines and Bailey [2]. [Yield: 34%. *Anal.* Found: C, 46.0; H, 4.0; N, 7.6; H<sub>2</sub>O, 9.0%. Calc. for C<sub>28</sub>H<sub>27</sub>N<sub>4</sub>O<sub>13.5</sub>ClCo: C, 46.1; H, 3.7; N, 7.7; H<sub>2</sub>O, 8.6%].

$\Delta, \Lambda$ -[Co(phen)<sub>2</sub>(*S*-(-)-malH)]ClO<sub>4</sub>·3½H<sub>2</sub>O was also synthesised using the published procedure [2]. [Yield: 20%. *Anal.* Found: C, 46.8; H, 3.6; N, 8.0; H<sub>2</sub>O, 8.4%. Calc. for C<sub>28</sub>H<sub>27</sub>N<sub>4</sub>O<sub>12.5</sub>ClCo: C, 47.1; H, 3.8; N, 7.8; H<sub>2</sub>O, 8.8%]. Our mixtures of diastereoisomers both contain an extra hemihydrate of crystallization compared to that reported [2]. The water contents of the salts were established by thermogravimetric methods using a Stanton Redcroft TG750 thermogravimetric balance. Elemental

\*Part 7 is reference [16].

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†Phen = 1,10-phenanthroline, bipy = 2,2'-bipyridyl, tartH<sub>4</sub> = tartaric acid, malH<sub>3</sub> = malic acid.

TABLE I. Electronic and C.D. Spectral Data<sup>a</sup> for the Complexes.

Complex	$\lambda_{\max}/\text{nm}$	$\log \epsilon_{\max}$	$\lambda_{\text{CD}}/\text{nm}$	$\Delta\epsilon_{\max}$	Ref.
$\Delta$ -[Co(phen) <sub>2</sub> ( <i>R,R</i> -(+)-tartH <sub>2</sub> )] <sup>+</sup> (aq)	520	3.12	530	-21.9	[3]
	515	3.27	543	-26.5(25)	this work
	272	5.67			[3]
	270	5.71			this work
			278 <sup>b</sup>	-478	[3]
			266	+382	[3]
			281 <sup>b</sup>	-1126(50)	this work
		267	+890(60)	this work	
$\Lambda$ -[Co(phen) <sub>2</sub> ( <i>R,R</i> -(+)-tartH <sub>2</sub> )] <sup>+</sup> (aq)	524	3.10	525	+50.5	[3]
	515	3.15	527	+66.8(23)	this work
	272	5.74			[3]
	270	5.73			this work
			278 <sup>b</sup>	+458	[3]
			265	-432	[3]
			279 <sup>b</sup>	+1000(14)	this work
		268	-942(14)	this work	
$\Delta$ -[Co(phen) <sub>2</sub> ( <i>S</i> -(-)-malH)] <sup>+</sup> (aq)	518	3.10	530	-68.8	[4]
	520	3.00	527	-54.7(61)	this work
			400	+28.0	[4]
			400	+23.1(30)	this work
	272	5.72			[4]
	270	5.70			this work
			280 <sup>b</sup>	-915.1	[4]
			267	+893.6	[4]
		282 <sup>b</sup>	-842(22)	this work	
		267	+894(25)	this work	
$\Lambda$ -[Co(phen) <sub>2</sub> ( <i>S</i> -(-)-malH)] <sup>+</sup> (aq)	517	3.12	540	+34.0	[4]
	512	3.03	539	+26.9(56)	this work
			400	+15.8	[4]
			400	+11.8(20)	this work
	272	5.72			[4]
	270	5.68			this work
			280 <sup>b</sup>	+1154	[4]
			267	-929.5	[4]
		281 <sup>b</sup>	+1037(45)	this work	
		267	-788(30)	this work	
$\Delta,\Lambda$ -[Co(phen) <sub>2</sub> ( <i>R,R</i> -(+)-tartH <sub>2</sub> )]ClO <sub>4</sub> ·3H <sub>2</sub> O <sup>c</sup>			521	+31.3	[2]
			515	+27.6(5)	this work
$\Delta,\Lambda$ -[Co(phen) <sub>2</sub> ( <i>S</i> -(-)-malH)]ClO <sub>4</sub> ·2H <sub>2</sub> O <sup>c</sup>			515	-20.7	[2]
			522	-18.9(5)	this work

<sup>a</sup>Units for  $\epsilon$  and  $\Delta\epsilon$  are  $\text{dm}^2 \text{mol}^{-1}$ . Errors calculated from multiple measurements. Electronic and C.D. spectra of other workers refer to solutions of the isolated monoperchlorate salts dissolved in H<sub>2</sub>O. All spectra in this work were recorded in 0.02 mol  $\text{dm}^{-3}$  aqueous NaCl. <sup>b</sup>Low energy  $\pi \rightarrow \pi^*$  transition. <sup>c</sup>Salts isolated in this study both contained 3.5 mol H<sub>2</sub>O of crystallization.

analyses were carried out by Mrs. A. Dams in the Department of Chemistry, Cardiff.

