Metallocarbene intermediates in rhodium(II)-catalyzed rearrangements of ethyl 2-butylcycloprop-2-ene-1-carboxylate

Muller, Paul; Graenicher, Christian; Klärner, Frank-Gerritt; Breitkopf, Volker

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METALLOCARBENE INTERMEDIATES IN RHODIUM(II)-CATALYZED REARRANGEMENTS OF ETHYL 2-BUTYLCYCLOPROP-2-ENE-1-CARBOXYLATE (*) (**)

PAUL MÜLLER (°) and CHRISTIAN GRÄNICHER
Département de Chimie Organique, Université de Genève, 30 Quai Ernest Ansermet, CH-1211 Genève 4, Switzerland

FRANK-GERRITT KLÄRNER and VOLKER BREITKOPF
Institut für Organische Chemie, Universität Essen, D-45117 Essen, Germany

Summary – Ethyl 2-butylcycloprop-2-ene-1-carboxylate, **1**, was rearranged thermally, photochemically and in the presence of Cu(I) and Rh(II) catalysts. The rearrangement leads to vinylcarbenes *via* ring opening. The products of the thermal and photochemical reactions derive from the more stable vinylcarbene **4** which, in turn, originates from cleavage of the more highly substituted cyclopropene single bond, while those of the transition metal-catalyzed rearrangement derive from cleavage of the less substituted bond through the vinylcarbenes (*E*)-**2**, (*Z*)-**2** and (*Z*)-**10**, respectively. When enantio-enriched **1** was rearranged with achiral [Rh$_2$(pfb)$_4$] the unreacted starting material retained the enantiomeric excess in the course of the reaction, while the product **3** was racemic. Rearrangement of **1** with the chiral Rh(II) catalysts [Rh$_2${(2S)-mepy}$_4$] or [Rh$_2$(*R*-bnp)$_4$] produced **3** in modest yield and modest enantiomeric excess (<52%).

The rearrangement of cyclopropenes to vinylcarbenes is of considerable interest for synthetic applications[1]. In the presence of certain transition metals, isolable metal-complexed vinylcarbenes may be obtained[2]. The first such complexes were prepared from cyclopropene rearrangements with titanocene and zirconocene precursors[3]. More recently, vinylcarbenes complexed to tungsten[4], rhenium[5] and ruthenium[6] have been generated from reactions with 3,3-diphenylcyclopropene.

In previous communications on cyclopropene rearrangements we have reported isomerizations of cycloprop-2-ene-1-carboxylates in the presence of [Rh$_2$(pfb)$_4$] [dirhodium(II) tetrakis(perfluorobutyrate)]. The most remarkable result of these studies was the formation of a cyclopentylidene, (*E*)-**3**, upon heating of ethyl 2-butylcycloprop-2-ene-1-carboxylate, **1**, in the presence of a catalytic amount of [Rh$_2$(pfb)$_4$] in refluxing benzene (see scheme 1)[7]. A reaction mechanism was proposed in which electrophilic attack of the catalyst affords a complexed vinylcarbene, (*E*)-**2**, which then inserts into one of the CH bonds of the aliphatic substituent. Reversible formation of **2** was assumed in order to account for the high regio- and stereoselectivity of the rearrangement. More detailed investigations revealed, however, that the product distribution is remarkably sensitive to the substitution pattern of the cyclopropene. Furans, dienoates and indenes may be produced in preference to cyclopentylidenes[8]. In some cases, ring opening was found to be highly regio- and stereo-

selective, while in others, products derived from all possible isomeric vinylcarbene intermediates were observed[9]. This communication deals with the role of the Rh(II)-catalyst in the rearrangement of **1**, by comparison of the reaction products with those occurring in thermal and photochemical rearrangements, and in its rearrangement catalyzed with Cu(I). In addition, the reversibility of the Rh(II)-catalyzed cyclopropene-vinylcarbene rearrangement was investigated, and the involvement of the metal in the CH insertion of the carbene was established[10].

