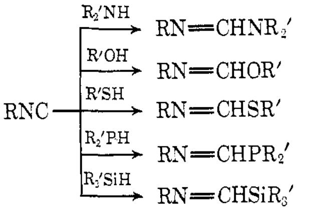
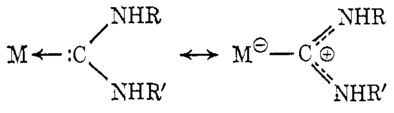
amine,[6] alcohol,[7] thiol,[8] phosphine,[9] and silane[10] in the presence of a catalytic amount of group IB and IIB metal compounds, *e.g.*, Cu, Ag, and Zn.



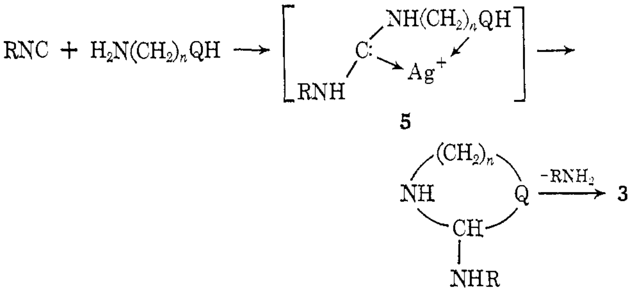
$$RNC \xrightarrow{R_2'NH} RN{=}CHNR_2' \quad (2)$$
$$RNC \xrightarrow{R'OH} RN{=}CHOR' \quad (3)$$
$$RNC \xrightarrow{R'SH} RN{=}CHSR' \quad (4)$$
$$RNC \xrightarrow{R_2'PH} RN{=}CHPR_2' \quad (5)$$
$$RNC \xrightarrow{R_3'SiH} RN{=}CHSiR_3' \quad (6)$$

The insertion of a carbon atom *via* an isonitrile by means of a metal catalyst in these formimidation reactions (eq 2–6) is mechanistically intriguing. Recently, Balch and Miller[11] reported the formation of an iron complex (**4**) having a coordinated carbene ligand in the reaction of the iron isonitrile complex with amine.



4

The heterocycle synthesis in the present study may well be interpreted by assuming a silver complex having a carbene-type ligand (**5**) as a key intermediate. Further studies are in progress to extend the potential of this synthetic method and to investigate the reaction mechanism.



5

(6) T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota, and H. Yoshioka, *Tetrahedron Lett.*, 6121 (1966).

(7) T. Saegusa, Y. Ito, S. Kobayashi, N. Takeda, and K. Hirota, *Tetrahedron Lett.*, 1273 (1967).

(8) T. Saegusa, S. Kobayashi, K. Hirota, Y. Okumura, and Y. Ito, *Bull. Chem. Soc. Jap.*, **41**, 1638 (1968).

(9) T. Saegusa, Y. Ito, and S. Kobayashi, *Tetrahedron Lett.*, 935 (1968).

(10) T. Saegusa, Y. Ito, S. Kobayashi, and K. Hirota, *J. Amer. Chem. Soc.*, **89**, 2240 (1967).

(11) (a) A. Burke, A. L. Balch, and J. H. Enemark, *J. Amer. Chem. Soc.*, **92**, 2555 (1970); (b) A. L. Balch and J. Miller, *ibid.*, **94**, 417 (1972); (c) J. Miller, A. L. Balch, and J. H. Enemark, *ibid.*, **93**, 4613 (1971).

Yoshihiko Ito, Yoshinori Inubushi, Michio Zenbayashi
Shimpei Tomita, Takeo Saegusa*
Department of Synthetic Chemistry, Faculty of Engineering
Kyoto University, Kyoto, Japan

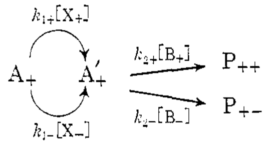
Received November 7, 1972

Nonreciprocal Kinetic Resolution. Kinetic Evidence for a Reactive Intermediate without Measurement of Rates