Electronic and circular dichroism (CD) spectra were recorded using a Pye-Unicam SP8-400 spectrophotometer and a Jobin-Yvon CNRS Dichrographe III, respectively. 360 MHz <sup>1</sup>H NMR spectra were

recorded on a Bruker WM 360 spectrometer and 200 MHz spectra on a Varian XL-200 instrument at 25 °C. Separations of the diastereoisomers were accomplished using a CM Sephadex<sup>®</sup> C-25 cation exchange column (30 × 1 cm) which had previously been prepared in the Na<sup>+</sup> cycle. Elution was carried

out with 0.02 mol dm<sup>-3</sup> aqueous NaCl. Fractions were collected from the column using an LKB 2070 Ultrarac® II fraction collector. The electronic and CD spectra of all fractions were recorded and cobalt concentrations therein determined by atomic absorption spectroscopy using a Varian AA-275 instrument. During all stages of separation and characterization of the spectral properties of the complexes, light was excluded, except that necessary for the recording of the spectral details. As was observed by Haines and Bailey [2] the complexes are sufficiently stable to permit these quantitative spectral measurements.

## Results and Discussion

Spectral results for the complexes are listed in Table I together with previously reported values. Our results for the electronic spectra of all diastereoisomers and the chiroptical parameters for  $\Delta$ - and  $\Lambda$ -[Co(phen)<sub>2</sub>(S-(−)-malH)]<sup>+</sup> are in good agreement with those reported by Tatehata [3, 4]. While the CD spectra of the *R,R*-(+)-tartaric acid complex isomers are generally of the same form as those reported earlier [3], we find somewhat higher values for  $\Delta\epsilon$ . However, our results are in accord with magnitudes predicted from exciton theory [6, 7] and indeed with those found previously for the S-(−)-malic acid compounds and for related Ru(II) complexes [8], as well as for analogous [Co(phen)<sub>2</sub>(aa)]<sup>n+</sup> species [1, 9].

Assignments of absolute configurations were made as has been done previously, on the bases both of the signs of the low-energy long-axis-polarized  $\pi \rightarrow \pi^*$  transitions in the UV region of the CD [6, 7] and on the signs of the lowest energy A  $\rightarrow$  E transitions in the visible CD spectra [10, 11].

The mixture of  $\Delta, \Lambda$ -[Co(phen)<sub>2</sub>(*R,R*-(+)-tartH<sub>2</sub>)]·ClO<sub>4</sub>·3½H<sub>2</sub>O diastereoisomers isolated using exactly the same experimental conditions as reported by Haines and Bailey [2] gives a maximum  $\Delta\epsilon$  of +27.6 dm<sup>2</sup> mol<sup>-1</sup> in the visible region of the CD spectrum. Using our observed values of  $\Delta\epsilon$  for the optically pure diastereoisomers, their ratio in the solid state in the isolated product,  $[\Delta\text{-}R,R]/[\Lambda\text{-}R,R]$ , is shown to be  $0.84 \pm 0.08$ . Taking the corresponding results of Haines and Bailey [2] we calculate this ratio in their product to be equal to  $0.68 \pm 0.06$ . Using an analogous synthetic method and by isolating the individual diastereoisomers, Tatehata found the corresponding ratio to be 0.75, but on the basis of his CD spectral data calculated this ratio to be only 0.38 for Haines and Bailey's solid. Tatehata suggested that this apparent difference in stereoselectivity might be due to differences in starting materials or reaction temperatures. However, detailed <sup>1</sup>H NMR studies on the product (see below) reveal that our results are

