A Mechanistic Puzzle: Variations on Decarboxylative Elimination

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Abstract: This experiment expands on a previous study of decarboxylative elimination. A number of cinnamic acids were subjected to alkene bromination. The resulting dibromides were given to pairs of students, who treated the acids with a weak base in either aqueous or organic solvent. The resulting products of decarboxylative elimination displayed different stereochemistries, depending not only on the conditions employed but also on the substituents present. The differences in stereochemistry of the alkenes formed can be understood in terms of carbocation stabilities as well as the electron-donating and electron-withdrawing effects of substituents on aromatic rings. In this application, the experiment was presented to the students as an open-ended investigation; that is, students did not know what the product of the reaction would be. A variety of instrumental techniques (^{1}H NMR, ^{13}C NMR/DEPT, IR, and GC–MS) was used to arrive at product structures and subsequently propose a reaction mechanism.

Introduction

Laboratory experiments that simulate the research process are valuable tools for endowing undergraduates with an understanding and appreciation of how science works. We describe here an organic chemistry laboratory experiment in which an unfamiliar reaction leads to an unexpected product. Several techniques of instrumental analysis are used in concert to arrive at the assignment of a chemical structure, a typical activity in organic chemistry. Upon reflection, the reaction makes chemical sense to the students. Furthermore, several different perturbations on the experiment are run, so that different students get unique results, an important factor in ensuring that students can make discoveries of their own (discovery-based experiments). Apart from this factor, these perturbations serve to illustrate important concepts in cation stability as well as electron-donating and electron-withdrawing effects on aromatic rings.

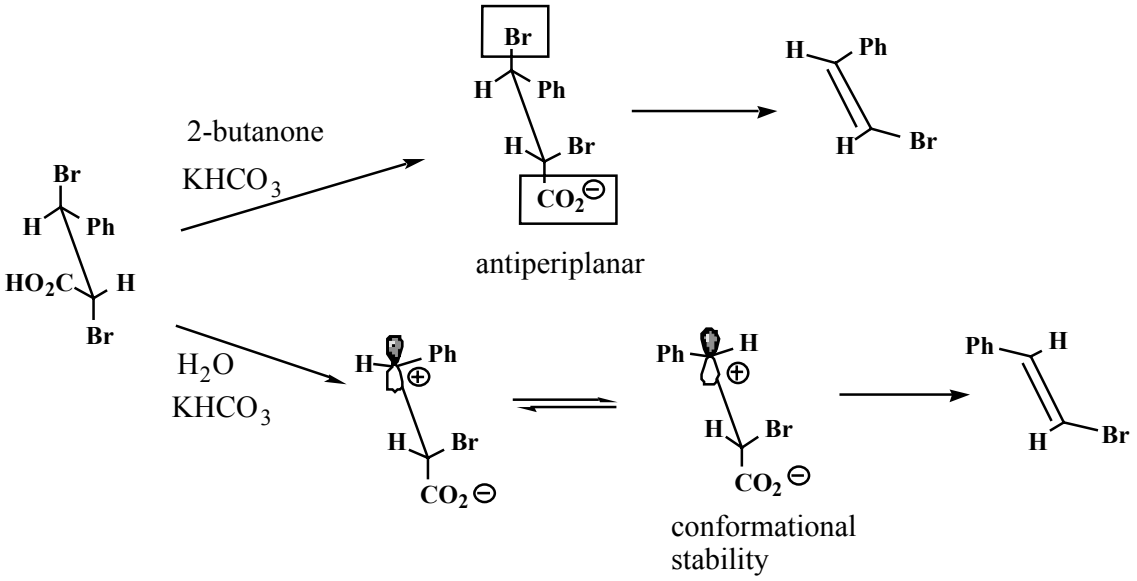
It has been reported previously that the decarboxylative elimination of a racemic mixture of (2*RS*,3*SR*)-2,3-dibromo-3-phenylpropanoic acid affords (*E*)- or (*Z*)-1-bromo-2-phenylethene depending upon the solvent employed (Scheme 1) [1–5]. This observation forms the basis of a classic experiment in physical organic chemistry as outlined in several organic laboratory texts [5]. Use of water, a protic solvent, leads to the *E* isomer via an E1-like mechanism in which loss of bromide ion at the benzylic position is followed by decarboxylation. In contrast, the reaction in 2-butanone forms the *Z* isomer via an E2-like mechanism in which decarboxylation occurs with concomitant loss of bromide. This difference in stereoselectivity stems from the requirement for a periplanar arrangement of proton and leaving group in an E2-like elimination. In the reported experiment, students know the structure of the product beforehand and can make use of the different magnitudes of the NMR coupling constants between cis and trans olefinic hydrogens in determining product stereochemistry.

