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CATALYTIC DECARBONYLATION, HYDROACYLATION, AND RESOLUTION OF RACEMIC PENT-4-ENALS USING CHIRAL BIS(DI-TERTIARY-PHOSPHINE) COMPLEXES OF RHODIUM(I)

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Summary

Attempts to decarbonylate racemic aldehydes catalytically using rhodium(I) complexes containing chiral di-tertiary-phosphine ligands are described. Incorporation of an alkenic moiety into the aldehyde, for subsequent probing of induced asymmetry by chiral shift reagents, leads instead to formation of optically active hydroacylated products via kinetic resolution of the precursor racemic aldehyde. For example, (*RS*)-2-methyl-2-phenylpent-4-enal (**1a**) yields, on treatment with [Rh(*S,S*-chiraphos)$_2$]Cl, 2-methyl-2-phenylcyclopentanone with up to 69% e.e. of the (−)-(*S*) optical isomer and remaining unreacted aldehyde which is possibly the enantiomerically pure (−)-(*R*) form. Extension of this cyclization reaction to a 3,3-disubstituted pent-4-enal similarly provides a synthesis for an optically active 3,3-disubstituted cyclopentanone. Decarbonylation by-products are also observed; those from **1a** appear as *E*- and *Z*-2-phenylpent-2-ene. The cyclization of **1a** is catalyzed also by Rh(chiraphos)(solvent)$_2^+$ but with lower e.e.

Introduction

Reports that cationic rhodium(I) bis(di-tertiary-phosphine) complexes of the type Rh(P–P)$_2^+$, where P–P = $Ph_2P(CH_2)_nPPh_2$, are effective catalysts for decarbonylation of aldehydes [1,2], coupled together with the earlier work of Walborsky and Allen [3] who showed that the stoichiometric decarbonylation of an optically active aldehyde using $RhCl(PPh_3)_3$ occurs with retention of configuration (eq. 1, P = PPh_3), suggested that a racemic aldehyde might be decarbonylated asymmetrically using a chiral catalyst of the type Rh(P*P)$_2^+$, where P*P represents a chiral di-tertiary-phosphine ligand. Such a process would provide an attractive route for the synthesis

$$R^1R^2R^3\overset{*}{C}\text{–CHO} \xrightarrow[-\,Rh(CO)ClP_2,\,-\,P]{RhClP_3} R^1R^2R^3\overset{*}{C}H \qquad (1)$$

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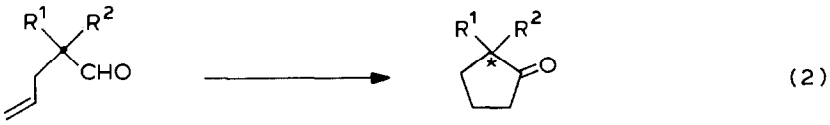
of optically active saturated hydrocarbons, since only catalytic amounts of chiral reagent (the P*P ligand) would be required. We have reported previously on the synthesis of the required rhodium complexes, such as $Rh(diop)_2^+$ [4,5], and thus the major problem for the project was synthesis of an appropriate precursor racemic aldehyde such that the optical purity of the anticipated chiral decarbonylation product could be readily determined.

This paper reports on our, as yet, unsuccessful efforts to accomplish this goal of asymmetric decarbonylation. Nevertheless, choice of a racemic alkenic aldehyde as substrate (in order to build in a functional group for resolution of optically active product by use of chiral shift reagents) has led to an interesting catalytic asymmetric synthesis of disubstituted cyclopentanones via a kinetic resolution process, for example eq. 2.



(2)

In retrospect, a second reason for carrying out the part of our studies that fortuitously led to the discovery of reaction 2 is provided by the earlier work of Sakai et al. [6] and Lochow and Miller [7], who reported on the conversion of pent-4-enal itself (eq. 2, $R^1 = H = R^2$) and substituted pent-4-enals to cyclopentanone derivatives using the $RhCl(PPh_3)_3$ complex. Incorporation of potential chirality into the system (two different substituents at C(2), and use of a chiral catalyst) would have provided an alternative raison d'etre for our discovery. Since the early reports there have been several other studies on the nonchiral systems [8–12], including intermolecular as well as the intramolecular reaction shown in eq. 2. A preliminary note on the present work has been published [13].

Experimental

Materials and methods. Allyl bromide was purified [14] and distilled before use, THF was distilled from sodium/benzophenone, and the benzonitrile used (Eastman Kodak) was aniline-free. The ethanol used in the optical rotation measurements was distilled from $Mg(OEt)_2$. All the other chemicals were at least reagent grade, and syntheses and catalysis experiments were performed under Ar unless otherwise noted. TLC was carried out on commercial silica gel plates (Bakerflex 1B2-F, J.T. Baker Co.), while column chromatography was effected using wet packed 230–400 mesh silica gel (E. Merck) columns (2.5 × 25 cm) and an eluent of 2% ethyl acetate in petroleum ether (35–60°C). Plates were developed using 5% dodecamolybdophosphoric acid in ethanol.