RESULTS AND DISCUSSION

1. THERMAL AND PHOTOCHEMICAL REARRANGEMENT OF 1

Flash-vacuum pyrolysis of **1** at 450 °C/5×10^{-5} Torr afforded a mixture of 5 products, ethyl (2*E*,4*E*)-octa-2,4-dienoate, **5**[11] (32%), the 2*Z*,4*E* and 2*E*,4*Z* isomers **6** (5%) and **7** (5%), the acetylene **8**[12] (6%) and the allene **9**[13] (21%) (see scheme 2). Products **5-7** originate from ring cleavage of the more highly substituted cyclopropene single bond to form the vinylcarbene **4** which undergoes 1,2-hydrogen migration. The preferential formation of the thermodynamically most stable 2*E*,4*E* diene **5** from **4** is typical for thermal rearrangements of cyclopropenes. Ring opening to the more stable vinylcarbene (*E*)-**4** should have a lower barrier than that to (*Z*)-**4**, although there are exceptions where electronic effects of electron-attracting substituents overrule the preference for formation of that vinylcarbene, which has the bulkier substituent *trans* to the carbenic centre[14].

SCHEME 1
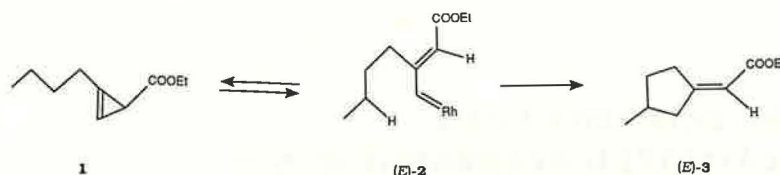
E Configuration at C(4), in turn, corresponds equally to formation of the thermodynamically most stable product. The other stereoisomers (2Z,4E)-6 and (2E,4Z)-7 also occur, but in much lower yield, while the 2Z,4Z isomer is not observed. In contrast, under catalysis with $[Rh_2(OAc)_4]$[15] or $[Rh_2(pfb)_4]$[16], the 1,2-hydrogen migration of carbenes often predominantly affords the less stable Z-configurated olefins. The formation of the allene 9 is readily rationalized by 1,2-migration of the olefinic hydrogen of 4. The occurrence of allenes upon pyrolysis of cyclopropenes has been reported in the literature[17]. The origin of the acetylene 8 is unknown. It could derive from an intermediate biradical[18]. However, more recent work on pyrolysis of 3,3-dimethylcyclopropene suggests the involvement of a vinylidenecarbene as more likely[19]. Acetylene formation has been observed in the pyrolysis of other cyclopropenes[20,21].

SCHEME 2
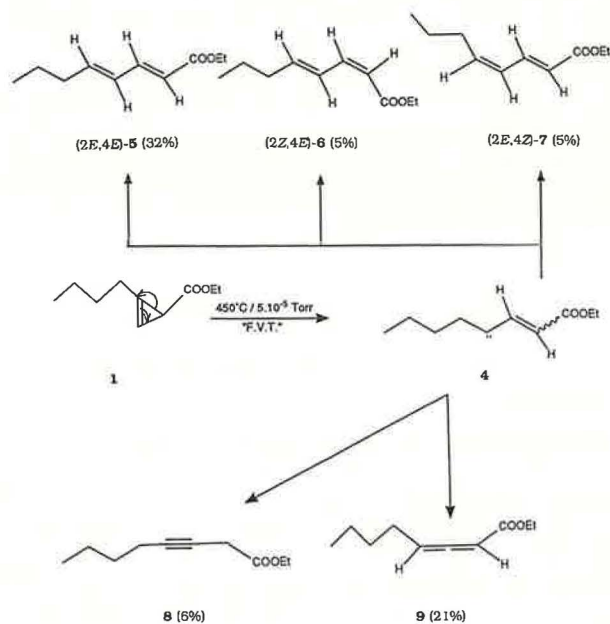
The photochemical rearrangement of 1 was carried out at 185 nm in a Suprasil A Quartz reactor under N_2 at −15 °C. The reaction was interrupted after low conversion owing to formation of polymeric material which could not be suppressed. The allene 9 (10%) was the only isolable product. In addition, acetylene 8 was identified as a secondary product in trace amounts in the ¹H NMR of the crude reaction mixture. Dienes 5-7 were not detected. If they were formed, they must have decomposed (polymerized) during irradiation. These results are consistent with those obtained in the photolysis of other cyclopropenes[21,22], where products derived from vinylcarbenes are observed upon direct irradiation.