TABLE II. <sup>1</sup>H NMR Spectral Data for the Complexes.<sup>a</sup>

	$\Lambda$ -[Co(phen) <sub>2</sub> ( <i>R,R</i> -(+)-tartH <sub>2</sub> )] <sup>+</sup>	$\Delta$ -[Co(phen) <sub>2</sub> ( <i>R,R</i> -(+)-tartH <sub>2</sub> )] <sup>+</sup>	$\Lambda$ -[Co(phen) <sub>2</sub> (S-(−)-malH)] <sup>+</sup>	$\Delta$ -[Co(phen) <sub>2</sub> (S-(−)-malH)] <sup>+</sup>
$\delta_A$	3.99	4.26	2.21	2.53
$\delta_B$	3.79	3.86	1.47	2.53
$\delta_X$			4.22	3.75
J <sub>AB</sub>	1.82	1.53	14.79	6.28 <sup>b</sup>
J <sub>AX</sub>			4.04	
J <sub>BX</sub>			8.75	

<sup>a</sup>All spectra were recorded in d<sub>6</sub>-DMSO, at 298.2 K. Chemical shifts relative to TMS  $\pm$  0.005 ppm, coupling constants  $\pm$  0.05 Hz. Tartrate complexes recorded at 200 MHz, malate complexes recorded at 300 MHz. <sup>b</sup> $\frac{1}{2}[J_{AX} + J_{BX}]$ .

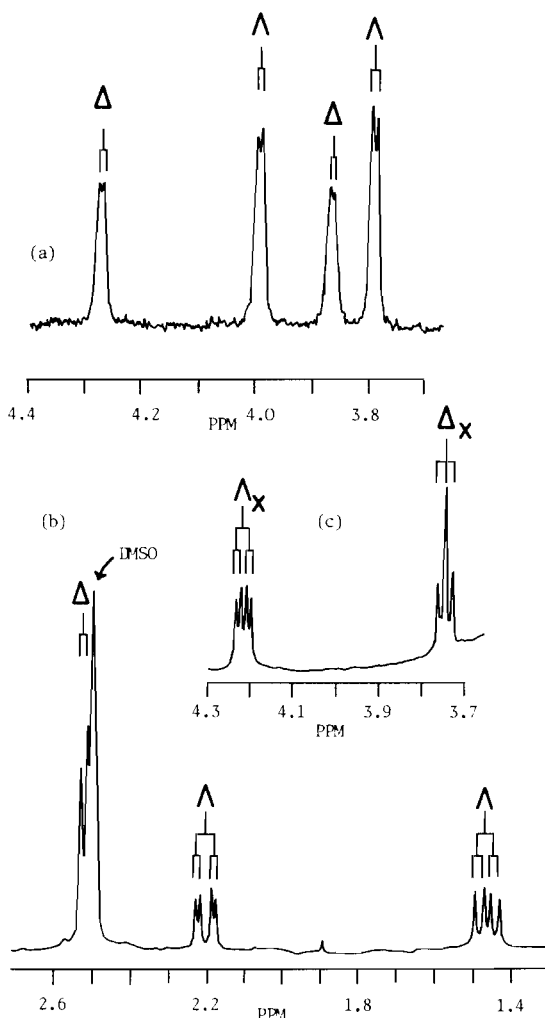


Fig. 1.  $^1\text{H}$  NMR spectra of a: the mixture of  $R,R$ -(+)-tartrate diastereoisomers in the aliphatic region recorded in  $d_6$ -DMSO at 200 MHz and b, c: the same region for the  $S$ -(-)-malate complexes recorded in  $d_6$ -DMSO at 360 MHz.

entirely self-consistent and that, therefore, our values of  $\Delta\epsilon$  for the complexes are close to absolute.

The aliphatic region of the 200 MHz  $^1\text{H}$  NMR spectrum of our isolated solid  $\Delta,\Lambda$ -[Co(phen) $_2$ ( $R,R$ -(+)-tartH $_2$ )]ClO $_4$ ·3½H $_2$ O dissolved in  $d_6$ -DMSO is shown in Fig. 1. Details are given in Table II. Spin decoupling experiments show that the doublet resonances at 4.26 and 3.86 ppm are due to one isomer and those at 3.97 and 3.79 ppm to the other. It has previously been concluded that both tartrate and malate coordinate to Co(III) in these complexes in a manner analogous to that of  $\alpha$ -amino acids [3, 4]. Integration of the above doublets, the former lower-field pair arising from the  $\Delta$ -diastereoisomer [8, 12], affords an independent check on the  $[\Delta,R,R]/[\Lambda,R,R]$  ratio. This is found to be  $0.76 \pm 0.05$  and

is in good agreement with that calculated on the basis of the chiroptical measurements.