The $[Rh(chiraphos)_2]X$ complexes ($X = Cl$, BF_4) were synthesized via the cyclooctene precursor $[RhCl(C_8H_{14})_2]_n$, and characterized as reported previously for other analogous bis(di-tertiary-phosphine) complexes [4]; further details on the X-ray structure of the ionic chloride complex and its reactivity toward small gas molecules (CO, H_2, O_2, HCl) will be reported elsewhere [15]. The complexes $[Rh(dpp)_2]SbF_6$ [4], [Rh(chiraphos)(COD)]BF_4 [16], $RhCl(PPh_3)_3$ and [RhCl-

$(PPh_3)_2]_2$ [17] were prepared by the literature methods referenced. The phosphines were used as received from Strem Chemicals. Silver trifluoroacetylacetonate (Ag(tfa)) was prepared by a literature method [18], black painted glassware being used throughout. The silver-modified lanthanide shift reagents were made according to the method of Sievers et al. [18,19] by dissolving the required amounts of Ag(tfa) and lanthanide reagent in 0.5 ml $CDCl_3$, centrifuging and transferring the clear supernatant to an NMR tube to which varying amounts of substrate could be added. The lanthanide reagents used, $Ln(fod)_3$, $Ln(facam)_3$ and $Ln(hfc)_3$ (Ln = Eu, Pr), were Aldrich products.

NMR spectra were obtained on Bruker WH 400, Varian XL 100 (for ^1H) and Varian CFT-20 (19.9 MHz, for ^{13}C) instruments, using tetramethylsilane as internal standard. IR were recorded using neat samples on a Perkin–Elmer Model 598. GC analyses were performed on a Carle 311 machine, fitted with a 6 ft 8% OV-101 on chromosorb column (125°C, heated inlet, He carrier, thermistor detectors). All catalytic yields are reported as uncorrected GC yields. Mass spectra were recorded on a Varian MAT CH4-B spectrometer, and a Perkin–Elmer 141 polarimeter was used to measure optical rotations. Elemental microanalyses were carried out by P. Borda of this department.

Synthesis of aldehydes

*(RS)-2-Methyl-2-phenylpent-4-enal (**1a**).* A mixture of 2-phenylpropanal (46.7 g, 0.35 mol), isopropylamine (21.0 g, 0.36 mol), and 4Å molecular sieve (70 g, 8–12 mesh) in CH_2Cl_2 (175 ml) was stirred for 24 h in a stoppered vessel. Removal of the sieve by filtration and washing with CH_2Cl_2 (80 ml) gave a clear filtrate that after evaporation of the solvent in vacuo yielded the pale yellow, water-sensitive imine. The imine (55.5 g, 0.30 mol) in THF (45 ml) was then added dropwise to a stirred solution of EtMgBr (0.30 mol) in THF (140 ml), C_2H_6 gas being evolved. After a 2 h reflux, the solution was cooled and treated dropwise with a solution of allyl bromide (36.0 g, 0.30 mol) in THF (80 ml). The resulting mixture was stirred under reflux for 22 h, and upon cooling was treated with an aqueous solution of oxalic acid (27.0 g, 0.30 mol in 250 ml H_2O) prior to a further refluxing for 2 h. The cooled reaction mixture was then extracted with ether (3 × 150 ml), and the ethereal phase washed with H_2O (4 × 150 ml), dried ($MgSO_4$) and evaporated in vacuo to yield crude **1a**. Vacuum distillation of the freeze-thaw deoxygenated material yielded 35.0 g (68%) of colorless, air-stable **1a** (b.p. 90°C, 0.55 mmHg). Anal. Found: C, 82.3; H, 8.1. $C_{12}H_{14}O$ calcd.: C, 82.7; H, 8.1%. ^1H NMR ($CDCl_3$): δ 1.44 (s, 3H, CH_3), 2.635 (A) and 2.691 (B) (*AB*MXY allyl, 2H, J_{AB} 13.6 Hz, $J_{AM} = J_{BM} = 7.2$ Hz, $J_{AX} = J_{BX}$ 1.0 Hz, diastereotopic $CH_2CH{=}CH_2$), 5.031 (X) and 5.056 (Y) (ABM*XY*, 2H, J_{MX}(*cis*) 10.1 Hz, J_{MY}(*trans*) 17.0 Hz, J_{XY} 1.9 Hz, $CH_2CH{=}CH_2$), 5.554 (AB*M*XY, 1H, $CH_2CH{=}CH_2$), 7.2–7.5 (m, 5H, Ph), 9.56 (s, 1H, CHO). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.85 (CH_3), 40.67 (C(3)), 53.34 (C(2)), 118.50 (C(5)), 127.16–128.84 (CH aromatic), 133.25 (C(4)), 139.64 (quat. aromatic), 201.59 (C(1)). IR (film, cm^{-1}): ν(C=O), 1710s; ν(C=C), 1635m; ν(=CH_2), 915s cm^{-1}. Mass spectrum; *m/e* 174(11%, M^+), 146(13), 145(100), 144(13), 143(12), 130(18), 129(15), 128(13), 121(16), 117(30), 115(15), 105(70), 103(20), 91(37), 77(46). This compound has been synthesized previously via other routes but spectroscopic details were not reported [20].