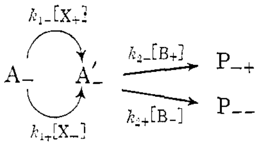
Sir:

We wish to describe a new method for showing the presence of a slowly formed, rapidly consumed intermediate. The reaction of a chiral reagent B_+ with an excess of a racemic substrate, $A_\pm$, may give two diastereomeric products, P_{++} and P_{-+} (from $A_+ + B_+$ and $A_- + B_+$, respectively). In general, kinetic resolution[1] is observed, *i.e.*, the amount of P_{++} formed differs from the amount of P_{-+}, and the unreacted A is enriched in the enantiomer corresponding to the less abundant diastereomer.[2] Most commonly, when the same reaction is performed using excess $B_\pm$ and, say A_+, the per cent stereoselectivity[2] is the same as that from the reaction of $A_\pm$ with B_+; we refer to such reactions as showing "reciprocal kinetic resolution."

Such a reciprocal relationship, however, need not always obtain. To illustrate, we take a process $A + X + B \rightarrow P$ reacting by the sequence $A + X \rightarrow A' + X'$ (k_1) and $A' + B \rightarrow P$ (k_2) in which $k_2 \gg k_1$; this is expanded below for the case in which A, A′, B, and X are chiral.



(1)



(2)

Note particularly that enantiomeric reactions (*e.g.*, A'_+ with B_+ *vs.* A'_- with B_-) have *identical* rate constants.[3]

When A_+ reacts with $B_\pm$ the ratio of the rates of formation of the products is (rate P_{++})/(rate P_{+-}) = $k_{2+}[B_+]/k_{2-}[B_-]$, whereas with $A_\pm + B_+$ (and X_+) the ratio is (rate P_{++})/(rate P_{-+}) = $k_{1+}[A_+]/k_{1-}[A_-]$. The consequences can perhaps be seen most clearly under "pseudo-first-order conditions," when the ratios of the diastereomers upon isolation become $P_{++}/P_{+-} = k_{2+}/k_{2-}$ and $P_{++}/P_{-+} = k_{1+}/k_{1-}$, *i.e.*, *the two reaction modes yield different product ratios* (or stereoselectivities).[4] Such a "nonreciprocal kinetic resolution" requires at least one reaction in which a chiral reactive intermediate reacts quickly *via* diastereomeric pathways.[6] It can readily be seen that nonreciprocal kinetic resolution also occurs in the simpler cases in which X is achiral (including racemic) or the first step, $A \rightarrow A'$, is unimolecular (in which cases $P_{++}/P_{-+} = 1$ for the reaction of $A_\pm$ with B_+).

Practical illustration is provided for the case in which $X \equiv B$ by the reaction of camphor-10-sulfonyl

---

(1) *Cf.* (a) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 65 ff; (b) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, New York, N. Y., 1966, p 122 ff; (c) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1971, p 28 ff.

(2) The extent of the kinetic resolution may be described[1b] by the "per cent stereoselectivity" = $100(P_{++} - P_{-+})/(P_{++} + P_{-+})$.

(3) We denote the sign of these rate constants by the sign of the product of the signs of the reacting enantiomers.

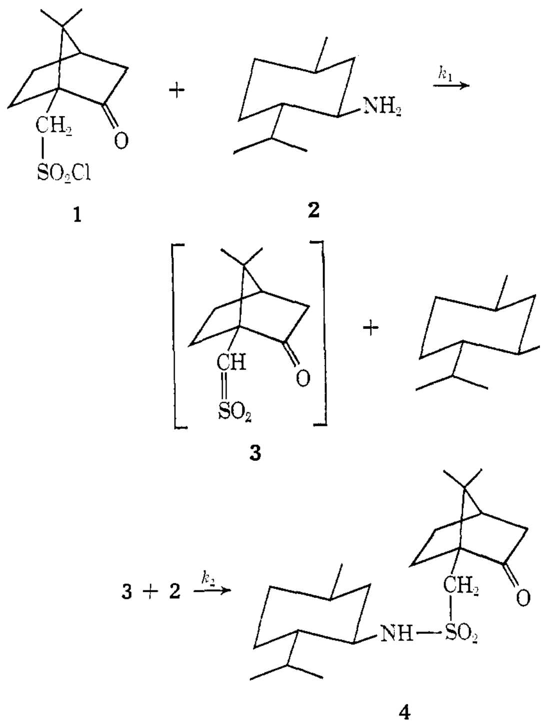
(4) It may be recalled that Horeau's ingenious "partial resolution" method for determining optical purity[5] specifically requires reciprocal kinetic resolution. It therefore cannot be used with reactions showing the nonreciprocal relationship noted here.