2. THERMOCATALYTIC REARRANGEMENT IN THE PRESENCE OF Rh(II) AND Cu(I)

The products of the rearrangement of ethyl 2-butylcycloprop-2-ene-1-carboxylate, 1, in the presence of Cu(I) $[[CuCl·2 MeCCSi(Me)_3]]$[23] or Rh(II) $([Rh_2(pfp)_4])$[24] differ from those of the thermal and photochemical reactions. With both metals the less substituted cyclopropene single bond is cleaved, whereby the less substituted (terminal) vinylcarbene forms. The configuration of the carbenes obtained from the metals is, however, different (see scheme 3). The furan 11, which results from Cu(I)-catalyzed decomposition derives from a vinylcarbene (Z)-10 in which the carboxylate group and the carbenic centre are cis. An analogous formation of a furan upon rearrangement of a cyclopropene-1-carboxylate with Cu(I) has been observed in the past[23]. In contrast, the cyclopentylidene (E)-3, which is obtained in the reaction with $[Rh_2(pfb)_4]$, derives from a carbene (E)-2 in which the carboxylate and carbenic centre are trans (see scheme 1). The preferential formation of the trans-configurated metallocarbene 2 in the rhodium-catalyzed reaction may be rationalized on the grounds of steric reasons. In the case of the Cu(I)-catalyzed rearrangement, coordination of the carboxylate group with a vacant coordination site of the metal could be involved. Such coordination may be responsible for the reported exclusive furan formation upon Cu(I)-catalyzed decomposition of ethyl 2,3-diorganylcyclopropenecarboxylates via Z-configurated vinylcarbenes[25]. Trapping of vinylcarbenes generated from cyclopropenes with Cu(I) revealed a preference for Z over E configuration of the carbene, with ratios varying from 1.3:1 (CuCl) to 4:1 $[(PhO)_3P·CuCl]$ according to the ligands. The structure of the dimeric Rh(II) complex does not allow such coordination and, accordingly, the rearrangement products deriving from E-configurated vinylcarbenes predominate with $[Rh_2(pfb)_4]$[9].

3. REVERSIBILITY OF THE Rh(II)-CATALYZED REARRANGEMENT

The reversibility of the ring cleavage was investigated with an enantio-enriched sample of S-configurated 1, which was synthesized by addition of
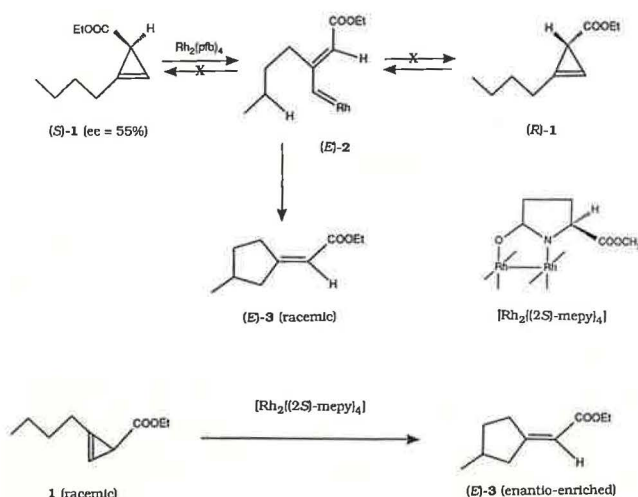
SCHEME 3