*(RS)-2-Methyl-2-phenylhex-5-enal (**1b**).* This aldehyde was prepared from 2-phenylpropanal (18 g, 0.13 mol) by a procedure similar to that described above for

1a, except that 4-bromobutene was employed in place of allyl bromide. Purification of the colorless liquid (14.0 g, 55%) was again by vacuum distillation (b.p. 72°C, 0.55 mmHg). Anal. Found: C, 82.8; H, 8.7. $C_{13}H_{16}O$ calcd.: C, 82.9; H, 8.6%. ^{1}H NMR ($CDCl_3$): δ 1.50 (s, 3H, CH_3), 1.95 (m, 4H, CH_2CH_2), 4.95–5.1 (m, 2H, $=CH_2$), 5.7–6.0 (m, 1H, CH=), 7.2–7.5 (m, 5H, Ph), 9.55 (s, 1H, CHO). IR (film, cm^{-1}): ν(C=O) 1710s, ν(C=C) 1633m, ν($=CH_2$), 910s. These data agree well with those reported for **1b**, made by another route [21].

(RS)-2-Methyl-2-phenylbutanal (1c). This compound was again prepared from 2-phenylpropanal (20 g, 0.15 mol) by the procedure described above for **1a**, but using ethyl bromide in the alkylation step. Purification by vacuum distillation (70°C, 0.55 mmHg) yielded a colorless liquid (20 g, 83%). Anal. Found: C, 81.2; H, 8.6. $C_{11}H_{14}O$ calcd.: C, 81.4; H, 8.7%. ^{1}H NMR ($CDCl_3$): δ 0.80 (t, 3H, J 8 Hz, CH_2CH_3), 1.44 (s, 3H, CH_3), 1.96 (overlapping q, 2H, J 8 Hz, CH_2CH_3), 7.2–7.5 (m, 5H, Ph), 9.56 (s, 1H, CHO). IR (film, cm^{-1}): ν(C=O) 1710s.

The pure (−)-*R* isomer has been reported previously [3].

(RS)-3-Ethyl-3-phenylpent-4-enal (2). The synthesis of this aldehyde, along with that of other 3,3-disubstituted analogues, is described elsewhere [22] and involves alkylation of 2-formyl-1,3-dithiane with 1-bromo-3-phenylpent-2-ene, followed by desulfurization using Raney nickel.

Catalysis apparatus and conditions. One-piece glass reaction vessels (ca. 4 ml volume), having gas-inlet tubes and a 20 cm water condenser with top sampling ports, were used. The vessel was typically charged with a solution of the substrate (0.5 g, 3.0 mmol for **1a**) and catalyst (30 mg, 0.03 mmol for $[Rh(chiraphos)_2]Cl$) in benzonitrile (0.5 ml), which was then deoxygenated by three freeze-thaw cycles. The reaction mixture was then stirred at constant temperature in the 130–180°C range under a slow flow of Ar. Some reactions were carried out using the neat aldehyde as solvent media, and a few reactions were performed in air. In several experiments, a −78°C trap placed after the condenser collected no condensate. The course of the reactions was monitored by periodic sampling (using long glass capillary tubing) and subsequent GC analysis. The catalyst could be recovered unchanged after completion of the reaction by the addition of diethyl ether. In the absence of a rhodium complex, solutions of the aldehyde remained unchanged under corresponding conditions.

Product isolation and characterization. The work-up for the disubstituted cyclopentanones was generally initiated when their yield was > 40%. The reaction mixture was absorbed onto the minimum amount of silica gel, and then the dry powder was loaded onto a chromatographic column of the same material and eluted with 2% ethyl acetate/light petroleum (~ 1.0 l). The collection of the fractions (~ 5–10 ml each) containing the disubstituted cyclopentanone (TLC with above solvent, R_f 0.05), followed by evaporation of the solvent in vacuo, yielded the pure cyclopentanone. Other reaction products from the catalysis experiments were characterized by a combination of techniques including: chromatographic isolation (as for the cyclopentanones) and subsequent IR, NMR and/or MS analysis; GC identification by co-injection with an authentic sample of the material; GC/MS analysis.