This procedure can be adapted easily to present a more open-ended exercise in which a variety of instrumental methods are employed in concert to determine the structure of the reaction product, which is not revealed to the students beforehand. In addition, the use of different carboxylic acid derivatives provides sufficient variation to simulate the process of solving a unique chemical problem. Decarboxylative elimination from similar derivatives have been reported previously [3].

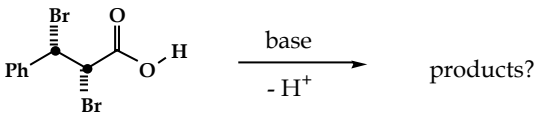
Results and Discussion

Pairs of students were given a sample of an enantiomeric mixture of a (2*RS,*3*SR*)-2,3-dibromocarboxylic acid, prepared beforehand via bromination of the corresponding α,β-unsaturated carboxylic acid. All of the carboxylic acids used were derivatives of cinnamic acid: 4-methoxycinnamic acid, 4-nitrocinnamic acid, 4-chlorocinnamic acid, 3-bromocinnamic acid, and cinnamic acid itself. Each student subjected their sample to treatment with potassium carbonate, either in water or in 2-butanone. A laboratory partner was assigned the same starting material but used the complementary solvent system. Students were not aware of the nature of the reaction being carried out, but were expected to determine the structure of the product and from the structure propose a reaction mechanism (Scheme 2). Product analysis included GC–MS, ^{1}H and ^{13}C NMR spectroscopy as well as a DEPT experiment, and IR spectroscopy[6]. Students were told to share their data with their partner but were responsible for an individual laboratory report.

The use of a variety of instrumental techniques to solve a problem reflects the manner in which instruments are frequently used in real-world research situations. Each of these instrumental methods contributed important data toward the establishment of the product structure. Initially, many students expected to see evidence for loss of HBr from their starting material, because the timing of this experiment coincided with the topic of dehydrohalogenations being covered in lecture;



Scheme 1. Decarboxylative elimination from (2*R*,3*S*)-2,3-dibromo-3-phenylpropanoic acid, showing the stereochemical course of the reaction. Elimination from the *2S,3R* enantiomer gives identical products.



Scheme 2. The problem as presented to students in the discovery-based experiment.

however, IR spectroscopy revealed the absence of C=O and O–H stretches, indicating loss of the carboxylic acid group. To underscore this point, students were asked to analyze their starting materials by IR spectroscopy as well. In addition, isotopic substitution patterns in the mass spectrum confirmed the loss of one bromine atom. The appearance of olefinic resonances in the NMR spectrum supported the formation of a double bond and provided coupling constants as indicated previously [1–5]. In all cases, coupling constants of 8 Hz were observed for the *Z* isomer, while coupling constants of 14 Hz were observed for the *E* isomer. Finally, data from the DEPT experiment clearly showed that each alkene carbon had one attached hydrogen; hence, there is no terminal olefinic CH_2 group, which several students inexplicably assumed would be present at first.

While some of this information may seem superfluous, it proved to be nontrivial in ruling out possible structures proposed by some students. Taken together, these data point to one unique structure for the product of the reaction. In each case, addition of base and heat has resulted in loss of the carboxylic acid moiety as carbon dioxide with concomitant loss of a bromide leaving group β to the carbonyl to form a double bond. Whether the *E* or *Z* isomer results depends on the reaction conditions as well as electronic factors specific to each compound used (Table 1).

