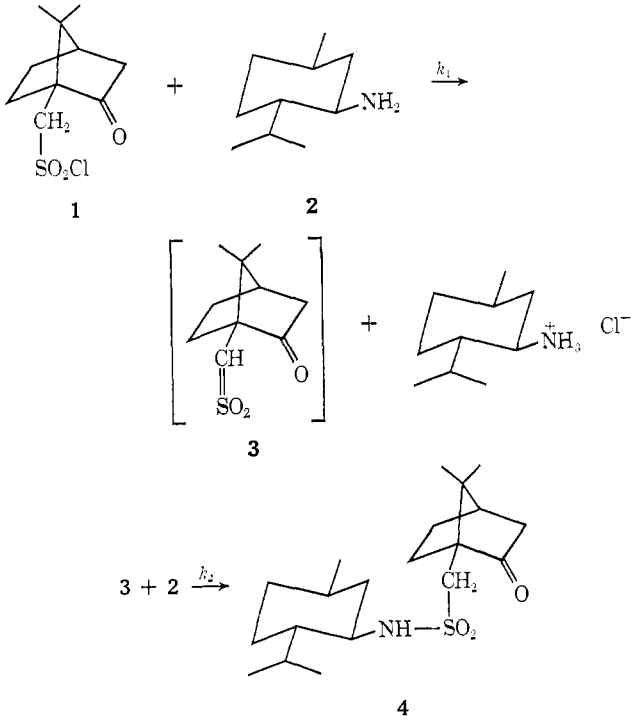
chloride (**1**) with menthylamine (**2**).[7,8] With $\mathbf{1}_+$ and $\mathbf{2}_\pm$ in toluene at $-10°$ we observed a stereoselectivity[9] of ~30%, in agreement with previous work,[7,8] whereas with $\mathbf{1}_\pm$ and $\mathbf{2}_-$ the stereoselectivity was negligible (1 ± 1%). These observations 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.

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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).

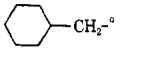
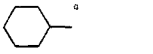
tertiary phosphines or carbon monoxide, are relatively slow, treatment of these complexes with 3 molar equiv of cupric chloride dihydrate in alcohol solution at 0° leads to the rapid precipitation of cuprous chloride[5] and the formation of the one carbon homologated ester. Yields are improved when the reaction is carried out in the presence of carbon monoxide. A similar transformation has recently been reported employing ceric ion.[4a]

$$FpR + CuCl_2 \xrightarrow[CO]{R'OH} RCOOR' + CuCl$$

$$Fp \equiv h^5\text{-}C_5H_5Fe(CO)_2$$

The results of such oxidative carboxylation reactions are summarized in Table I.

Table I

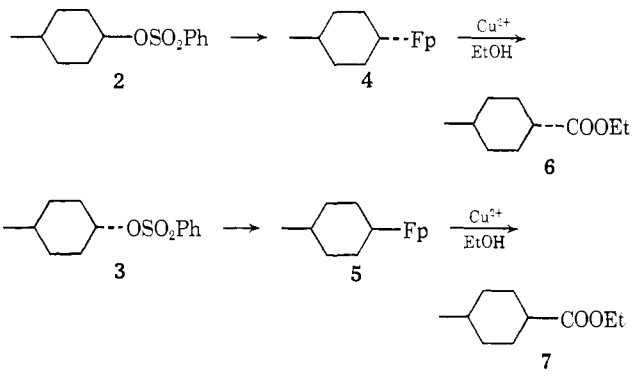
FpR	Alcohol (R'OH)	% yield of ester RCOOR'[c,e]
	EtOH	85
	i-PrOH	60
	t-BuOH[b]	5
$PhCH_2CH_2$-[d]	EtOH	70
	MeOH	64
	EtOH	48

[a] Satisfactory spectral and analytical data were obtained. [b] With THF as cosolvent. [c] Yield of product isolated after chromatography. [d] D. J. Ehntholt, G. F. Emerson, and R. C. Kerber, *J. Amer. Chem. Soc.*, **91**, 7547 (1969). [e] Esters were characterized by their nmr, ir, and mass spectra.

