Decarboxylative Elimination of 2,3-Dibromo-3-phenylpropanoic Acid to *E* or *Z* 1-Bromo-2-phenylethylene (β-Bromostyrene)

An Experiment Illustrating Solvent Effect on the Stereochemical Course of a Reaction

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The nature of the solvent has often a determining influence on the course of an organic reaction. A classical laboratory experiment illustrates the solvent dependence of reaction kinetics[1], but there is a lack of examples demonstrating that the nature of the reaction products may also depend on the solvent. In the simple laboratory experiment presented here, the same reaction selectively leads to either one or the other of the *E* and *Z* isomers of the product, depending on the solvent in which this reaction is performed.

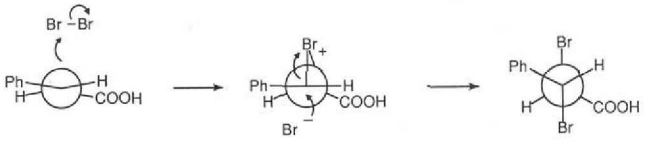
The preparation of 1-bromo-2-phenylethylene consists in stereospecific bromination of (*E*)-cinnamic acid, followed by decarboxylative elimination of the resulting bromoacid; the latter reaction leads to (*Z*)-β-bromostyrene as practically the only product when it is run in butanone, whereas in water the major product is the *E* isomer.

$$PhCH{=}CHCOOH + Br_2 \rightarrow PhCHBr{-}CHBrCOOH$$

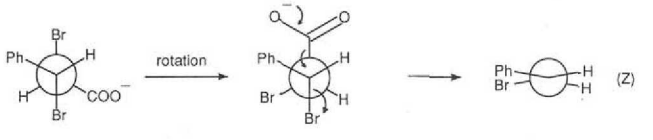
$$PhCHBr{-}CHBrCOOH \xrightarrow[\text{butanone}\ \text{water}]{CO_3^{2-},\ \Delta} \text{Ph-Br} + \text{Ph-Br}$$

The stereochemical course of these reactions can be easily rationalized in terms of well-known types of mechanism, as shown in the following schemes (Newman representations):

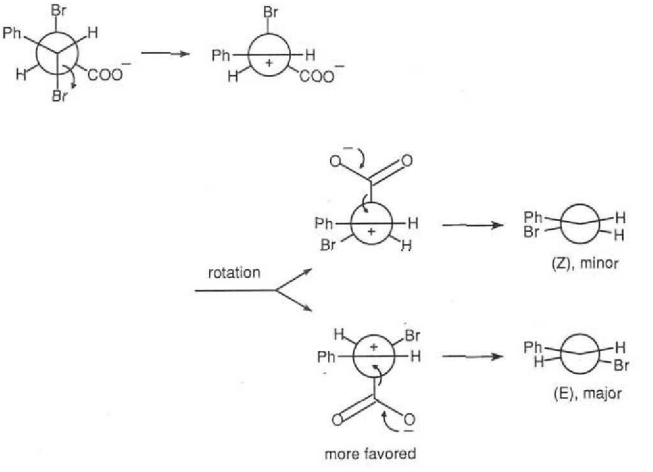
(1) *Anti addition of bromine to the double bond of* (*E*)-cinnamic acid, leading to (*RS*, *SR*)-2,3-dibromo-1-phenylpropanoic acid:



(2) Decarboxylative elimination:
In butanone:



In water:



In both solvents the first step is deprotonation of the acid by carbonate ion to give the carboxylate, which then eliminates Br^- and CO_2. If the polarity of the solvent is low or intermediate, as is the case for butanone, elimination of CO_2 and Br^- occurs in a single-step, concerted reaction (E2 type). In order to provide the most favorable geometry for the corresponding transition state (i.e., maximal overlap between the occupied σ orbital of the cleaving C–C bond and the empty σ^* orbital of the C–Br bond) the bromine substituent and the carboxyl group must be in anti position to each other, leading exclusively to the *Z* isomer.

In a highly polar solvent such as water, bromide loss occurs first (E1 type) to give the intermediate zwitterion, in which the positive charge is stabilized by delocalization on the aromatic ring. Free rotation around the C–C bond is allowed in this intermediate. In a second step carbon dioxide leaves perpendicularly to the plane of the cation (which provides the maximal overlap between the occupied σ orbital of the cleaving C–C bond and the empty p orbital of the positively charged carbon). Of the two possible transition state geometries the one in which the most bulky groups phenyl and bromine are opposite to each other, leading to the *E* isomer, is slightly more favored than the other. Therefore this mechanism leads mainly to the most stable *E* isomer.