2-Methyl-2-phenylcyclopentanone (3). Anal. Found: C, 82.7; H, 8.0. $C_{12}H_{14}O$ calcd.: C, 82.7; H, 8.1%. ^{1}H NMR ($CDCl_3$): δ 1.40 (s, 3H, CH_3), 1.95, 2.35, 2.55 (three multiplets of 3H, 2H, 1H, respectively, $CH_2CH_2CH_2$), 7.3–7.5 (m, 5H, Ph).

IR (film, cm^{-1}): ν(C=O) 1740 s. Mass spectrum; *m/e* 175 (6%), 174 (39, M^+), 131 (20), 119 (12), 118 (100), 117 (26), 116 (7), 115(11), 103 (17), 102 (5), 91 (14), 78 (13), 77 (16). Optical rotation measurements used solutions of ca. 40 mg/ml (Literature [23], (*R*)-**3**, $\alpha_D^{25°}$ +95.30°, *c* 3.89, ethanol).

Z-2-Phenylpent-2-ene (4). ^{1}H NMR ($CDCl_3$): δ 0.92 (t, 3H, J_{45} 7.5 Hz, C(5)H_3), 2.01 (d, 3H, J_{13} 1.5 Hz, C(1)H_3), 2.05 (dq, J_{34} 7.5 Hz, C(4)H_2), 5.42 (tq, 1H, =CH), 7.2–7.5 (m, 5H, Ph). Mass spectrum; *m/e* 146 (M^+).

E-2-Phenylpent-2-ene (5). ^{1}H NMR ($CDCl_3$): δ 1.05 (t, 3H, J_{45} 7.5 Hz, C(5)H_3), 2.05 (d, 3H, J_{13} 1.5 Hz, C(1)H_3), 2.15 (dq, J_{34} 7.5 Hz, C(4)H_2), 5.75 (tq, 1H, =CH) 7.2–7.5 (m, 5H, Ph). Mass spectrum; *m/e* 146 (M^+).

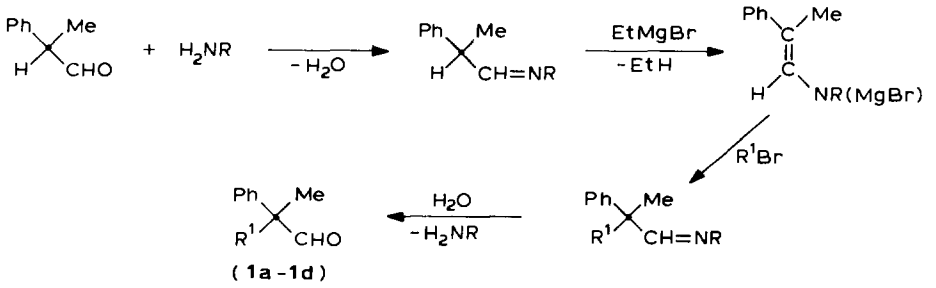
trans-2-Methyl-2-phenylpent-3-enal (1d). This compound is the major product when the catalytic reaction with **1a** is carried out in air at 160°C. ^{1}H NMR ($CDCl_3$): δ 1.51 (s, 3H, CH_3), 1.81 (dd, 3H, J_{45} 7.0 Hz, J_{35} 3.0 Hz, C(5)H_3), 5.58 (dq, 1H, J_{34} 16.4 Hz, =C(4)H), 5.81 (dq, 1H, =C(3)H), 7.2–7.5 (m, 5H, Ph), 9.54 (s, 1H, CHO). IR (film, cm^{-1}): ν(C=O) 1725s, ν(C=C) 1600m. Mass spectrum; *m/e* 174 (M^+). The compound polymerizes at 0°C in ~ 1 d. In the absence of a rhodium complex, aerial oxidation of **1a** yielded acetophenone and other unidentified gaseous fragments.

Biphenyl. In some reactions, this compound was isolated by column chromatography. M.pt., NMR, IR, and GC were identical to those of an authentic sample. Mass spectrum; *m/e* 154 (M^+).

3-Ethyl-3-phenylcyclopentanone (6). Anal. Found: C, 82.8; H, 8.5. $C_{13}H_{16}O$ calcd.: C, 82.9; H, 8.5%. ^{1}H NMR ($CDCl_3$): δ 0.67 (t, *J* 7.5 Hz, 3H, CH_3), 1.693 (septet, dq, J_{AB} 14.0 Hz, J_{AX_3} 7.5 Hz, 1H, diast. H of Et), 1.783 (septet, dq, J_{AB} 14.0 Hz, J_{BX_3} 7.5 Hz, 1H, diast H of Et), 2.30–2.50 (m, 4H, CH_2CH_2), 2.575 (dd, AB pattern, δ_A 2.502, δ_B 2.653, J_{AB} 17.75 Hz, 2H, diast. CH_2CO), 7.10–7.30 (m, 5H, Ph). IR (film, cm^{-1}): ν(C=O) 1745s.