EtOOC ... CuCl . 2 MeCCSi(Me)$_3$ / CH$_2$Cl$_2$ 40°C ... (Z)-10 ... 11

1
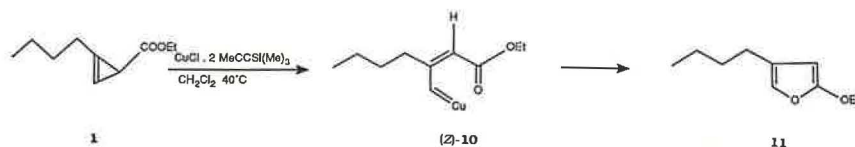
ethyl diazoacetate to hex-1-yne in the presence of a chiral Rh(II) catalyst, [Rh$_2$[(2S)-mepy]$_4$][26] [dirhodium tetrakismethyl 2(S)-pyrrolidinone carboxylate] in 83% yield and with ee of 55%[27]. The cyclopropene was rearranged in refluxing benzene in the presence of 3.4 mol% of [Rh$_2$(pfb)$_4$], and samples were withdrawn after 5, 10, 20, and 30 min, corresponding to 30, 52, 85, and 100% conversion, respectively. The ee of the unreacted cyclopropene was measured by GC, using a chiral Lipodex E column. No change in enantiopurity of **1** was detected. In contrast, the cyclopentylidene was racemic according to GC (Lipodex E column) and HPLC (Chiracel OD column). This shows that the cyclopropene-vinylcarbene rearrangement is irreversible under our reaction conditions, and that the rearrangement proceeds via an achiral intermediate (see scheme 4). This intermediate could be a metallocarbene **2** or a free carbene. In order to distinguish between these possibilities, the rearrangement was carried out in the presence of a chiral Rh(II) catalyst. The presently known catalysts which are most efficient for asymmetric carbenoid reactions have pyrrolidinone or oxazolidinone ligands. They are much less electrophilic than [Rh$_2$(pfb)$_4$] and, accordingly, are less suited for cyclopropene rearrangements. Thus, with [Rh$_2$[2(S)-mepy]$_4$] in refluxing benzene the cyclopentylidene (E)-**3** was formed in only 4% yield, but with an ee of 52%. Increase of the temperature to 110 °C (refluxing toluene) afforded a higher yield of **3** (9%), but an ee of only 32%. A slightly more electrophilic catalyst, [Rh$_2$[(R)-bnp]$_4$] [dirhodium(II) tetrakisbinaphtholphosphate][28] afforded a yield of 25% (ee 5%) at 80 °C, and a yield of 14% (ee 14%) at 40 °C. These results demonstrate unambiguously that the CH insertion occurs from a metal-complexed rather than from a free carbene. The asymmetric inductions achieved in these reactions compare rather unfavourably with those of other intramolecular CH-insertions of diazo esters with [Rh$_2$[2(S)-mepy]$_4$] where ee's in the range of 95% have been reported. However, the pyrrolidinone catalyst is equally inefficient in intramolecular CH-insertions of diazo ketones[29]. A low yield of furan **11** (2%) was also detected in the reaction mixture when **1** was rearranged with [Rh$_2$[(2S)-mepy]$_4$] in refluxing benzene. It derives from the complexed carbene (Z)-**2** (see scheme 5), which prefers cyclization to **11** over insertion to (Z)-**3**.

Our initial mechanism for the [Rh$_2$(pfb)$_4$]-catalyzed rearrangement of **1** to **3** involved reversible formation of an Rh-complexed vinylcarbene **2**[7]. Reversibility was proposed in order to account for the stereo- and regioselectivity of the ring-opening.

Subsequent studies involving systematic variations of the cyclopropene substituents, casted serious doubts on this hypothesis[8,9]. The present experiments show that under our reaction conditions [[Rh$_2$(pfb)$_4$], refluxing benzene] ring cleavage is irreversible. Once reversible formation of the vinylcarbene is eliminated, the reasons for the stereoselectivity of the ring-opening must be addressed again. It may be due either to a stereoselective attack of the catalyst to the less hindered face of the cyclopropene, followed by stereoselective disrotatory ring-opening[9], or to rapid cis/trans isomerization of the vinylcarbene. Such isomerizations reportedly occur thermally[30] or photochemically[31] with Cr(CO)$_5$-complexed vinylcarbenes. There is some evidence that cis/trans isomerizations should be slow in comparison to the product-forming step in the rearrangements catalyzed by [Rh$_2$(pfb)$_4$], but definitive proof is lacking[9]. Unfortunately, the ring-opening of cyclopropenes does not allow the generation of vinylcarbenes having predetermined configuration, so that this question must be investigated by another approach.

SCHEME 4

EtOOC ... Rh$_2$(pfb)$_4$ ... (S)-**1** (ec = 55%) ... (E)-**2** ... (R)-**1** ... (E)-**3** (racemic) ... [Rh$_2$[(2S)-mepy]$_4$] ... **1** (racemic) ... [Rh$_2$[(2S)-mepy]$_4$] ... (E)-**3** (enantio-enriched)

Our observation of irreversible ring cleavage may not be general. Formation of cyclopropenes from vinylcarbenes is a well-established reaction[32] and an example of an [Rh$_2$(OAc)$_4$]-catalyzed transformation of an allylic diazo ketone into a cyclopropene (methyl 2-t-butylcyclopropene-1-carboxylate) via a vinylcarbene has been reported recently[33]. The reaction conditions of this latter transformation were however significantly milder (refluxing CH$_2$Cl$_2$) than those used in the cyclo-

propene rearrangements, and since the substitution pattern of the cyclopropene is different, this result should have no direct implications on our conclusions.

