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THE PREPARATION OF cis-CINNAMIC ACID  
DIBROMIDE AND ITS CONVERSION  
TO beta-BROMOSTYRENE

A THESIS

Presented to  
the Faculty of the Graduate Division

by  
Spyros P. Theophilou

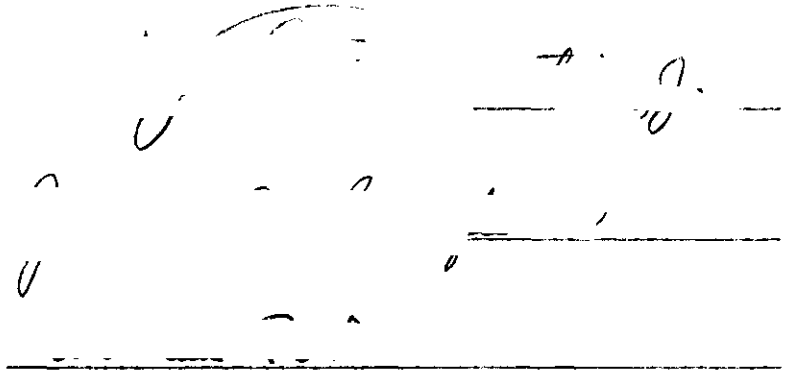
In Partial Fulfillment  
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Master of Science in Chemistry

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THE PREPARATION OF cis-CINNAMIC ACID  
DIBROMIDE AND ITS CONVERSION  
TO beta-BROMOSTYRENE

Approved:

A large, handwritten signature in dark ink is written over several horizontal lines. The signature is somewhat cursive and difficult to decipher, but it appears to consist of several words. There are also some smaller initials or marks scattered around the main signature.

Date Approved by Chairman: June 8, 1954

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## SUMMARY

The purpose of this investigation was to improve the method of preparation of cis-cinnamic acid dibromide and to study the stereochemistry of the conversion of this compound to beta-bromostyrene, in the solvents absolute ethanol, dry acetone, and water.

The initial step of this work was the irradiation of trans-cinnamic acid in a saturated methanolic solution with light from a quartz mercury lamp. The resulting mixture of cis- and trans-cinnamic acids was analyzed by an infrared technique. The conversion to cis-isomer was found to be  $51 \pm 2$  per cent in a 10 hour period of irradiation.

The separation of the two isomers was effected by fractional extraction and crystallization from n-hexane. The crude cis-cinnamic acid was further purified through its aniline salt.

An improved method of preparation of cis-cinnamic acid dibromide was devised. This consisted of addition of bromine to cis-cinnamic acid in glacial acetic which was about one molar in hydrogen bromide. The separation of cis-cinnamic acid dibromide from its higher melting diastereoisomer was effected by extraction with carbon disulfide followed by recrystallization from n-hexane. The yield of cis-cinnamic acid dibromide was 50 per cent of product of m.p.  $88.0-92.5^{\circ}$  which from a mixed melting point curve was calculated to be  $95.5 \pm 1.0$  per cent cis-cinnamic acid dibromide.

Alkali metal salts of cis-cinnamic acid dibromide were converted to beta-bromostyrene by heating in appropriate solvents.

The results are shown in the table below.

Olefins from the Alkali Metal Salts of  
cis-Cinnamic Acid Dibromide

Solvent	Composition of cinnamic acid dibromide % <u>cis</u> -dibromide	Yield of <u>beta</u> - bromostyrene %	Composition of <u>beta</u> -bromostyrene	
			<u>cis</u> %	<u>trans</u> %
Acetone	95.5 $\pm$ 1.0	85.0	4.7	95.3
Abs. ethanol	95.5 $\pm$ 1.0	64.7	2.6	97.2
water	91.0 $\pm$ 1.0	64.0	4.8	95.2

Calculations show that all of the cis-beta-bromostyrene formed in the runs in dry acetone and absolute ethanol can be attributed to the trans-cinnamic acid dibromide present in the starting material. For the run in water the product contained about 3 per cent of cis-beta-bromostyrene which is calculated to arise from the cis-cinnamic acid dibromide itself. The greater tendency of cis- over trans-cinnamic acid dibromide to undergo decarboxylative elimination by a stereospecific concerted trans-mechanism is attributed to less steric hindrance in the corresponding transition state for cis-cinnamic acid dibromide.