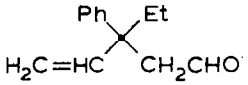
Results and discussion

The synthesis of the aldehydes **1a–1c** is straightforward and follows Scheme 1. The reaction of the imine with EtMgBr effects deprotonation of the α-carbon, and subsequent treatment of the Grignard complex with the appropriate alkenyl or alkyl bromide produces the imine of the desired aldehyde, which is liberated upon hydrolysis. The aldehydes decompose on heating in air.



SCHEME 1. Synthesis of the aldehydes **1a** ($R^1 = CH_2CH{=}CH_2$), **1b** ($R^1 = CH_2CH_2CH{=}CH_2$), **1c** ($R^1 = CH_2CH_3$); **1d** ($R^1 = CH{=}CHCH_3$) is an isomerization product of **1a** (see text).

Structures of other substrates and reaction products obtained under various conditions are given below:



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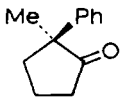

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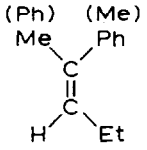
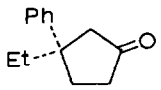


(4(*Z*-), 5(*E*-))



(6)

Treatment of the racemic alkenic aldehyde **1a** with chiral rhodium(I) phosphine catalysts in the 130–180°C range under a stream of argon results in two main types of products: those from decarbonylation, and those from intramolecular addition of the aldehyde group to the alkene bond. The important finding in the studies is that the latter hydroacylation products, substituted cyclopentanones, are optically active, one of the enantiomers of the racemic aldehyde precursor cyclizing preferentially. Thus the process constitutes a kinetic resolution of the racemic aldehyde, and indeed examination of unreacted aldehyde at various stages of the reaction (see below) shows it to be optically active.

Table 1 summarizes some data concerning formation of (*S*)-(−)-2-methyl-2-phenylcyclopentanone (**3**), from (*RS*)-2-methyl-2-phenylpent-4-enal (**1a**), while Fig. 1 and 2 show, respectively, a typical GC trace for a final product analysis, and a composition versus time profile. The disubstituted cyclopentanone **3** has been synthesized previously as the pure *R* enantiomer via resolved 2-methyl-2-phenylhexanedioic acid [23]. As shown in Fig. 1 and 2, the anticipated potentially chiral decarbonylation product, 4-phenylpent-1-ene, is not observed but its isomerization products (*Z*)- and (*E*)-2-phenylpent-2-ene (**4**,**5**), formed via double-bond migration,

TABLE 1

INTRAMOLECULAR HYDROACYLATION OF **1a** TO **3** [a]

Temperature (°C)	Time (h)	Yield of **3** (%) [b]	e.e. of (*S*)-**3**
150	6	17	69
150	10	24	67
150	19	40	58
155	17	40	61
155 [c]	39	10	[d]
160	3	15	69
160	4	19	67
160	24	58	38
160 [e,f]	10	34	52
180 [e,g]	1.5	48	41
180 [e,h]	9	46	52
130 [i]	7	44	30
130 [h,i]	24	20	25

[a] In PhCN using [Rh(chiraphos)$_2$]Cl with [**1a**]/[Rh] = 100, unless noted otherwise. [b] Based on [**1a**]. [c] Using [Rh(chiraphos)$_2$]BF_4; the major products were **4** and **5** via decarbonylation. [d] Not measured. [e] Using neat **1a** as solvent. [f] [**1a**]/[Rh] = 900. [g] [**1a**]/[Rh] = 500. [h] [**1a**]/[Rh] = 200. [i] Using Rh(chiraphos)(solvent)$_2^+$ formed via pretreatment of [Rh(chiraphos)(COD)]BF_4 with H_2 for 30 min at 20°C [24].

are found in low yield; the isomerization, which may be rhodium-catalyzed but is almost certainly assisted via conjugation with the phenyl group, thwarts attempts to demonstrate asymmetric decarbonylation using **1a** as substrate. Formation of **3** is effected in benzonitrile solution or using neat **1a** as solvent, although the latter tends to give more trace products (unidentified, occurring near **4** in the GC). *trans*-2-Methyl-2-phenylpent-3-enal (**1d**), a simple alkene isomerization product of **1a**, is also formed in low yield (Fig. 1, 2) and indeed is essentially the only product if the reaction is carried out in the presence of air rather than argon. This isomerization definitely requires also the rhodium; such alkene isomerization requiring rhodium