The reaction mechanism dicussed so far makes no mention of possible metallacyclobutenes (12) as reaction intermediates. Evidence for such species has been presented for several transition metal-catalyzed rearrangements of cyclopropenes[34,35], and some of them have been characterized by spectroscopic means[36] or by X-ray crystallography[37]. A mechanism for Rh(I)-catalyzed cyclopropene rearrangements involving electrocyclic ring opening of an intermediate cyclopropyl cation to a complexed vinylcarbene, followed by electrocyclic ring-closure of the latter to a metallacyclobutene has been proposed by Padwa[38], and could also apply to Rh(II). Direct insertion of the metal in one of the single bonds of the cyclopropene is however also concievable. Unfortunately, our present approach provides no insight into the possible involvement of metallocyclobutenes.

SCHEME 5
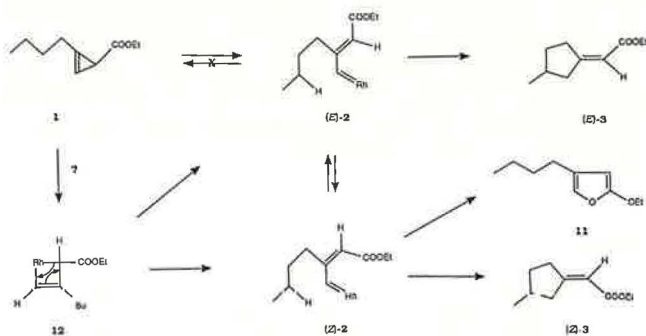
EXPERIMENTAL

GENERAL

See ref. 39.

THERMAL REARRANGEMENT OF 1

Ethyl 2-butylcycloprop-2-ene-1-carboxylate, 1[7] (132.1 mg 0.79 mmol) was subjected to flash vacuum pyrolysis by passing through a 40 cm quartz tube heated to 450 °C at 5×10^{-5} Torr. A mixture of products (107.4 mg) was collected in a cold trap, consisting of 5 (32%), 6 (5%), 7 (5%), 8 (6%) and 9 (21%) (by gas chromatography and NMR). Flash chromatography (silica gel, 1:1 CH$_2$Cl$_2$/hexane) allowed separation of pure 6, a mixture of 7 and 8 (12 mg), and a mixture of 5 and 9 (70 mg). Pure 5 was isolated by column chromatography (silica gel, 1:1 CH$_2$Cl$_2$/hexane).

Ethyl (2E,4E)-octa-2,4-dienoate, 5[11] – IR (CH$_2$Cl$_2$): 3054m, 2965m, 2931m, 1960w, 1706s, 1642m, 1617w, 1421w, 1368w, 1302w, 1143m, 1002m, 896w cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz), δ: 0.92 (t, J=7.4 Hz, 3 H); 1.29 (t, J=7 Hz, 3 H); 1.30-1.50 (m, 2 H); 2.10-2.20 (m, 2 H); 4.19 (q, J=7 Hz, 2 H); 5.78 (d, J=15.5 Hz, 1 H); 6.00-6.24 (m, 2 H); 7.25 ppm (d×d, J=5.2, 15.5 Hz, 1 H). ^{13}C NMR (CDCl$_3$), δ: 13.6 (q); 14.3 (q); 21.9 (t, 35.0 (t); 60.1 (t); 119.2 (d); 128.5 (d); 144.5 (d); 145.1 (d); 167.3 ppm (s). MS, m/z: 169 (6, [M+1]$^+$), 168 (53), 139 (7), 126 (15), 125 (92), 123 (57), 111 (11), 98 (40), 97 (100), 95 (58), 94 (19), 93 (21), 81 (47), 79 (22), 77 (14), 53 (22).

Ethyl (2Z,4E)-octa-2,4-dienoate, 6[11] – ^{1}H NMR (CDCl$_3$, 200 MHz), δ: 0.8-1.0 (t, 3 H); 1.25 (t, J=7, 3 H); 1.40-1.55 (m, 2 H); 2.10-2.30 (m, 2 H); 4.19 (q, J=7 Hz, 2 H); 5.55 (d, J=11.3 Hz, 1 H); 6.06 (d×t, J=15, 7.3 Hz, 1 H); 6.54 (d×d, app. t, J=11.4 Hz, 1 H); 7.25-7.44 ppm (m, 1 H).