In a typical experiment, the complex (0.20 mmol) in 10 ml of absolute ethanol was cooled to 0° as a rapid stream of carbon monoxide was passed into solution. Cupric chloride dihydrate (0.66 mmol) was then added. After 1 hr at 0°, cuprous chloride was removed by filtration and the solution was worked up by dilution with water, ether extraction, and chromatography on alumina. No attempt has been made to optimize yields, but these evidently decline with the use of secondary and tertiary alcohols and when the reaction is carried out on a complex possessing a secondary alkyl–metal bond.

In order to define the stereochemistry of this transformation, *cis*- and *trans*-4-methylcyclohexyl benzenesulfonate (**2** and **3**)[6] were each converted to the corresponding organometallic complex (**4** and **5**) by treatment with sodium dicarbonylcyclopentadienylferrate. Evidence has previously been provided that metalation of alkyl benzenesulfonates or halides with dicarbonylcyclopentadienylferrate[1c] and with other complex organometallic anions[2c,d] proceeds generally with inversion. The present results add further support for this conclusion. Thus, the trans ester (**3**) gave the cis complex (**5**) as a yellow oil in 26% yield (nmr (CS_2) τ 5.4 (s, 5, Cp), 7.4 (m, 1, FpCH), 7.9–8.7 (m, 9, CH_2, CH), 9.0 (d, 3, J = 7 Hz, Me)) while the cis ester (**2**) gave the trans complex (**4**) in very low yield (nmr (CS_2) τ 5.4 (s, 5, Cp), 7.3–9.1 (m, 10, CH_2, CH), 9.2 (d, 3, J = 5 Hz, Me)). The relative chemical shifts of the methyl protons in **5** and **4** conform to the relative values for the corresponding methyl protons in *cis*- and *trans*-4-*tert*-butylmethylcyclohexane and in the low-temperature nmr spectrum of 1,4-dimethylcyclohexane.[7]

Treatment of **5** with cupric chloride in ethanol gave an ethyl ester in 42% yield. This was shown to be ethyl *cis*-4-methylcyclohexanecarboxylate (**7**) by saponification to *cis*-4-methylcyclohexanecarboxylic acid, mp 28–29.5° (87%) (lit. mp 30–31,[8] 28–29.5[9]). The acid was further characterized by conversion to its *p*-bromophenacyl ester, mp 110–111° (lit.[8] mp 111–112°).



In a similar manner the trans isomer (**4**) was converted to the trans ester (**6**) in 40% yield. Saponification gave *trans*-4-methylcyclohexanecarboxylic acid, mp 103–108° (97%) (lit.[8] mp 110–111°).

Gas chromatographic analysis[10] of the crude product from each of the oxidative carboxylation reactions failed to reveal the presence of epimeric ester. Since under conditions of analysis 1% of the cis ester could be detected in the presence of the trans isomer while approximately 10% of trans ester could be detected in the presence of the cis isomer, the oxidative carboxylation reaction for each of the reactants must be highly stereospecific.

It seems probable that the reaction proceeds through the oxidized organometallic as the first intermediate[4a] and that ligand transfer within such a species is greatly facilitated by the increased electron deficiency at the carbonyl carbon atom due to diminished back-bonding from the metal. The effect of coordinating metal cations in accelerating the rate of ligand transfer reactions in $RFe(CO)_4$ anion[11] may be due to a similar polarization of the carbonyl ligand. Subsequent nucleophilic attack by alcohol on the intermediate cationic metal–acyl complex resulting from the ligand transfer reaction results in the formation of the observed product.

Further extensions and applications of these reactions are being examined.

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(5) Analyzed by titration with potassium bromate. *Anal.* Calcd for CuCl: Cu, 64.2. Found: 63.6.

(6) Prepared from pure (98%) *cis*- and *trans* 4-methylcyclohexanol (Aldrich Chemical Co.).

(7) N. Muller and W. C. Tosch, *J. Chem. Phys.*, 37, 1167 (1962).

(8) H. van Bekkum, A. A. B. Kleis, A. A. Massier, D. Medema, P. E. Verkade, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, 80, 595 (1961).

(9) M. Tichy, J. Jonas, and J. Sicher, *Collect. Czech. Chem. Commun.*, 24, 3436 (1959).

(10) Retention time on a 6 ft 5% SE-30 on Chromosorb W column, column temp 100°: cis ester (7), 7.5 min; trans ester (6), 8.8 min.

(11) J. P. Collman, J. N. Cowse, and J. I. Brauman, *J. Amer. Chem. Soc.*, 94, 5905 (1972).

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