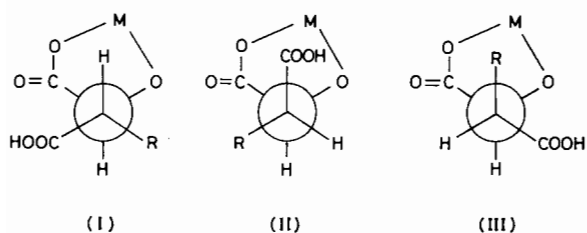
Using a higher frequency spectrometer it also has been possible to record the aliphatic region of the spectrum of  $\Delta,\Lambda$ -[Co(phen) $_2$ ( $S$ -(-)-malH)] $^+$  which also is shown in Fig. 1. Again spectral details are given in Table II. The spectrum shown is that of the isolated mixture of  $\Delta$ - and  $\Lambda$ -diastereoisomeric salts. It was found previously in analogous Ru(II) complexes containing  $S$ -aspartic acid that the coordinated amino acid gives rise in both isomers to an ABX splitting pattern [8]. In the above Co(III) species however, the  $\Delta$ -isomer displays a 'deceptively simple' ABX pattern, the AB portion of which has its resonances very close to those of the  $d_5$ -DMSO solvent impurity. The  $\Lambda$ -isomer shows an AMX splitting pattern. Integration of the appropriate signals yields for the isolated solid a value of  $1.16 \pm 0.05$  for the  $[\Delta,S]/[\Lambda,S]$  ratio of diastereoisomers. Using our chiroptical data this ratio is calculated to be  $1.2 \pm 0.1$  and the results are consistent with those reported by Tatehata [4]. Applying our  $\Delta\epsilon$  values for the optically pure isomers to the product reported by Haines and Bailey [2] we find that this same ratio in their complex would be equal to  $1.3 \pm 0.1$ .

We wish to emphasise that the above ratios do not necessarily reflect equilibrium conditions, and in turn they could not be used to determine chiral discrimination energies for the pairs of diastereoisomers. It has been pointed out [1] that any distribution of isomers obtained from the reaction of  $\Delta,\Lambda$ -[Co(phen) $_2$ CO $_3$ ] $^+$  with  $S$ -aspartic or  $S$ -glutamic acid is kinetically determined and that in aqueous solution, the isomers  $\Delta$ - and  $\Lambda$ -[Co(phen) $_2$ ( $aa$ )] $^{n+}$  are thermodynamically unstable with respect to [Co(phen) $_3$ ] $^{3+}$  and [Co( $aa$ ) $_3$ ] $^{n+}$ . In addition Haines and Bailey mentioned [2] that the *bis*-phen tartrate and malate complexes are photosensitive both in solution and in the solid state, a fact that we have confirmed. If any of the diastereoisomers is dissolved in buffers of pH ranging from 4 to 9 and the solutions are kept in the dark, no decomposition is observed (by measurement of CD spectra) during 72 hours. At pH values higher than 11 these complexes do decompose in the dark, but at a considerably faster rate if light is admitted to their solutions. Thus the pattern of isomer distributions found here and by other workers may reflect not only variations in synthetic conditions employed, but a different degree of photochemical decomposition may occur during reaction and work-up if the photosensitivity of each isomer is different.

A detailed analysis of the  $^1\text{H}$  NMR spectra of the tartrate and malate complexes (Table II) indicates that intramolecular hydrogen bonding is significant and this may explain some of the chemical behaviour of the various species. It is also possible that Co(II) intermediates are involved in the ligand dispropor-

tionations since exposure of solutions used to record the PMR spectra of the tartrato-complexes to light causes the loss of all signals except those derived from HDO and solvent impurities. This phenomenon is accompanied by a change of solution colour from pink-orange to yellow.

An analysis of rotamer distributions of the coordinated hydroxyacid in some of the complexes was carried out using the data given in Table II. The coupling constants  $J_{gauche} = 2.9$  Hz and  $J_{trans} = 14.6$  Hz were used in these calculations for *S*-(-)-malic acid [13], and the assumption was made that these quantities show no appreciable change upon coordination. The three possible staggered conformers are shown in (I)–(III). Here, R is H for *S*-(-)-malic acid or would be OH for *S,S*-(-)-tartaric acid. Mole fractions of rotamers were calculated using published