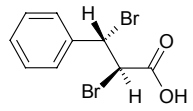
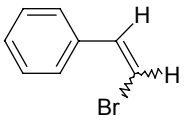
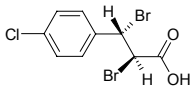
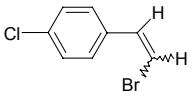
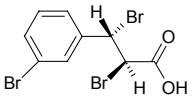
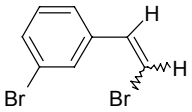
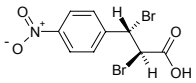
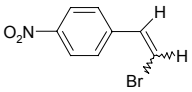
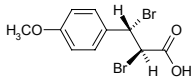
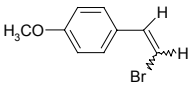
The data in Table 1 clearly illustrate the solvent dependence of the stereospecificity of this reaction. As noted by Mestdagh and Puechberty [2], decarboxylation of (*R,S*)-2,3-dibromo-3-phenylpropanoic acid, **1**, in an aprotic solvent such as 2-butanone occurs via an E2-like mechanism and requires an antiperiplanar arrangement of groups to be eliminated; thus, the (*Z*)-β-bromostyrene predominates (95% by GC analysis). In contrast, heterolysis of the benzylic carbon–bromine bond in water obviates the need for a periplanar arrangement, and so elimination occurs predominately through the more stable conformation of the intermediate carbocation to give the *E* product (85%).

These results, originally reported for **1**, are also observed in the 3'-bromo and 4'-chloro derivatives. For the *m*-bromo derivative, *m*-**2**-Br in Table 1, reaction in 2-butanone gives an E:Z ratio of 5:95; in water the ratio is 60:40. Using the *p*-chloro starting material, *p*-**2**-Cl in Table 1, gives an E:Z ratio in 2-butanone of 5:95 and in water of 83:17.

Structural assignments for the products of these three reactions are greatly enhanced by mass spectrometry. Some students are tempted to hypothesize loss of both bromine atoms, but the 1:1 pattern of molecular ions at *m*/*z* 184 and 182 in the product of decarboxylation of **1** indicates that one bromine atom remains. In addition, a single peak at *m*/*z* 103 corresponds to the loss of both bromine atoms. In the decarboxylation product resulting from *m*-**2**-Br, the 1:2:1 pattern at *m*/*z* 264, 262, and 260 indicates two bromine atoms are present, while the decarboxylation of *p*-**2**-Cl yields a product with a 3:4:1 ratio of molecular ions at *m*/*z* 220, 218, and 216, suggesting the presence of one bromine and one chlorine.

These results indicate a subtle difference in the selectivity of the *m*-bromo compound, *m*-**2**-Br, as compared to **1** and *p*-**2**-Cl. This difference is derived from electronic trends in substituted benzenes as commonly taught in chapters on the chemistry of aromatics; such effects have also been reported for related reactions of cinnamic acid derivatives [7–11]. Chlorine and bromine are both electronegative σ-withdrawing groups that could potentially destabilize carbocations. In addition, both chlorine and bromine are also moderate π donors that can effectively place electron density at positions ortho or para to themselves. As a result, π donation onto the carbocation that is

Table 1. Product Distribution from Decarboxylation of 2,3-dibromocarboxylic Acids

Starting Material	Product	E:Z Ration in water*	E:Z Ration in 2-butanone*
 **1**	 **3**	85:15 (84:16)	5:95 (6:94)
 *p*-**2**-Br	 *p*-**4**-Cl	83:17 (80:20)	5:95 (8:92)
 *m*-**2**-Br	 *m*-**4**-Br	60:40 (65:35)	5:95 (5:95)
 *p*-**2**-NO_2	 *p*-**4**-NO_2	10:90 (5:95)	2:98 (5:95)
 *p*-**2**-OMe	 *p*-**4**-OMe	98:2 (>99:1)	64:36 (67:33)

*determined by gas chromatography and (in parentheses by ^{1}H NMR spectroscopy

para to the chlorine in *p*-**2**-Cl stabilizes the positive charge by delocalization; however, the bromine meta to the benzylic carbocation in *m*-**2**-Br is unable to place electron density adjacent to the positive charge. The net effect in this case is that the *m*-bromine substituent is an electron-withdrawing group that acts to destabilize the benzylic carbocation. Consequently, in water, the E1-like pathway is relatively higher in energy than in the other cases, and so it is accompanied by a significant degree (40%) of E2-like elimination.