Ethyl (2E,4Z)-octa-2,4-dienoate, 7[11] (from mixture with 8) – ^{1}H NMR (CDCl$_3$, 200 MHz), δ: 0.85-1.10 (t, 3 H); 1.20-1.35 (t, 3 H); 1.35-1.50 (m, 2 H); 2.10-2.40 (m, 2 H); 4.05-4.25 (q, 2 H); 5.70-6.30 (m, 2 H); 5.85 (d, J=15.5 Hz, 1 H); 7.60 ppm (d×d, J=15.3, 15.0 Hz, 1 H).

Ethyl oct-3-ynoate, 8[13] – Characteristic ^{1}H NMR signal: 3.22 ppm (t, J=2.5 Hz).

Ethyl octa-2,3-dienoate, 9[12] (from mixture with 5) – IR (CH$_2$Cl$_2$): 1972s, 1718s cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz), δ: 0.87 (t, J=7.2 Hz, 3 H); 1.25 (t, J=7.2, Hz, 3 H); 1.20-1.50 (m, 4 H); 2.10 (m, 2 H); 4.15 (q, J=7.2 Hz, 2 H); 5.50-5.60 ppm (m, J=6 Hz, 2 H). ^{13}C NMR (CDCl$_3$), δ: 13.7 (q); 14.2 (q); 21.9 (t); 27.1 (t); 30.7 (t); 60.7 (t); 88.2 (d); 95.3 (d); 166.3 (s); 212.3 (s).

PHOTOCHEMICAL REARRANGEMENT OF 1

A solution of 1 (206 mg, 206 mmol) in purified, dried and degassed pentane (240 ml) was degassed and irradiated in a Suprasil A-Quartz photolysis apparatus (Heraeus) by means of a low-pressure mercury lamp (Osram HNS, 10 W) at –15 °C. Cooling jacket and lamp compartment were cooled with dry N$_2$. Progress of the reaction was followed by GC. Irradiation was stopped after 4 h, when product formation ceased. The solvent was distilled (0 °C/15 Torr) and the residue (ca. 50 mg) was purified by column chromatography (silica gel, 50:1 cyclohexane/ethyl acetate). The main fraction contained 9 (ca. 20 mg, 10%), identified by ^{1}H- and ^{13}C NMR (see above) and by GC/MS; m/z: 140 (7), 139 (8), 125 (45), 123 (18), 112 (17), 98 (100), 97 (82), 81 (57), 79 (21), 67 (41), 55 (43), 41 (30), 29 (67). A trace amount of acetylene 8 was identified in the ^{1}H NMR spectra of the reaction mixture (t at 3.22 ppm).

REARRANGEMENT OF 1 IN THE PRESENCE OF [Rh$_2$(pfb)$_4$]

To a refluxing mixture of [Rh$_2$(pfb)$_4$] (0.01 mmol) in dry benzene under N$_2$ (5.0 ml) were added simultaneously, by means of a syringe pump, in 15 h solutions of 1 (0.50 mmol) in benzene (5.0 ml) and [Rh$_2$(pfb)$_4$] (0.005 mmol) in benzene (5.0 ml). After the addition, the mixture was refluxed for an additional 4 h and then filtered through a plug of silica gel (CH$_2$Cl$_2$) under N$_2$. The solvent was evaporated, and the yield (44%) was determined by GC, using an authentic sample of 3 as standard. The reaction mixture contained, in addition, unreacted 1 (2%) and ethyl 2-(cyclohepta-2,4,6-trienyl)hept-2-enoate (5 to 40%)[7].

Ethyl (E)-(3-methylcyclopentylidene)acetate, 3 – ^{1}H NMR (CDCl$_3$), 400 MHz), δ: 1.02 (d, J=6.4 Hz, 3 H); 1.28 (t, J=7.2 Hz, 3 H); 1.30-1.38 (m, 1 H); 1.89-1.99 (m, 1 H); 2.00-2.10 (m, 2 H); 2.55-2.73 (m, 2 H); 2.92-3.02 (d×m, 1 H); 4.15 (q, J=7.2 Hz, 2 H); 5.77-5.78 ppm (m, 1 H). For other spectral data, see ref. 7.