## CHAPTER I

## DISCUSSION

Preparation of cis-Cinnamic Acid. -- cis-Cinnamic acid was prepared in the present work by irradiation of methanolic solutions of trans-cinnamic acid with ultraviolet light from a quartz mercury arc lamp. This synthesis of cis-cinnamic acid was first effected by Stoermer<sup>1</sup> who irradiated a benzene solution of trans-cinnamic acid for eight days with ultraviolet light to give a 25-30 per cent yield of cis-cinnamic acid (m.p. 58°). Later, Guy<sup>2</sup>, working on infrared absorption and Raman spectra of cis- and trans-cinnamic acids, repeated Stoermer's method of preparation of cis-cinnamic acid. Havinga and Rivard<sup>3</sup> irradiated a dilute solution of trans-cinnamic acid in benzene for six days with a mercury lamp, but gave no statement of yield.

Tanasescu<sup>4</sup>, working on photochemical behavior of o-nitrocinnamic acid, states that a solution of o-nitrocinnamic acid (in ethyl alcohol, acetone, pyridine, ether, etc.) exposed to sun light is rapidly colored red, but although insolation was continued for several weeks there was no further change in the solution. No explanation of these results is given by the author.

---

(1) E. Stoermer, Ber., 42, 4875-71 (1909).

(2) M. J. Guy, Bull. Soc. Chim. (France), 731-42 (1949).

(3) E. Havinga and R. J. F. Rivard, Rec. Trav. Chim., 67, 340-54 (1948).

(4) J. Tanasescu, Bull. Soc. Chim., 41, 1074 (1927).

Vaidya<sup>5</sup> has studied in detail the isomerization of trans- to cis-cinnamic acid using a quartz mercury vapor lamp equipped with suitable filters such that light of only 313  $m\mu$ . was employed. He found that for a 0.003 M aqueous solution the conversion proceeded to 72 per cent cis acid at photochemical equilibrium. The isomerization at the start of the reaction was zero order in trans-cinnamic acid and proceeded with a quantum efficiency of 0.61. From isolation of the product from five days' irradiation of a methanolic solution of trans-cinnamic acid, Vaidya obtained 25-30 per cent yield of cis-cinnamic acid.

In the present work with a non-filtered quartz mercury arc lamp, a somewhat different state of photochemical equilibrium was attained. A plot of the percentage conversion to cis- acid against the time of exposure is given in Figure 1, p. 4. It will be seen that the rate of change is directly proportional to the time of exposure for the first 6 hours, after which it gradually falls off until the equilibrium value is reached. The equilibrium point after 10 hours exposure corresponds to 56 per cent cis- and 44 per cent trans-cinnamic acid; however, these acids constituted only about 91 per cent of the total starting acid, sweet smelling oily by-products being formed. This formation of by-products reduces the effective conversion to  $51.2$  per cent in 10 hours exposure.

Longer periods of exposure increase the extent of by-product formation (13 per cent in 20 hours). Moreover the color of the product deepens with exposure time from colorless to yellow (6 hours) to light

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(5) B. K. Vaidya, Proc. Roy. Soc., (A) 129, 299 (1930).

brown (20 hours). The nature of the by-products was not determined; the sweet odor suggests that in part they consist of esters. Irradiation of crystalline trans-cinnamic acid is known to give cinnamic acid dimers<sup>6</sup> (alpha-Truxillic acid and less beta-Truxillic acid).

A partial separation of cis and trans acids from the mixture of products from 6 hours irradiation was effected by fractional extraction and crystallization from n-hexane. The crude product was isolated in a yield of  $52 \pm 2$  per cent which according to infrared analysis was 76.5 per cent cis- and 20.9 per cent trans-cinnamic acid. Purification through the aniline salt gave  $28 \pm 2$  per cent of 99 per cent pure cis- cinnamic acid (the yield being based on the amount of trans- cinnamic used). An alternative procedure in which carbon tetrachloride was used for the extractions of the cis from the crude cis- trans mixture in place of n-hexane gave similar results but permitted a more ready extraction of the cis- from the trans-cinnamic acid.

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(6) H. Stobbet and F. K. Steinberger, Ber., 55, 2228 (1922).