An additional example of electronic perturbations on this elimination is illustrated by the reaction of the *p*-nitro derivative, *p*-**2**-NO_2, which gives predominately *Z* stereochemistry regardless of the reaction conditions. This outcome neatly reflects the results of a previous report involving the meta derivative, *m*-**2**-NO_2 [11]. Thus, in water the E:Z ratio was observed to be 10:90, and in 2-butanone it was 2:98. This result is a wonderful illustration of electron-withdrawing effects by a strongly π-accepting aromatic substituent. The *p*-nitro group strongly destabilizes the benzylic cation that would result from loss of bromide ion in an E1-like mechanism, consequently, the reaction proceeds primarily through an E2-like pathway in either solvent. Hence, students working with this compound needed to recognize that the E1-like pathway would be severely restricted due to poor cation stability and that the E2-like elimination would require antiperiplanar elimination.

A nice complementary result is obtained in the decarboxylative elimination reaction of the *p*-methoxy derivative, *p*-**2**-OMe. In this case, elimination in water gives entirely the *E* isomer as expected; however, elimination in 2-butanone still favors the *E* isomer over the *Z* isomer by a 2:1 ratio. Clearly, the cation afforded by heterolysis at the benzylic position is significantly stabilized by π donation from the *p*-methoxy group, leading to a lower energy pathway for E1-like elimination even in an aprotic solvent.

In conclusion, this experiment represents an investigation of a mechanism in which there is sufficient variation to preserve a "discovery" aspect for all the students involved. Alternatively, the data could be combined into a larger project, in which the effects of different aromatic substituents on the course of the reaction are outlined and explained. In other variations, the σ-withdrawing versus π-donating abilities of different substituents could be separated from the positional dependence of resonance effects by using other compounds, such as the *p*-bromo or *m*-chloro derivatives. In all of these cases, an array of instrumental techniques is used to clearly determine product structure and stereochemistry. This effort provides the students with a challenging chemical problem, as well as practice with spectroscopic analysis.

Experimental

General Procedures. Reagents and starting materials were obtained from commercial suppliers and used without further purification. All melting points were determined using a Mel-Temp capillary-melting-point apparatus. A Varian Gemini 2000 NMR spectrometer (300 MHz) was used for all proton and carbon NMR spectra. Unless otherwise noted, the solvent employed was $CDCl_3$, and chemical shifts are reported relative to deuterochloroform (7.26 ppm for ^{1}H, 77.0 ppm for ^{13}C). Infrared spectroscopy was performed using diffuse reflectance with KBr mull on Mattson Galaxy 3000 spectrometers. Mass spectra were determined using a Varian Saturn 2000 GC–MS with Varian 8200 autosampler. GC–MS samples were prepared in pesticide grade dichloromethane at an approximate concentration of 1 ppm. Gas chromatography was performed under isothermal conditions at a 240 °C oven temperature on a Shimadzu GC-8A chromatograph. Chromatograms were run using 10% OV-210 on Chromsorb WAW in a 6-foot column with 3.25 kg/cm^2 carrier-gas pressure. Samples were prepared by diluting extracts in TBME to an approximate concentration of 1 ppt. Typical retention times for the β-bromostyrenes ranged from 3 to 6 min; however, in the case of the parent compound in the series, **3**, retention times were just under 2 min; improved resolution in this case was found at 220 °C with 2.40 kg/cm^2 carrier-gas pressure, with retention times around 7 min.

Bromination of Cinnamic Acid and Derivatives [12]**.** Sixty millimoles of the carboxylic acid was dissolved in 130 mL of glacial acetic acid with good stirring. Sixty-six millimoles of pyrdinium bromide perbromide was introduced, and the solution was heated in an oil bath at a temperature of 85 ^{0}C for one hour during which time the reaction mixture became homogeneous. Water (ca. 100 mL) was added to the hot reaction mixture until it became cloudy. After cooling to room temperature and then with an ice bath, the resulting solid was suction-filtered and washed with water until it was a white solid. Yields were consistently in the 90% range.