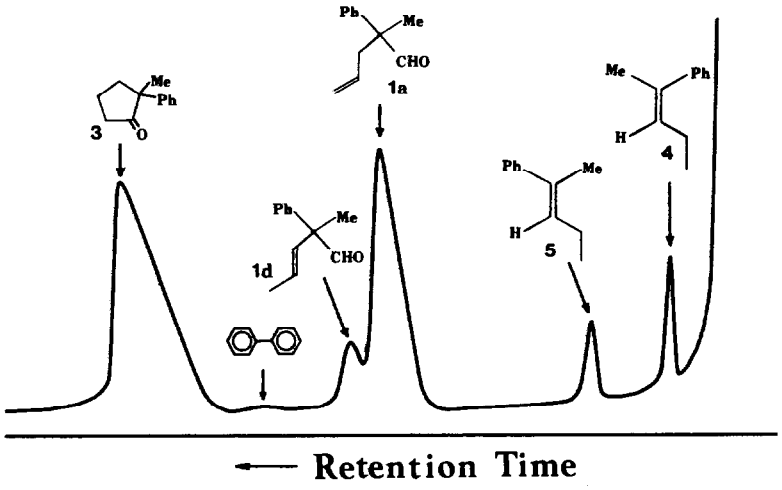


Fig. 1. The GC trace for a final product analysis of the 24 h experiment at 160°C listed in Table 1.

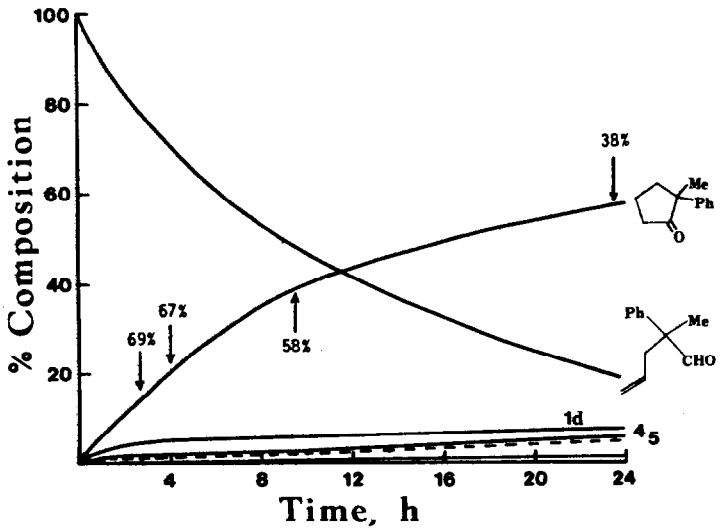
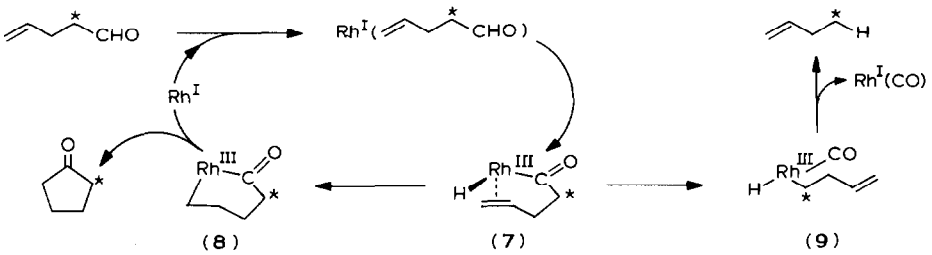


Fig. 2. Composition vs. time curves for the 24 h/160°C experiment listed in Table 1. The line closest to the abscissa axis shows the increase in biphenyl concentration (~ 1.5% at 24 h). The percentages noted on the 2-methyl-2-phenylcyclopentanone curve refer to enantiomeric excess.

and trace O_2 has been noted by others [25], and probably results from new complexes generated by the removal of phosphine as phosphine oxide [26].

The noted intramolecular hydroacylation reaction **1a** → **3** has been accomplished with up to ~ 70% e.e., although this degree of optical purity is achieved only at relatively low conversions (see Table 1); the e.e. falls with increasing conversion and at the best yields obtained (50–60%), the optical purity obtained is in the 40% range. A maximum product yield of about 50% (based on the initial concentration of **1a**) suggests that only one enantiomer of **1a**, that of *S*-configuration, undergoes the hydroacylation reaction, and indeed recovery of unreacted **1a** by column chromatography after the longer reactions and determination of its optical rotation ($\alpha_D^{25°}$ −26.5°, *c* 2, $CHCl_3$) shows that the recovered 2-methyl-2-phenylpent-4-enal is of very high optical purity. The formation of this aldehyde in 8 ± 2% e.e. (α_D^{25} 1.8°, *c* 2, $CHCl_3$) via alkylation of 2-phenylpropanal using a $PdCl_2$(diop) catalyst has been reported by Fiaud et al. [27]; the assigning of the negative rotation to the *R*-enantiomer results from our data. Such high enantiomeric discrimination, in terms of choice of substrate enantiomer, is noteworthy and deserves further comment. Although no kinetic work on the intramolecular hydroacylation reaction (with non-chiral reagents) has been reported, some labelling studies [9] and data on oxidative addition of aldehydes to rhodium(I) phosphine complexes [11,12] strongly suggest a basic mechanism of the type included in Scheme 2 (written for unsubstituted pent-4-enal, with an unspecified Rh^I catalyst).