(5) A. Horeau, *Bull. Soc. Chim. Fr.*, 2673 (1964).

(6) Note that the mere observation of different product ratios does not in itself establish a nonreciprocal resolution, since they could arise if the reaction, for example, were first order in A and second order in B; this may be readily distinguished experimentally from a true nonreciprocal resolution.

chloride (1) with menthylamine (2).[7,8] With $\mathbf{1}_+$ and $\mathbf{2}_\pm$ in toluene at −10° we observed a stereoselectivity[9] of ~30%, in agreement with previous work,[7,8] whereas with $\mathbf{1}_\pm$ and $\mathbf{2}_-$ the stereoselectivity was negligible (1 ± 1%). These observations are consistent with Scheme I in which $k_2 \gg k_1$, $k_{1+}/k_{1-} = 1.0$, and $k_{2+}/k_{2-} = 0.4$, and

Scheme I



provide evidence of a new kind for the intermediacy of a sulfene in such reactions. The following experiments confirm this conclusion. (a) Reaction of camphor-10-sulfonyl-*10-d*$_2$ chloride with $\mathbf{2}_-$ (or $\mathbf{2}_+$) gave largely the sulfonamide with one C-10 deuterium atom, as expected for a sulfene reaction.[10] (b) The observed second-order rate constants[11] (k_r) for the reaction of $\mathbf{1}_+$ with $\mathbf{2}_+$ and $\mathbf{2}_-$ in toluene at −10° were respectively 2.49×10^{-2} and 2.41×10^{-2} M^{-1} sec^{-1}, $k_{r+}/k_{r-} = 1.03$.[12] This ratio agrees with the ratio $k_{1+}/k_{1-} = 1.0$ derived above, as required by the above mechanism (from which it is evident that $k_r = k_1$). (c) For the reaction of 1,4-diazabicyclo[2.2.2]octane (DABCO) with 1 (using 2-propanol as the sulfene trap), $k_r = 2.26 \times 10^{-1}$ M^{-1} sec^{-1}, and hence in a reaction of $\mathbf{1}_+$ with DABCO and $\mathbf{2}_\pm$ (molar ratio 1:4:2) most of the **3** formed would come from reaction of $\mathbf{1}_+$ with DABCO. We found the stereoselectivity the same with or without DABCO, again, just as expected from Scheme I.

The advantage of nonreciprocal kinetic resolution as a mechanistic tool lies in the fact that no rate determinations are required (unlike, for example, the related "rate-product criterion"[13]), and in certain cases it may therefore be the most convenient or even the only adequate method.

Two useful variations may be noted. (i) The final product(s) need not be chiral; there must, however, be chiral diastereomeric transition states, and the stereoselectivity determinable from unreacted B. (ii) If the product ratio can be determined by an "achiral" measurement (*e.g.*, nmr, as above), the experiment may be done using *racemic* A with racemic and chiral B, respectively, since the ratio $(P_{++} + P_{--})/(P_{+-} + P_{-+})$, obtained from the former reaction, approximates the ratio P_{++}/P_{+-} obtained from reaction of A_+ with excess $B_\pm$.[14]

Acknowledgments. We thank Mr. L. S. K. Li for preliminary experiments and the National Research Council of Canada for financial support.

---

[7] J. Read and R. A. Storey, *J. Chem. Soc.*, 2761 (1930).

[8] K. Okamoto, E. Minami, and H. Shingu, *Bull. Chem. Soc. Jap.*, **41**, 1426 (1968).

