Asymmetric Induction in the Pyrolysis of β-Hydroxy Olefins¹

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Pyrolysis of (R)-(-)-(E)-1,4-diphenyl-3-penten-1-ol (3) at 460 °C leads to benzaldehyde and (R)-(-)-3-phenyl-1-butene, formed in 25.6% enantiomeric excess. While the results support a concerted cyclic reaction, the direction of asymmetric induction is not that expected on the basis of a transition state conformation resembling chair cyclohexane. It is concluded that the chair model is a poor one for thermal reactions involving hydrogen transfer.

Among the large family of concerted thermal organic reactions, the fragmentation of β -hydroxy olefins (eq 1) is one of the earliest discovered,² now well-recognized³ subclassifications. The generality of the reaction was established and the accepted mechanism first proposed by Arnold;⁴ the concerted cyclic nature of the process, which may be described as a symmetry allowed suprafacial 1,5-hydrogen migration, has been confirmed by a large body of kinetic⁵ and stereochemical⁶

$$R_{1} - CH = CH - CH_{2} - CR_{2}R_{3} \xrightarrow{}$$

$$= R_{1} - CH_{2} - CR_{2}R_{3} \xrightarrow{}$$

$$= R_{1} - CH_{2} - CH_{2} + R_{2}COR_{3} \quad (1)$$

OTT

evidence. The reaction is reversible⁷ and has been extended to β -hydroxyacetylenes.⁸

A stereochemical feature which this fragmentation shares with a number of [3,3]-sigmatropic rearrangements is the possibility of taking place through a transition state of geometry approximating that of either chair or boat cyclohexane (Chart I). In an elegant example provided by Ohloff,^{6b} the

Chart I. Possible Transition State Conformations Resembling Chair and Boat Cyclohexanes



pyrolysis of (+)-terpin-1-en-4-ol to (S)-(+)-2,6-dimethyl-7-octen-3-one (eq 2) is forced to occur via a boat transition



state; normally in sigmatropic rearrangements of acyclic molecules free to adopt either conformation, chairlike conformations are preferred, and β -hydroxy olefin pyrolysis has been specifically proposed to involve the chair conformation.⁸

The transition state geometry of reactions occurring via six-membered cyclic transition states may be deduced by following the stereochemistry of reactant and product double bonds, as in Doering and Roth's⁹ original investigation of the Cope rearrangement. An alternative method to probe transition-state topology is to trace the direction and magnitude of asymmetric induction with a chiral substrate. This method has been used to show that the Claisen,¹⁰ Cope,¹¹ amino-Claisen,¹² orthoester, and Eschenmoser rearrangements¹³ proceed primarily by chairlike transition states. A further conclusion that can be drawn from these investigations is that of the two possible chair forms, that conformation which places substituents on saturated carbons of the reactant in equatorial positions is greatly preferred. It is surprising for a six-membered transition state in which all six atoms have at least some sp² character that the rules of cyclohexane conformational analysis should apply so well, but Perrin and Faulkner have shown¹⁴ that it is possible to predict quantitatively the cis/trans ratios of Claisen and Cope products from the axial/equatorial free-energy differences in substituted cyclohexanes.

We report here the application of the asymmetric induction probe to β -hydroxy olefin pyrolysis and the unexpected finding that the results are not in accord with conformational predictions.

Results and Discussion

The substrate selected for this study was the homoallylic alcohol 3, which could easily be prepared by the Julia-Johnson rearrangement¹⁵ of the cyclopropylcarbinol 2. Alcohol 2 was prepared by methyl Grignard addition to the known¹⁶ cyclopropyl ketone 1 (Scheme I) and solvolyzed in dilute formic acid to afford 3. Although two geometric isomers are possible, the product was homogeneous by TLC and VPC, gave a single crystalline phthalate, and showed a single methyl peak in the NMR spectrum. It had been reported¹⁷ that carbinols of type 2 rearrange specifically to that homoallylic alcohol with alkyl groups cis, and this was confirmed by spectroscopic analysis of 3. The uv maximum at 247 nm (log ϵ 4.19) is consistent with the E configuration, according to Cram's data on the 2-phenyl-2-butenes¹⁸ and related olefin pairs in which the Z isomer absorbs some 8-15 nm lower because of twisting out of coplanarity.¹⁹ Moreover, the chemical shift of the vinyl proton in 3, δ 5.70, is in good agreement with the value calculated by Simon's rules²⁰ (E, 5.80; Z, 5.36).