SCHEME 2. Mechanism for intramolecular hydroacylation and decarbonylation.

Coordination of the aldehyde via the carbonyl, or more probably the olefinic group, followed by oxidative addition of the CHO would yield eventually a rhodium(III) acylhydride species **7**; subsequent hydrometallation to the metallocycle **8**, followed by reductive elimination of the C–C fragment to give cyclopentanone, completes the catalytic cycle [12]. Substrate labelling studies using the $RhCl(PPh_3)_3$ catalyst [9] tend to rule out an alternative addition of Rh–CO across the alkene link followed by C–H reductive elimination to give cyclopentanone. In either case, chirality at position 2(★) is not influenced by any steps of the process (Scheme 2). Kinetic resolution of an initially racemic aldehyde with the chiral catalyst could result from preferred binding of the olefinic group within a set of diastereotopic species, although further discussion on this point requires details of the structure of the catalyst, a study now in progress [15]. Such preferential binding of one side of an olefinic face was initially considered to be the source of optical induction in catalytic asymmetric hydrogenation, where orientation of phenyl groups within the catalyst and substrate was a key feature [28]. Whether the corresponding phenyl groups, which are present in our hydroacylation work, are important for the chiral dis-

crimination requires studies on further substrates and catalysts. If the unreacted aldehyde (**1a**) is pure *R*, then catalysis via Scheme 2 only implies production of **3** as the pure *S* form. Preliminary data suggest that the optical purity of **3** decreases on standing at 160°C (cf. Fig. 2), and side-reactions are clearly present also during the catalysis. The trace biphenyl detected may result from a process associated with racemization of **3**; the biphenyl certainly implies a radical pathway of some kind, although addition of radical inhibitors has essentially no effect on the intramolecular hydroacylation, and other workers have ruled out radical mechanisms for this process [8,9]. The decarbonylation products (**4,5**) must result from an alkenyl (carbonyl)hydride intermediate such as **9** (Scheme 2) formed from **7**, an overall migratory elimination process. With pent-4-enal itself and $RhCl(PPh_3)_3$ catalyst, some decarbonylation occurs to give the expected but-1-ene product [9,12] and there is no subsequent isomerization of the hydrocarbon fragment. The catalysis cycle for decarbonylation is completed by loss of CO from the rhodium; the $Rh(chiraphos)_2^+$ complex has been found to be completely unreactive toward 1 atm CO at or above room temperature [15], which implies that any $Rh(CO)(chiraphos)_2^+$ intermediate formed in a catalytic cycle would be thermodynamically unstable with respect to loss of CO. In an intermediate such as **9**, a coordination number of seven for rhodium(III) can be avoided (if necessary) by one of the diphosphine ligands becoming monodentate. Such behavior has been invoked previously in catalytic cycles [1,29], and such complexes have been isolated even with dpe [30] which, like chiraphos, is normally expected to form the favored five-membered chelate ring.

That the hydroacylation and decarbonylation processes invoke the same intermediate (**7**) augurs well for eventual success in producing optically active hydrocarbons via decarbonylation using a chiral complex, at least via a kinetic resolution as shown in Scheme 2. For a non-olefinic aldehyde, asymmetric induction at position-2 would have to be realized via (a) preferential formation of a diastereomeric hydrido(acyl) complex (cf. **7**), (b) at the CO de-insertion stage (**7** → **9**), the reverse reaction being known to occur with complete retention [31], or (c) during reductive elimination of the hydride(alkyl) fragment, although within catalytic asymmetric hydrogenation systems the reductive elimination step of the final hydrocarbon product is not usually found to be involved in chiral recognition [28,32,33].

It should be noted that the Cl^- salt of $Rh(chiraphos)_2^+$ is a much more effective catalyst for the hydroacylation than the BF_4^- salt; indeed, the latter is for practical purposes inactive (Table 1). Anion effects such as this are common also in asymmetric hydrogenations catalyzed by rhodium-chiral phosphine complexes, where Cl^- has been shown to have either positive [34] or more commonly negative [28,35] effects, depending on the particular catalyst and substrate. Coordination of a Cl^- within the primary or secondary coordination sphere of an intermediate must modify the activity. If Cl^- is in the primary coordination sphere of an intermediate such as **7** (or **9**), hexacoordination could be achieved by a single bidentate chiraphos ligand; experiments using $Rh(chiraphos)(solvent)_2^+BF_4^-$ show higher conversions than the corresponding bis(chiraphos) systems (Table 1) and, within the previously reported non-chiral systems using pent-4-enal, the most active catalysts also contained two coordinated phosphorus atoms per Rh, Cl^- again being a better counter-ion than BF_4^- [8]. Whether the bis(bidentate phosphine)systems give better optical yields requires further study; such species will almost certainly be more effective for the decarbonylation process [1].