REARRANGEMENT OF 1 IN THE PRESENCE OF [CuCl·2MeCCSi-(Me)$_3$]

To CuCl (10.5 mg, 0.106 mmol, Fluka, 99.99% pure) under Ar and 3-(trimethylsilyl)prop-1-yne (24 mg, 0.215 mmol) in degassed CH$_2$Cl$_2$ (5.0 ml) was added under reflux a solution of 1 (209 mg, 1.25 mmol) in CH$_2$Cl$_2$ (5.0 ml) within 15 h. After the addition, refluxing was continued further for 4 h. The mixture was filtered through Celite under N$_2$ (hexane, followed by degassed CH$_2$Cl$_2$). The solvents were evaporated (oil pump). ^{1}H NMR revealed the presence of 11 (53%). Distillation (bulb-to-bulb, 60 °C/0.1 Torr) afforded 70 mg (33%) of 98% pure 11.

2-ethoxy-4-butylfuran, 11 – IR (CH$_2$Cl$_2$): 2930m, 2290w, 1620s, 1575s, 1380m, 950m. ^{1}H NMR (CDCl$_3$, 200 MHz), δ: 0.91 (t, 3 H); 1.38 (t, 3 H); 1.25-1.58 (m, 4 H); 2.32 (d×t, 2 H); 4.04 (q, 2 H); 5.03 (d, J=1.3 Hz, 1 H); 6.64 (q, J=1.2 Hz, 1 H). ^{13}C NMR (CDCl$_3$), δ: 13.8 (q); 14.5 (q); 22.3 (t); 25.3 (t); 31.7

(t); 66.5 (t); 81.8 (d); 126.7 (s); 128.3 (d); 160.6 (s). MS, *m/z*: 170 (10.5, [M+2]⁺), 169 (95.4), 168 (89.5), 141 (12), 126 (69), 111 (11), 98 (100), 70 (19), 55 (36). HRMS, *m/z*: 168.1139 [$C_{10}H_{16}O_2$]⁺, calc. 168.1152).

REARRANGEMENT OF ENANTIO-ENRICHED 1

A solution of enantio-enriched (*S*)-**1** (ee 55%)[27] (47 mg, 0.28 mmol) and [Rh₂(pfb)₄] (10 mg, 0.01 mmol, 3.4%) was refluxed in benzene (10.0 ml) under N_2 with stirring. Aliquots (1.0 ml) were withdrawn after 5 (soln. 1), 10 (soln. 2), 20 (soln. 3), and 30 (soln. 4) minutes, filtered through a plug of silica gel (CH_2Cl_2) and analyzed by GC (chiral Lipodex E column). Composition of solns.: soln 1: **1** (70%, ee 54%), **3** (30%, racemic); soln. 2: **1** (48%, ee 55%), **3** (52%, racemic); soln. 3: **1** (15%, ee 54%), **3** (85%, racemic); soln. 4: **1** (0%), **3** (100%, racemic).

REARRANGEMENT OF 1 IN THE PRESENCE OF CHIRAL Rh(II)-CATALYSTS

To [Rh₂[(2*S*)-mepy]₄][26] (8.0 mg, 0.01 mmol) in refluxing benzene (10.0 ml) was added **1** (60.2 mg, 0.36 mmol) in benzene (5.0 ml) in 15 h. After the addition, stirring and heating were continued for 75 h, until all **1** had disappeared. The mixture was filtered through silica gel (CH_2Cl_2). After bulb-to-bulb distillation (120 °C/0.01 Torr) a complex mixture of products containing **3** (4%, by GC) and **11** (2%) was obtained. The ee of **3** was determined by GC (Lipodex column) to 52%. When the reaction was carried out in refluxing toluene (110 °C) reaction was complete in 20 h, and it afforded 9% of **3** with an ee of 32% and 7% of **11**.

With [Rh₂(*R*-bnp)₄][28] in refluxing benzene the yield of **3** was 25% (ee 5%) after 17 h. At 60 °C, a yield of 21% (ee 8%) was obtained after 18 h. When the reaction was carried out at 40 °C, the yield of **3** was 14% (ee 14%) after 48 h. The ee of **3** obtained in the reactions with [Rh₂(*R*-bnp)₄] was determined by HPLC (Chiracel OD column, solvent 200:1 hexane/isopropanol).

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