methods [14]. For the  $\Delta$ -*S*-malate complex the calculated rotamer populations are  $M_I = 0.097$ ,  $M_{II} = 0.403$  and  $M_{III} = 0.499$ , respectively. Both rotamers (II) and (III) have an arrangement ideal for the formation of an intramolecular hydrogen bond between the uncoordinated carboxyl group and the coordinated  $\alpha$ -hydroxyl oxygen atom. This is illustrated in Figs. 2(a) and 2(b). It seems probable that these bonds would stabilize the conformers and thus account for their relatively high abundance. It has been proposed that the existence of analogous intramolecular hydrogen bonds between the free carboxylate groups and the coordinated amine groups in  $\Delta$ , $\Lambda$ -[Ru(diimine)<sub>2</sub>-(*S*-aspartate)]<sub>(aq)</sub><sup>o</sup> complexes [8] affects the relative thermodynamic stabilities of their diastereoisomers. Rotamer (I), shown in Fig. 2(c), in which the two carboxylate groups are *cis*- to each other and the side chain is extended, is the least favoured conformation of the *S*-(-)-malate ligand in the  $\Lambda$ -isomer.

A detailed analysis of rotamer distributions for the  $\Delta$ -[Co(phen)<sub>2</sub>(*S*-(-)-malH)]<sup>+</sup> diastereoisomer was not possible because of the nature of the NMR results obtained. However, molecular models suggest that rotamers (II) and (III) may be formed although there are some non-bonded interactions between the oxyacid side chain and the H(2) proton of a phenanthroline ligand. Such steric interactions have been shown to be important in related complexes of Ru(II) [5].

Both diastereoisomers of the *R,R*-tartaric acid complex (Table II) have  $J_{AB}$  coupling constants close

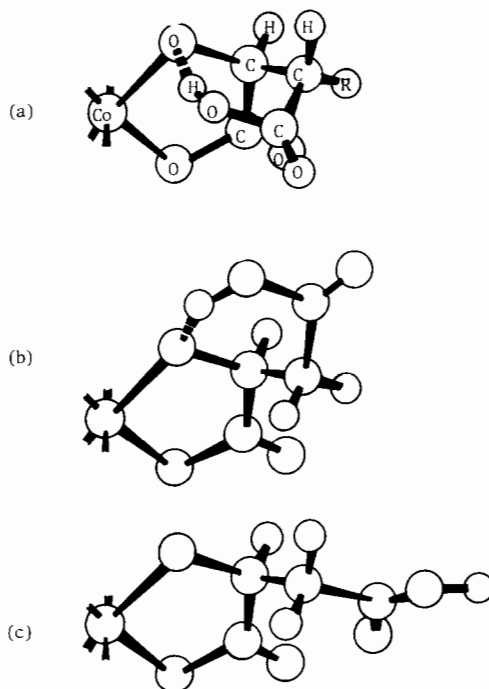


Fig. 2. A representation of the three staggered conformers of coordinated *S*-malic (R = H) or *S,S*-tartaric (R = OH) acids.

to those predicted for an essentially *gauche* arrangement of the C–H atoms on adjacent carbons [15]. For the two isomers, this result precludes any significant population of rotamer (I), after allowing of course for the mirror relationship between the tartrate enantiomers. Thus, in aqueous solution, the results parallel those found for the distribution of rotamers in the *S*-(-)-malH<sub>3</sub> isomers. The two possible conformers corresponding to the mirror images of the structures shown in Figs. 2(a) and (b) are those which may participate in intramolecular hydrogen bonding.

These results may explain the instability of the various isomers at high pH in the absence of light. If the intramolecular hydrogen bonds serve to stabilize the complexes towards decomposition, then removal of the protons involved (at pH > 11) will disrupt the structures. In addition, non-bonded contacts present in the  $\Delta$ -*S* forms of the diastereoisomers may tend to destabilize the H-bonded structure(s). Thus in the solid state, other hydrogen bonds to the perchlorate anion may be present, as is the case in the solid state structure of  $\Delta$ , $\Lambda$ -[Ru(bipy)<sub>2</sub>(*S*-alanine)]·ClO<sub>4</sub>·½H<sub>2</sub>O [16]. Such an arrangement might result in a slight preference for the  $\Delta$ -*S* diastereoisomers in the *solid state* simply as a result of solubility differences. In this connection it is worth noting that when the products were isolated, both in this work and previously [2], the solids were washed copiously at filtration. Any slight difference in solubility, which would of course be reflected in the pattern of

distribution of isomers obtained, could easily be accounted for by variations imposed by hydrogen bonding requirements.

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