2,3-Dibromo-3-phenyl-propanoic acid (**1**). ^{1}H NMR: δ 7.70 (2H, d, *J* = 6.6 Hz), 7.38 (3H, m), 7.09 (1H, d, *J* = 8.4 Hz), 6.44 (1H, d, *J* = 8.1 Hz). IR: 3081 (s, br), 1724 (s) cm^{-1}.

2,3-Dibromo-3-(4′-chlorophenyl)-propanoic acid (*p*-2-Cl). ^{1}H NMR: δ 7.62 (2H, d, *J* = 8.5 Hz), 7.35 (2H, d, *J* = 8.7 Hz), 7.02 (1H, d, *J* = 8.2 Hz), 6.46 (1H, d, *J* = 8.2 Hz). IR: 3038 (s, br), 1718 (s) cm^{-1}.

2,3-Dibromo-3-(3′-bromophenyl)-propanoic acid(*m*-**2**-Br). ^{1}H NMR: δ 7.83 (1H, t, J = 0.9 Hz), 7.60 (1H, dm, J = 7.7 Hz), 7.50 (1H, dm, J = 7.7 Hz), 7.25 (1H, t, J = 7.7 Hz), 7.01 (1H, d, J = 8.2 Hz), 6.50 (1H, d, J = 8.2 Hz) ppm. IR: 3032 (s, br), 1707 (s) cm^{-1}.

2,3-Dibromo-3-(4′-nitrophenyl)-propanoic acid (*p*-**2**-NO_2). ^{1}H NMR: δ 8.24 (2H, d, *J* = 9.0 Hz), 7.82 (2H, d, *J* = 8.5 Hz), 7.15 (1H, d, *J* = 8.2 Hz), 6.68 (1H, d, *J* = 8.2 Hz). IR: 3001 (s, br), 1720 (s) cm^{-1}.

Bromination of 4′-Methoxycinnamic Acid (*p*-2-OMe). To a mixture of 1 mmol of 4-methoxycinnamic acid suspended in 5 mL of ethyl acetate at 0 °C, 1 mmol of bromine was added dropwise. As the reaction proceeded the solution became homogeneous. When addition of bromine was complete the reaction mixture was allowed to stir at room temperature for 0.5 h. The organic layer was washed sequentially with 5% NaHSO3 and brine. The organics were dried with sodium sulfate and removed at reduced pressure to afford **2**-O-Me in 96% yield. ^{1}H NMR (CD_3OD): δ 7.33 (2H, d, *J* = 8.8 Hz), 6.92 (2H, d, *J* = 8.8 Hz), 5.33 (1H, d, *J* = 11.7 Hz), 4.84 (1H, d, *J* = 11.7 Hz), 3.78 (3H, s). mp 154–155 °C.

Decarboxylative Elimination from (RS,SR)-2,3-Dibromocarboxylic Acid Derivatives in Water. All reactions were performed as in the formation of β-bromostyrene **(3)**. To a 5-mL round-bottom flask was added 2,3-dibromo-3-phenylpropanoic acid (0.62 g, 2 mmol), potassium carbonate (0.69 g, 5 mmol) and deionized water (3 mL). The flask was equipped with an air condensor and heated to 90 to 100 °C for 10 min. The cooled mixture was extracted with *t*-butyl methyl ether (2 × 3 mL) and the collected organics were dried with sodium sulfate and concentrated. ^{1}H NMR analysis indicated 84% *E* isomer (85% by GC). ^{1}H NMR: δ 7.31 (5H, m), 7.11 (1H, d, *J* = 14 Hz), 6.77 (1H, d, *J* = 14 Hz). ^{13}C NMR (DEPT): δ 102 (1H), 122 (1H), 124 (1H), 125 (1H), 133 (1H). IR: 3077 (m), 3025 (m), 1607 (m), 941(s), 733 (s) 691 (s) cm^{-1}. GC–MS: *m*/*z* 184, 182, 103, 77.