The phthalate ester of **3** was resolved with α -phenylethylamine and hydrolyzed to afford both enantiomers of **3**. To determine the absolute configuration and optical purity of these samples, each isomer was ozonized to β -hydroxy- β phenylpropionic acid (4). Based on the maximum rotation,



 $[\alpha]$ D 21.1° (c 2.2, ethanol), reported²¹ for 4 and its known (R)-(+) configuration,²² (R)-(-)-3, $[\alpha]^{25}$ D -42.1° (ethanol), is 80.1% optically pure, while (S)-(+)-3, $[\alpha]^{25}$ D 40.3° (ethanol), is 77.7% optically pure.

Pyrolysis was carried out at 460 °C in a Vycor tube packed with glass beads by injecting a toluene or cyclohexane solution of 3 under a positive nitrogen flow and collecting the products at -74 °C. Distillation gave 3-phenyl-1-butene (5), further purified by VPC to afford 51–63% of the pure olefin. From the pyrolysis of (S)-(+)-3 the sample of 5 isolated had $[\alpha]^{24}$ D 1.09°, while pyrolysis of (R)-(-)-3 gave 5 with $[\alpha]$ D -1.26°.

The absolute configuration of 5 has been established as (R)-(-), and from the rotation of the optically pure hydrocarbon²³ (6.39°, neat) the optical purities of the dextro- and levorotatory pyrolysis products are calculated to be 17.1 and 19.7%, respectively. These conclusions were confirmed by oxidation of (R)-(-)-5 to (S)-(+)-hydratropic acid²⁴ (6) of 20.5% optical purity, based on the maximum rotation recorded²⁵ of 81.1°.

Pyrolysis of the optically active homoallylic alcohol 3 consequently furnishes olefin 5 with 25.6% retention of optical activity. Three conclusions from this result may be noted.

(1) The retention of appreciable optical activity during the formation of 5 from 3 provides additional evidence that β -hydroxy olefin pyrolysis proceeds (at least partly) through a cyclic transition state in a concerted reaction, as opposed to, e.g., initial homolytic cleavage to a radical pair followed by hydrogen atom transfer. The observed asymmetric induction (a "self-immolative" asymmetric synthesis²⁶) requires a chiral transition state in which the original asymmetric center in 3 is not lost before exerting its influence on the creation of the new asymmetric center in 5. While Ohloff had provided an earlier example^{6b} of a self-immolative β -hydroxy olefin pyrolysis, the present case is the first involving a nonrigid, acyclic substrate.

(2) The degree of conservation of optical purity, about 25%, is at first sight low by comparison with optical yields found in other thermal reactions which occur via six-membered cyclic transition states, e.g., 94–96% in the Cope rearrangement¹¹ and greater than 90% in the orthoester and Eschenmoser rearrangements.¹³ However, it is of the same order of magnitude as the few published cases involving *hydrogen* transfer in six-membered transition states: 15% optical yield in the 1,5-intramolecular hydride transfer to carbonium ions;²⁷ apparently low optical yields in the intermolecular ene reaction.²⁸ Moreover, those hydride reductions, such as the Meerwein–Ponndorf–Verley and Grignard reductions, which transfer a hydrogen atom in a six-membered cyclic complex containing a metal atom as well also occur with variable but generally low optical yields.²⁹

The low optical yield does not necessarily imply a nonconcerted component to the mechanism, but rather that several transition states of small energy differences, leading to products of opposite configuration, are available. It appears that in this case, and possibly the other hydrogen-transfer reactions cited above, the presence of a hydrogen atom in the cycle results in marked lowering of energy differences between puckered transition-state conformations, and perhaps in flattening of these conformations.

(3) The four transition-state conformations for pyrolysis of (R)-(-)-3 resembling chair and boat cyclohexanes are shown below:





On the basis of the published cases cited earlier, in which product formation seems to be governed by principles of cyclohexane conformational analysis, it would have been anticipated that conformation 7, a chairlike conformer with equatorial phenyl, would be the preferred transition state, leading to a predominance of the S enantiomer of 5. The observed preference for (R)-5 is the first case of a thermal rearrangement involving a six-membered cyclic transition state in which the direction of asymmetric induction is incorrectly predicted by conformational arguments.

