

Preliminary communication

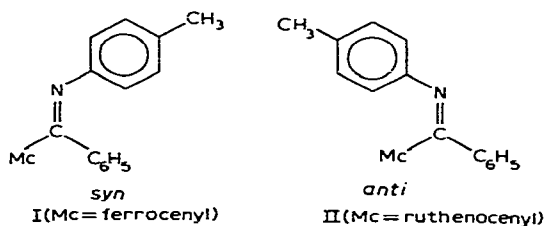
The *syn-anti* isomerization of imines of benzoylferrocene and benzoylruthenocene

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A recent paper by Yamakawa and Hisatome¹ reporting on the separation of the *syn* and *anti* isomers of four acylferrocene oximes prompts our communication of a study of the *syn-anti* isomerization of the *p*-tolyl imines of benzoylferrocene and benzoylruthenocene I and II (in this communication, the *syn* isomer is the one with both aryl groups *syn*).

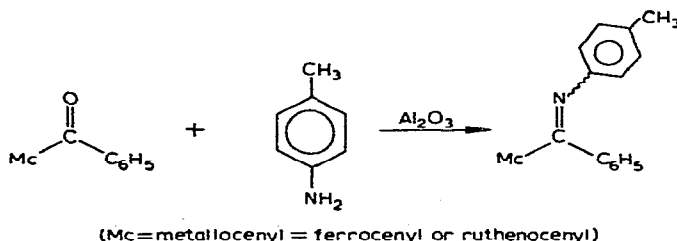


Yamakawa and Hisatome's study was aimed at the separation and spectroscopic characterization of the *syn* and *anti* oximes. The impetus for our study derived from two sources: (1) Schlögl & Mechter's²⁻³ report of the resolution of diferrocenylcarbodiimide, and (2) the possibility of maximizing the importance of the dipolar rotational

mechanism (going through a transition state like: $\begin{matrix} \oplus & \ominus \\ \text{C} & \text{---} & \text{N} \\ \diagup & & \diagdown \end{matrix}$) for *syn-anti* isomerization⁴. The first source suggests a large effect of a ferrocenyl group adjacent to nitrogen on the configurational stability of nitrogen. The second takes cognizance of the remarkable stabilizing effect of a metallocene group on a neighboring carbonium center^{5,6}.

Imines I and II have been prepared by a method developed by Hetnarski and Grabowski⁷:

★Other experimental studies to assess the effect of the ferrocenyl moiety on the configurational stability of nitrogen are in progress. Based on these studies, we feel that Schlögl and Mechter's original observation may be incorrect³.



The yields of I and II, 52% and 59.5% (m.p. 138–139° and 100–100.5°) (after purification), respectively, were considerably higher than those obtained when alumina was replaced by phosphorus pentachloride⁸. Spectral and analytical data confirm the structures I and II.

Examination of the temperature dependent NMR spectra of I and II provide evidence for the *syn-anti* isomerization process. The room temperature spectra are given in Table 1. As the spectrum temperature is raised the signals assigned to methyl groups coalesce into a singlet. The coalescence temperatures are given in Table 2, along with some comparative data from reference 6. These data are entirely consistent with observations by other workers^{4,8}. The interpretation to such observations suggests that *syn-anti* isomerization is occurring.

TABLE 1

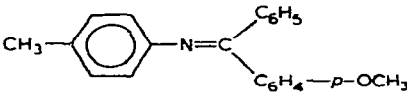
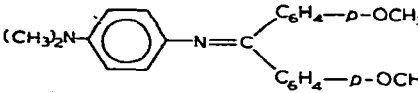
ROOM TEMPERATURE NMR OF COMPOUNDS I AND II

	δ (CH ₃) ^{a,c}	δ (C ₆ H ₄)	δ (C ₆ H ₅)	δ (unsubstituted Mc) ^a	δ (substituted Mc) ^b
I	2.10(s)/2.30(s)	6.65(q)	7.15(s)	4.17(s)/4.05(s)	4.32(t)/4.47(t)
II	2.16(s)/2.30(s)	6.67(q)	7.15(s)	4.62(s)/4.53(s)	4.70(t)/4.93(t)

^a These signals are of unequal intensity; see Table 3. ^b Both I and II have small signals upfield of the unsubstituted Mc signals. These are weak, though undoubtedly the signals of the substituted Mc of the minor isomer. ^c s = singlet, t = triplet, q = quadruplet.

TABLE 2

COALESCENCE TEMPERATURES FOR SELECTED IMINES

Compound	Coalescence temperature ^{a,b}
I	53° for CH ₃
II	62° for CH ₃
	69° for OCH ₃ 50° for CH ₃
	78.8° for OCH ₃

^a Data for compounds III and IV are from Ref. 8. ^b Data are based on repeated temperature runs. The coalescence phenomenon is reversible and has been observed with all three doubled signals.

TABLE 3

Syn-anti ISOMER DATA

Compound	NMR δ (CH ₃)	Area ratios of CH ₃	NMR δ (unsubstituted Me)	Area ratios of unsubstituted Me	IR peaks in 700 cm ⁻¹ ^a	
					solution	solid
I	2.10/2.30	10/1	4.17/4.05	7/1	693(m), 703(sh)	702(m), 714(s)
II	2.16/2.30	6/1	4.62/4.53	6/1	692(m), 699(sh)	710(s), 701(m)

^a sh = shoulder, s = strong, m = medium

Other data bearing on the question of the *syn-anti* isomers of I and II are listed in Table 3. It is clear that in both I and II, one isomer predominates in solution. Using the infrared criterion of Curtin^{4,8,9}, we tentatively suggest that the predominant isomer is *anti*.

Our data are consistent with an interpretation suggesting that at room temperature compounds I and II exist as mixtures of *syn* and *anti* isomers. As the temperature is raised, sufficient energy is supplied to overcome the energy barrier separating the isomers and they begin to rapidly interconvert. Because the *syn-anti* ratios of I and of II are not equal to one, we cannot calculate a rate constant for the isomerization process. The similarity of coalescence temperatures in Table 2 suggests a similarity in isomerization mechanism. Concomitantly, these data suggest that the dipolar rotational mechanism (*vide supra*) is not of prime importance even in systems like I and II. We, therefore, favor a lateral shift mechanism⁴ for the *syn-anti* isomerizations of I and II.

We are at present carrying out a complete line shape analysis of our data to accurately determine barrier heights. In addition, we are continuing our studies of the effect of neighboring organometallic groups on nitrogen configurational stability.

ACKNOWLEDGEMENTS

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