p-Chloro-β-bromostyrene (*p*-**4**-Cl). ^{1}H NMR analysis indicated 80% E-isomer (83% by GC). ^{1}H NMR: δ 7.30 (2H, d, *J* = 8 Hz), 7.23 (2H, d, *J* = 8 Hz), 7.06 (1H, d, *J* = 14 Hz), 6.76 (1H, d, *J* = 14 Hz). ^{13}C NMR (DEPT): δ 101 (1H), 122 (1H), 124 (1H), 132 (1H). IR: 3077 (s), 2950 (s) 1900 (m), 1744 (m), 1490 (s) cm^{-1}. GC–MS: *m*/*z* 220, 218, 216, 137,101, 85, 71, 57.

m-Bromo-β-bromostyrene (*m*-**4**-Br). ^{1}H NMR analysis indicated 65% E-isomer (60% by GC). ^{1}H NMR: δ 7.42 (2H, m), 7.21 (2H, m), 7.03 (1H, d, *J* = 14 Hz), 6.80 (1H, d, *J* = 14 Hz). ^{13}C NMR (DEPT): δ 103(1H), 120 (1H), 124 (1H), 126 (1H), 127 (1H), 132 (1H). IR: 3075 (m), 2924 (s), 1470 (m), 787 (s), 673 (s) cm^{-1}. GC–MS: *m*/*z* 264, 262, 260, 183, 181, 102.

p-Nitro-β-bromostyrene (*p*-**4**-NO_2). ^{1}H NMR analysis indicated 95% Z isomer (90% by GC). ^{1}H NMR: δ 8.25 (2H, dt, *J* = 8 Hz, 2 Hz), 7.83 (2H, dt, *J* = 8 Hz, 2 Hz), 7.16 (1H, d, *J* = 8 Hz), 6.68 (1H, d, *J* = 8 Hz). ^{13}C NMR (DEPT): δ 106(1H), 119 (1H), 125 (1H), 126 (1H). IR: 3071 (s), 2925 (s), 1930 (m), 1593 (s), 1518 (s), 656 (m) cm^{-1}. GC–MS: *m*/*z* 229, 227, 199, 197, 102, 76.

p-Methoxy-β-bromostyrene (*p*-**4**-OMe). ^{1}H NMR analysis indicated 100% E-isomer. ^{1}H NMR: δ 7.22 (2H, d, *J* = 8.8 Hz), 7.03 (1H, d, *J* = 13.9 Hz), 6.86 (2H, d, *J* = 8.8 Hz), 6.60 (1H, d, *J* = 13.9 Hz), 3.80 (3H, s). ^{13}C NMR (DEPT): δ 136 (1H), 128 (1H), 114 (1H), 104 (1H), 55 (3H). IR: 3014 (s), 2964 (s), 2038 (m), 1897 (m), 1610 (s), 1258 (s), 1032 (s) cm^{-1}. GC–MS: *m*/*z* 214, 212, 199, 197, 171, 169, 133, 90, 77, 63.

Decarboxylative Elimination from (RS,SR)-2,3-Dibromocarboxylic Acid Derivatives in 2-Butanone. All reactions performed as in the formation of β-bromostyrene **(3)**. To a 25-mL round-bottom flask was added 2,3-dibromo-3-phenylpropanoic acid (0.62 g, 2 mmol), potassium carbonate (0.69 g, 5 mmol) and 2-butanone (10 mL). The flask was equipped with an air condenser and brought to reflux for 1.25 hours. The cooled mixture was extracted with *t*-butyl methyl ether (2 × 3 mL) and the collected organics were washed with water (2 mL), then dried with sodium sulfate and concentrated. Yield: ^{1}H NMR analysis indicated 94% Z isomer (95% by GC). ^{1}H NMR: δ 7.69 (2H, dt, *J* = 7 Hz, 2 Hz), 7.37 (3H, m), 7.08 (1H, d, *J* = 8 Hz), 6.77 (1H, d, *J* = 8 Hz) ppm. ^{13}C NMR (DEPT, $CDCl_3$): δ 102(1H), 121 (1H), 124 (1H), 125 (1H), 134 (1H). GC–MS: *m*/*z* 184, 182, 103, 77.