The experimental procedure for these reactions has been adapted from described experiments[2,3] in such a way that it proves suitable for undergraduate laboratory course; in particular, butanone is used instead of acetone as a low polarity solvent since its higher boiling point allows a shorter reaction time. The decarboxylative elimination products are easily analyzed via GLC and/or ^1H NMR spectroscopy.

[1] (a) Herbrandson, H. F. *J. Chem. Educ.* **1971,** *48*, 706. (b) Landgrebe, J. A. *Theory and Practice in the Organic Laboratory*, 3rd ed.; Heath: 1982; p 424.

[2] Bromination of cinnamic acid: *Vogel's Textbook of Practical Organic Chemistry*, 4th ed.; Longman: 1978; p 349.

[3] Decarboxylative elimination: (a) Grovenstein, E. Jr.; Lee, D. E. *J. Am. Chem. Soc.* **1953,** *75*, 2639. (b) Cristol, S. J.; Norris, W. P. *J. Am. Chem. Soc.* **1953,** *75*, 2645.

None of the starting materials is expensive; (*E*)-cinnamic acid may be either purchased or synthesized via Perkin reaction, a straightforward laboratory experiment.[4]

Experimental Procedure

Bromination of Cinnamic Acid

A 10 M stock solution of bromine in chloroform is prepared before the laboratory session.

Caution: Bromine and bromine solutions are highly corrosive and toxic. They should be handled with thick gloves under a well-ventilated hood.

In a 150-mL Erlenemeyer flask, commercial *trans*-cinnamic acid (7.5 g, 50 mmol) is dissolved in the minimum amount of chloroform (~50 mL) with magnetical stirring and slight heating in a hot water bath. After complete dissolution the water bath is removed, and the bromine solution (5.5 mL, 1.1 equiv.) is slowly added. The bromine color is gradually discharged, and a white solid appears. After 10–15 min stirring at room temperature, the mixture is cooled in an ice–salt bath to complete crystallization. The resulting dibromide is then filtered, washed with a few milliliters of precooled chloroform, and dried. The yield is 50–70%, mp 204 °C, corresponding to (*RS*, *SR*)-2,3-dibromo-3-phenylpropanoic acid (the (*RR*, *SS* isomer melts at 91–93 °C).

Decarboxylative Elimination

In butanone. A suspension of anhydrous potassium carbonate (2.0 g) in a solution of (*RS*, *SR*)-2,3-dibromo-3-phenylpropanoic acid (2.0 g, 6.5 mmol) in butanone (30 mL) is refluxed 1.3 h with efficient magnetical stirring. The mixture is cooled, poured in water (20 mL), and extracted with diethyl ether (2 × 30 mL). The combined organic phases are dried over anhydrous magnesium sulfate and filtered. The resulting solution is analyzed by GLC. Evaporation of the solvents leads to ~1.1 g of a colorless/yellowish oil, corresponding to a 93% yield.

In water. A solution of (*RS*, *SR*)-2,3-dibromo-3-phenylpropanoic acid (2.0 g, 6.5 mmol) in 10% aqueous sodium carbonate (30 mL) is refluxed 20 min, then cooled to room temperature and extracted with diethyl ether (2 × 30 mL). After drying, filtering, and GLC analysis as above, evaporation of the solvent provides ~0.85 g of a yellowish oil, corresponding to a 70% yield.

Product Analysis

GLC analyses are performed using a 11-ft, 10% SE30 column, oven temperature 160 °C, carrier gas pressure 1.5 bar. Under those conditions the retention times of *Z*- and *E*-1-bromo-2-phenylethylene are, respectively, 8.4 and 9.0 min.

The structures and proportions of the reaction products can be confirmed by ^{1}H NMR; *E* or *Z* structure of the major product obtained from each experiment is easily assigned from the value of the coupling constant between the two vinylic hydrogens.

E isomer: δ = 7.20 (s, 5H), 7.01 (d, 1H, J = 14 Hz), 6.63 (d, 1H, J = 14 Hz) ppm.

Z isomer: δ = 7.7–7.5 (m, 2H), 7.4–7.1 (m, 3H), 6.90 (d, 1H, J = 8 Hz), 6.32 (d, 1H, J = 8 Hz) ppm.

Note also the difference in the pattern of the aromatic ring: in the *Z* isomer the ortho hydrogens are deshielded by the proximity of the bromine atom.

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[4] Yip, M. T.; Dalton, D. R. *Organic Chemistry in the Laboratory;* Van Nostrand: 1979; p 115.