What is responsible for this failure of conformational prediction? It should be noted, first of all, that the energy differences involved are quite small; $\Delta\Delta G^{\pm}$ for a reaction giving 25.6% asymmetric induction at 460 °C corresponds to 0.76 kcal/mol. Mislow has cogently warned of the dangers of predicting the direction of asymmetric induction when the energy differences are small and the transition state conformation imperfectly understood.³⁰ In the present case, the substitution of oxygen and hydrogen for two of the carbon atoms in the cyclohexane model, as well as the ring flattening induced by the sp² carbons, conspire to severely weaken the validity of the model. The 1.3-diaxial interactions which are responsible for the normal preference of equatorially substituted cyclohexanes vs. their axially substituted conformers are absent in transition states 7 and 8, and Dreiding models reveal no obvious preference for either. In any case, the cyclohexane model which has served so well for [3,3]-sigmatropic rearrangements is apparently a poor model for the six-membered cycles involved in thermal hydrogen transfer.

Experimental Section³¹

Methylphenyl(2-phenylcyclopropyl)carbinol (2). The Grignard reagent was prepared in the usual way from 0.9724 g of magnesium turnings and 5.68 g of methyl iodide in 30 ml of ether. To this solution was added an ethereal solution of 7.0 g of 1-benzoyl-2-phenylcyclopropane¹⁶ and the mixture was stirred for 1 h, then heated to reflux for 20 min. The reaction mixture was hydrolyzed with saturated aqueous NH₄Cl, the layers separated, and the aqueous layer extracted with ether. The combined ether solutions were washed with water, dried (MgSO₄), and distilled, yielding 6.27 g (82%) of **2**: bp 147–155 °C (0.4 mm); ir (neat) 3450, 3000, 1610, 1500, 765, 700 cm⁻¹; NMR (CCl₄) δ 7.15 (m, 10 H), 2.60 (br s, 1 H, OH), 1.95 (m, 1 H), 1.4 (s, 3 H), 0.9 (m, 3 H); t_R 21.5 on a 10 ft × 0.125 in. Carbowax column, 160 °C, 80 psi He.

Anal. Calcd for $C_{17}H_{18}$ O: C, 85.67; H, 7.61. Found: C, 85.92; H, 7.44. (*E*)-1,4-Diphenyl-3-penten-1-ol (3). A mixture of 2.0 g of 2, 90 ml of water, 36 ml of dioxane, and 0.81 g of formic acid was heated under reflux for 1.5 h, then cooled and extracted with several portions of ether. The combined extracts were washed with water, dried (MgSO₄), and distilled, affording 1.93 g (96%) of 3: bp 145–160 °C (0.4 mm); ir (neat) 3360, 2980, 1600, 1505, 1060, 765, 705 cm⁻¹; NMR (CDCl₃) δ 7.2 (m, 10 H), 5.70 (triplet of quartets, 1 H, J = 7.3 and 1.3 Hz), 4.59 (t, 1 H, J = 6.5 Hz), 2.9 (s, 1 H, OH), 2.5 (triplet of quartets, 2 H, J = 6.5 and 1.15 Hz), 1.85 (s, 3 H); uv (cyclohexane) λ_{max} 247 nm (log ϵ 4.19); t_R 18.0 on a 5 ft \times 0.125 in. Carbowax column, 160 °C, 60 psi He; mass spectrum M⁺ m/e 238.

The hydrogen phthalate was prepared by heating a mixture of 3 (5.88 g), phthalic anhydride (3.67 g), and pyridine (4.1 ml) under reflux for 1.5 h. The mixture was cooled, acidified with 0.1 N HCl, and extracted with ether. The extracts were dried (MgSO₄) and concentrated under reduced pressure, leaving 9.54 g of crude product. This was taken up in a small volume of CHCl₃ and unreacted phthalic anhydride allowed to crystallize; the residue was crystallized from acetic acid-water (9:1) and then from ethyl acetate. The product (8.15 g, 85%) was collected as colorless prisms: mp 130–131 °C; mmp with

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phthalic anhydride (mp 131-132 °C) was 105-112 °C; ir (CCl₄) 3050, 1740, 1700, 1595, 1295, 1135, 705 cm⁻¹; NMR (CDCl₃) δ 12.6 (s, 1 H), 7.3 (m, 14H), 6.15 (t, 1 H, J = 6.8 HZ), 5.75 (t, 1 H, J = 7.2 Hz), 2.9 (m, 2 H), 1.9 (s. 3 H).