[9] As determined by two or more of the following: (i) $[\alpha]_D$ of recovered 2·HCl, (ii) $[\alpha]_D$ of mixed 4, (iii) relative areas of the AB quartets due to the C-10 hydrogens in the nmr of 4, (iv) relative areas of the NH doublets in 4.

[10] *Cf.* J. F. King and T. Durst, *J. Amer. Chem. Soc.*, **87**, 5684 (1965); W. E. Truce and R. W. Campbell, *ibid.*, **88**, 3599 (1966).

[11] As determined by rate of formation of titrable chloride: J. F. King and T. W. S. Lee, *J. Amer. Chem. Soc.*, **91**, 6524 (1969); *Can. J. Chem.*, **49**, 3724 (1971).

[12] Okamoto, *et al.*,[8] tried to estimate k_{r+} by multiplying their measured k_{r-} by a factor derived, in effect, from the percent stereoselectivity. This, however, is clearly inadmissible because, as we show here, the rate- and product-determining steps are different.

[13] L. C. Bateman, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 881 (1938); L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *ibid.*, 979 (1940); see also M. L. Bender, *Tech. Org. Chem.*, **8**, 1480 (1963); R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **9**, 751 (1970).

[14] This has been confirmed experimentally.

J. F. King,* S. K. Sim
Department of Chemistry, University of Western Ontario
London, Ontario N6A 3K7, Canada

Received February 7, 1973

Transformations of Dicarbonyl Cyclopentadienyl(alkyl)iron Complexes. Stereochemistry of Oxidative Carboxylation

Sir:

The mechanism and stereochemistry of reactions occurring at carbon–metal bonds in transition metal complexes have been investigated for a number of such complexes[1,2] and remains a subject of considerable interest and some controversy.[2] It has, however, been shown that triphenylphosphine or carbon monoxide promoted ligand transfer reactions[3] in alkylmetal carbonyl complexes proceed with retention of configuration at the migrating carbon center.[1a–c]

We now wish to report that oxidatively induced ligand transfer reactions[2f,4] in dicarbonyl*pentahapto*-cyclopentadienyl(alkyl)iron complexes (**1**) also proceed stereospecifically with *retention* of configuration.

While alkyl transfer reactions in **1**, promoted by

---

[1] (a) R. F. Heck, *J. Amer. Chem. Soc.*, **85**, 1460 (1963); (b) J. P. Collman, S. R. Winter, and D. R. Clark, *ibid.*, **94**, 1788 (1972); (c) G. M. Whitesides and D. J. Boschetto, *ibid.*, **91**, 4313 (1969); (d) K. Noack and F. Calderazzo, *J. Organometal. Chem.*, **10**, 101 (1967).

[2] (a) G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, **93**, 1529 (1971); (b) R. G. Pearson and W. R. Muir, *ibid.*, **92**, 5519 (1970); (c) F. R. Jensen, V. Madan, and D. H. Buchanan, *ibid.*, **93**, 5283 (1971); (d) R. W. Johnson and R. G. Pearson, *Chem. Commun.*, 986 (1971); (e) D. Dodd and M. D. Johnson, *ibid.*, 571 (1971); (f) S. N. Anderson, D. H. Ballard, J. Z. Chrzastowski, D. Dodd, and M. D. Johnson, *J. Chem. Soc., Chem. Commun.*, 685 (1972).

[3] Reactions of general form ZMR → MZR have been referred to in the literature as Z-insertion reactions, but the weight of evidence suggests that these processes bear little mechanistic resemblance to reactions such as methylene insertion but occur by the transfer of R from the metal to Z (see, for example, ref 1d). We therefore have chosen to refer to these reactions as *ligand transfer processes.* A similar suggestion has been made by F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1968, p 578.

[4] (a) S. N. Anderson, C. W. Fong, and M. D. Johnson, *J. Chem. Soc., Chem. Commun.*, 163 (1973); (b) P. Abley, E. R. Dockal, and J. Halpern, *J. Amer. Chem. Soc.*, **94**, 659 (1972).