Treatment of **1a** with $[RhCl(PPh_3)_2]_2$ (80°C, 1.5 h) resulted in a stoichiometric decarbonylation, the organic product appearing as the isomerization products **4** and **5** (in a 1/3 ratio), and the rhodium being converted to the well-known $RhCl(CO)(PPh_3)_2$ complex [36]; no cyclopentanone product was observed. 2-Methyl-2-phenylbutanal (**1c**) was similarly decarbonylated stoichiometrically to 2-phenylbutane, as reported previously [3]. The rhodium carbonyl complex is thermally very stable with respect to loss of CO and this prevents any effective catalytic decarbonylation process under relatively mild conditions [37]. It should be noted here that use of the Ag-lanthanide chiral shift reagents with 2-phenylbutane at varying mole ratios at $\leqslant 20$°C did not split sufficiently any of the ^1H NMR resonances of the phenylbutane to distinguish successfully the optical isomers, although shifts of ca. 0.2 ppm to high field were observed at a shift reagent: substrate ratio of about 2.0. Chiral hydrocarbon decarbonylation products which contain only a phenyl functional group are thus unlikely to be amenable to NMR analysis, at least using the Ag shift reagents listed in the Experimental Section.

Larock and co-workers [8] reported that the $[RhCl(PPh_3)_2]_2$ dimer was the most effective complex for the hydroacylation of pent-4-enal (much better, for example, than a BF_4^- salt or in situ RhCl(dpe)), but effected neither hydroacylation or decarbonylation of 2-methyl-substituted 4-pentenals; however, these workers were using long reaction times (days) at ambient temperatures and the reactions were never catalytic [8], and it is difficult to make comparisons with the present work.

Using conditions comparable to those noted in Table 1, we found that the $Rh(dpp)_2^+$ complex was completely unreactive towards **1a**. This dpp complex is the most effective catalyst reported for decarbonylation of benzaldehydes and aliphatic aldehydes of the type RCH_2CHO. However, increasing substitution at the α-carbon atom decreases activity, and tertiary aldehydes such as 2-methyl-2-phenylbutanal (**1c**) gave turn-overs of only about 1 h^{-1} at 180°C [1]. We did test racemic **1c** with $[Rh(chiraphos)_2]Cl$ at 180°C, but over 8 h the decarbonylation product, 2-phenylbutane, was not detected and some decomposition of the complex to metal was observed; binding of the olefinic group within olefinic aldehydes, a key step in the hydroacylation process, may also act to stabilize the rhodium as rhodium(I) within an aldehyde complex or as rhodium(III) within an intermediate such as **7** (see Scheme 2). However, olefinic groups are not essential for prevention of metal production within chiraphos systems, since 2-phenylpropanal was cleanly decarbonylated catalytically to ethylbenzene using $[Rh(chiraphos)_2]Cl$ at 200°C (turnover 20 h^{-1}).

Attempts to produce 2,2-disubstituted cyclohexanones from 2-methyl-2-phenylhex-5-enal using $[Rh(chiraphos)_2]Cl$ have not been successful. An important requirement for the cyclization reactions appears to be the formation of favored 5.5- and 6-membered ring Rh intermediates and the cyclopentanone ring, as noted by others [6–9].

3-Ethyl-3-phenylpent-4-enal (**2**) appeared to be an attractive substrate for asymmetric decarbonylation since (a) the anticipated product would have no migrateable hydrogen atom on the resulting tertiary carbon atom, thus avoiding the isomerization problem encountered with **1a**, and (b) aldehydes containing two α-hydrogens were in general most readily decarbonylated (see above). However, in benzonitrile at 160°C for 5 h, **2** with $[Rh(chiraphos)_2]Cl$ (cf. Table 1) gave in about 70% yield the cyclization product **6**; this 3,3-disubstituted cyclopentanone is a new compound and

is unambiguously characterized by the ^1H NMR, particularly by the sets of diastereotopic CH_2 protons adjacent to the asymmetric carbon center. The hydroacylation product is optically active ($\alpha_D^{25} = -1.9°$, c 4.0, ethanol) but thus far we have not found a satisfactory shift reagent to determine the optical purity. The catalytic production of **6** is accompanied by formation of five other by-products in small yields (up to 6%); some of these with short GC retention times may well be decarbonylation products (cf. Fig. 1), but we need to obtain these in larger amounts before they can be characterized.

Conclusions

While seeking the possibility of asymmetric decarbonylation of racemic aldehydes using chiral rhodium catalysts, we have discovered a route to optically active 2,2- and 3,3-disubstituted cyclopentanones. The full scope of such syntheses (variation in unsaturated aldehyde substrate and chiral catalyst) remains to be established, including potential use in synthesis of prostaglandins that commonly contain a five-membered ketone-containing ring substituted at the 2- and 3-positions [6,38]. The studies reveal also a novel method for kinetic resolution of racemic alkenic aldehydes.

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