Anal. Calcd for C25H22O4: C, 77.70; H, 5.74. Found: C, 77.82; H, 5.56. Resolution of Alcohol 3. A mixture of 45.2 g of the above acid phthalate and 14.17 g of (+)- α -phenylethylamine in 500 ml of ether and 250 ml of acetone was brought to reflux, filtered, and kept in the dark for 24 h. The salt (27.6 g, mp 131-136 °C) which had precipitated was collected and recrystallized seven times from acetone-ether at room temperature, affording 22.3 g, mp 142-143 °C, [α]²⁸D -28.0° (c 1.03, ethanol). The salt was decomposed with 1 N HCl and the phthalate extracted into ether. Removal of the ether left the phthalate (16.5 g) as an oil, $[\alpha]^{25}$ D -9.22° (c 7.0, ethanol).

The combined mother liquors from the recrystallization of the amine salt were concentrated to dryness and decomposed with 1 N HCl as above to furnish 24.2 g of crude phthalate, $[\alpha]^{28}$ D 2.66° (ethanol). This was resolved with (-)- α -phenylethylamine (7.69 g) as described above, recrystallizing the salt five times, to give a salt of mp 142–143 °C, $[\alpha]^{25}$ D 26.07° (c 1.12, ethanol), which yielded 18.2 g of oily phthalate, $[\alpha]^{25}$ D 9.05° (c 7.0, ethanol).

A mixture of the levorotatory phthalate (3.24 g) and 0.84 g of NaOH in 70 ml of ethanol and 130 ml of water was heated under reflux for 7 h, cooled, and extracted with ether. The combined extracts were washed with water, dried (MgSO₄), and distilled to yield 1.54 g (77.7%) of (-)-3, $[\alpha]^{25}$ D -42.1° (c 5.69, ethanol).

Hydrolysis of the dextrorotatory phthalate in the same way gave (+)-3, in 97% yield, $[\alpha]^{26}$ D 40.32° (c 6.51, ethanol).

Ozonolysis of 3. A solution of 1.1 g of (-)-3, $[\alpha]^{25}D$ -42.1°, in 25 ml of CH_2Cl_2 was ozonized in a Welsbach Model T-408 ozonator at 74 °C, using an ozone flow rate of 0.16 mol/min for 40 min. The solvent was then removed at reduced pressure, 3.1 ml of 90% HCOOH and 3.0 ml of 30% H_2O_2 were added, and the mixture was heated to reflux for 1 h. The reaction mixture was concentrated under reduced pressure, and the residue was taken up in 1 N NaHCO_3 and washed with ether, then acidified with HCl and extracted with ether. Concentration of the extracts left 0.585 g (76%) of (R)-(+)- β -hydroxyβ-phenylpropionic acid (4): mp 116-117 °C (lit.²¹ mp 117-118 °C) after crystallization from CHCl₃; ir (KBr) 3000 (br), 1680, 1390, 1260, 1045, 1005, 755, 690 cm⁻¹; NMR (acetone- d_6) δ 7.4 (m, 5 H), 4.8 (t, 1 H), 3.4 (s, 1 H, OH), 2.85 (d, 2 H); $[\alpha]^{24}$ D 16.9° (c 1.73, ethanol); the maximum rotation reported²¹ is 21.1° (c 2, ethanol). The methyl ester, bp 120–128 °C (4 mm, Kugelrohr), $[\alpha]^{25}$ D 16.3° (c 2.39, ethanol), lit. $[\alpha]$ D 18.3° (c 4.78, ethanol), 22c was prepared with ethereal diazomethane.

Ozolysis of the antipode of 3, $[\alpha]^{26}$ D 40.32° (ethanol), by the same procedure gave (S)-(-)-4 in 86% yield, mp 116–117 °C, $[\alpha]^{24}$ D –16.4° (c 3.70, ethanol), methyl ester bp 115–124 °C (2.0 mm, Kugelrohr), $[\alpha]^{25}$ D -16.2° (c 2.1, ethanol).

Pyrolysis of 3. The apparatus used was essentially that described by Bailey and Hewitt³² for ester pyrolysis. A 2×100 cm vertical Vycor tube, with an injection port and gas inlet near the top, was heated by a Lindberg tube furnace. The heated zone was packed with glass beads supported by a constantan wire. The bottom of the tube was connected to a condenser connected in turn to three vacuum traps at 74 °C and a gas bubbler. The temperature was controlled by a calibrated external voltage and thermocouple gauges. Before each run the tube was thermally equilibrated at 450-470 °C for 1 h. During a run the rate of nitrogen flow was held constant, and the product gases were condensed in the first and second traps.