p-Chloro-β-bromostyrene (*p*-**4**-Cl). ^{1}H NMR analysis indicated 92% Z isomer (95% by GC). ^{1}H NMR: δ 7.62 (2H, d, *J* = 9 Hz), 7.34 (2H, d, *J* = 9 Hz), 7.02 (1H, d, *J* = 8 Hz), 6.46 (1H, d, *J* = 8 Hz) ppm. ^{13}C NMR (DEPT, $CDCl_3$): δ 103(1H), 124 (1H), 126 (1H), 127 (1H). GC–MS: *m*/*z* 220, 218, 216, 137,101, 85, 71, 57.

m-Bromo-β-bromostyrene (*m*-**4**-Br). ^{1}H NMR analysis indicated 95% Z isomer (95% by GC). ^{1}H NMR: δ 7.83 (1H, t, J = 2 Hz), 7.60 (1 H, d, J = 8 Hz),7.46 (1H, ddd, J = 8 Hz, 1 Hz, 1 Hz), 7.25 (1H, t, J = 8 Hz), 7.01 (1H, d, J = 8 Hz), 6.49 (1H, d, J = 8 Hz) ppm. ^{13}C NMR (DEPT): δ 104(1H), 123 (1H), 125 (1H), 126 (1H), 127 (1H), 128 (1H) ppm. GC/MS: m/z 264, 262, 260, 183, 181, 102.

p-Nitro-β-bromostyrene (*p*-**4**-NO_2). ^{1}H NMR analysis indicated 95% Z isomer (98% by GC). ^{1}H NMR: δ 8.25 (2H, dt, J = 8 Hz, 2 Hz), 7.83 (2H, dt, J = 8 Hz, 2 Hz), 7.16 (1H, d, J = 8 Hz), 6.68 (1H, d, J = 8 Hz) ppm. ^{13}C NMR (DEPT): δ 106(1H), 119 (1H), 125 (1H), 126 (1H) ppm. GC/MS: m/z 229, 227, 199, 197, 102, 76.

p-Methoxy-β-bromostyrene (*p*-**4**-OMe). ^{1}H NMR analysis indicated 33% Z isomer. ^{1}H NMR: δ 7.67 (2H, d, J = 8.6 Hz), 6.99 (1H, d, J = 8.1 Hz), 6.91 (2H, d, J = 8.8 Hz), 6.30 (1H, d, J = 8.0 Hz), 3.82 (3H, s) ppm. GC/MS: m/z 214, 212, 199, 197, 171, 169, 133, 90, 77, 63.

Safety and Disposal Information.

Potassium carbonate: Irritating to skin, eyes, and respiratory tract. Aqueous wastes can be neutralized and disposed of in sewer.

2-Butanone: Extremely flammable. Harmful if inhaled or absorbed through skin. Affects central nervous system. Flammable, nonhalogenated wastes can be collected together and sent to chemical waste disposal facility.

t-Butyl methyl ether: Extremely flammable. Harmful if swallowed, inhaled, or absorbed through skin. May affect central nervous system, blood, kidneys. Flammable, nonhalogenated wastes can be collected together and sent to a chemical waste disposal facility.

Sodium sulfate: Mildly toxic by ingestion. Nonhazardous, solid wastes can be collected together and disposed of in trash.

Chloroform ($CDCl_3$): May be fatal if swallowed. Affects central nervous system, cardiovascular system, liver, and kidneys. Possible cancer hazard. Halogenated wastes can be collected together and sent to a chemical waste disposal facility.

Dichloromethane: May be fatal if swallowed. Affects central nervous system, cardiovascular system, liver, and kidneys. Suspect cancer hazard. Halogenated wastes can be collected together and sent to chemical waste disposal facility.

Note Added on Logistics of Obtaining Data

Students obtained their own IR spectra and GC traces using three gas chromatograms and two infrared spectrometers available in the organic laboratory. Each student prepared and submitted an NMR sample and a GC–MS sample for analysis. The GC–MS samples were loaded into an autosampler and the data were downloaded onto the campus PC network for use by the students. A TA ran the NMR samples and forwarded the students' FIDs to workstations located in computer laboratories for student use (Fourier transform, phasing, integration, peak picking). Because of the time involved in data acquisition, one DEPT experiment was run on a representative sample of each product and plots of the data were available in the laboratory on the day of the experiment.

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12. While not part of the laboratory experiment, this information is included for the purposes of laboratory preparation.