A solution of 1.5 g of (S)-(+)-(E)-1,4-diphenyl-3-penten-1-ol in 2 ml of toluene was injected into the tube at 460-465 °C over a period of 30 min. After the tube had cooled, the tube and traps were rinsed with ether; after removal of the solvent, the dark residue was purified by VPC on a 10-ft Carbowax 20M on Chromosorb W 60/80 column at 140 °C 40 psi He. 3-Phenyl-1-butene (5), 0.425 g (51%), was collected at $t_{\rm R}$ 6 min and redistilled: bp 172–180 °C (Kugelrohr); the product showed a single peak on two different VPC columns (5-ft SE-30 column at 150 °C, $t_{\rm R}$ 4; 10-ft SDC 710 column at 150 °C, $t_{\rm R}$ 10), with retention times identical with those of an authentic sample; the ir spectrum was identical with that reported by Cram;²³ NMR (CCl₄) δ 7.10 (s, 5 H), 5.88 (m, 1 H), 4.95 (m, 2 H), 3.32 (m, 1 H), 1.26 (d, 3 H); uv (hexane) λ_{max} 245 nm (log ϵ 2.98); mass spectrum M⁺ m/e 132; [α]²⁴D 1.09° (c 1.0, ethanol); reported [α]²²D 6.39° (ethanol).²³

Pyrolysis of the antipode of 3, $[\alpha]^{25}D - 42.1^{\circ}$, gave (R) - (-) - 3-phenyl-1-butene in 62% yield, $[\alpha]^{24}$ D -1.26° (c 5.15, ethanol).

Oxidation of 5. To a vigorously stirred solution of 1.243 g of K₂CO₃ in 100 ml of water was added 0.396 g of (R)-(-)-5, $[\alpha]^{24}D$ -1.26°. A solution of 5.13 g of NalO₄ and 0.633 g of KMnO₄ in 100 ml of water was added and the solution adjusted to pH'8.5 with 2 N NaOH. After stirring for 16 h, the solution was extracted with ether. The aqueous layer was acidified with HCl to pH 2.5, NaHSO3 added to destroy the MnO₂, and the solution extracted with ether. The extracts were dried (MgSO₄), concentrated, and distilled to give 0.319 g (71%) of (S)-(+)-hydrotropic acid (6): bp 119–125 °C (4.2 mm, Kugelrohr); $[\alpha]^{23}$ D 16.6° (c 1.1, ethanol); reported $[\alpha]^{20}$ D 81.1° (c 3.108, ethanol).²⁵ The ir and NMR spectra were identical with those of an authentic sample.

Registry No.—1, 1145-92-2; 2, 58692-65-2; (±)-3, 58692-66-3; (±)-3 hydrogen phthalate, 58692-67-4; (-)-3, 58717-80-9; (-)-3 hydrogen phthalate, 58717-81-0; (-)-3 hydrogen phthalate (+)- α -phenylethylamine salt, 58692-69-6; (+)-3, 58717-82-1; (+)-3 hydrogen phthalate, 58717-83-2; (+)-3 hydrogen phthalate (-)- α -phenvlethvlamine salt. 58717-84-3; (R)-(+)-4, 2768-42-5; (R)-(+)-4 methyl ester, 58692-70-9; (S)-(-)-4, 36567-72-3; (R)-(-)-5, 36617-88-6; (S)-(+)-5, 58717-85-4; (S)-(+)-6, 7782-24-3; (+)- α -phenylethylamine, 3886-69-9; (-)- α phenylethylamine, 2627-86-3.

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- ratus and are uncorrected. NMR spectra were recorded on a Varian HA-100 spectrometer by Mr. C. Pape; chemical shifts are reported as δ units, against tetramethylsilane as an internal standard. Ir spectra we on Perkin-Elmer Models 257 and 621 spectrophotometers and uv spectra on a Perkin-Elmer Model 202 spectrometer. Optical rotations were measured on a Perkin-Elmer Model 141 polarimeter; c is expressed as g/100 ml solution. A Varian Aerograph Model 90P gas chromatograph was used in VPC analyses. Elemental analyses were performed at the University of Georaia
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