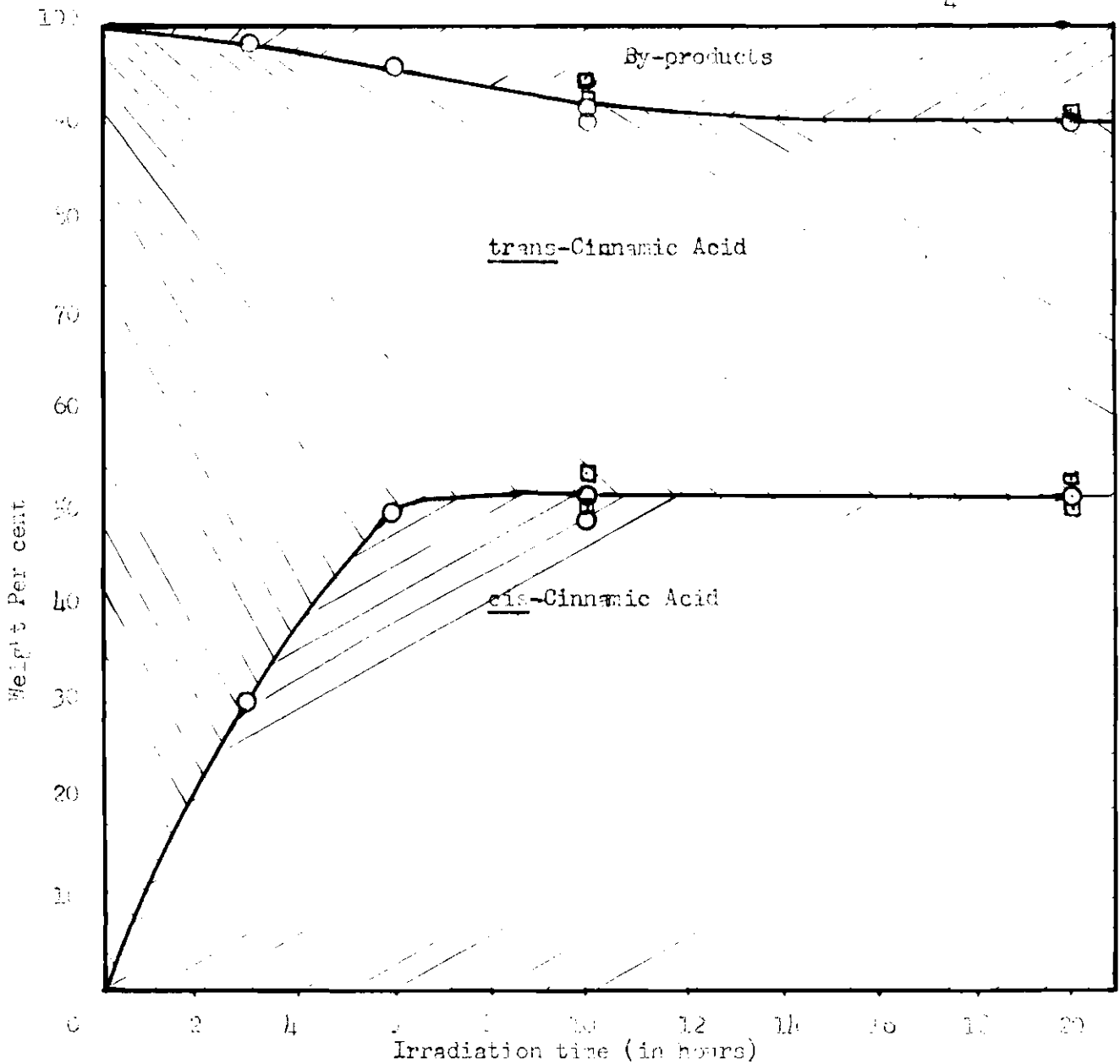


Figure 1. Conversion of trans-cinnamic acid to cis-cinnamic acid upon irradiation. The scale of ordinates measures the amount in per cent by weight and the scale of abscissas gives the time of conversion in hours. The vertical width of a band at a given time measures the per cent by weight of the corresponding compound.

The Preparation of cis-Cinnamic Acid Dibromide.-- Liebermann<sup>7</sup> first reported the preparation of cis-cinnamic acid dibromide (m.p. 91-93°) in yield of about 30 per cent by bromination of cis-cinnamic acid in carbon disulfide in absence of light; the remainder of the product was trans-cinnamic acid dibromide. In the present work under similar conditions, the yield of trans-cinnamic acid dibromide was about 53 per cent; however, at best, only impure cis-cinnamic acid dibromide was obtained in a yield not exceeding 25 per cent of a product of m.p. 55-80°.

The kinetics of the addition of bromine to trans-cinnamic acid in acetic acid as solvent have been reported by Williams<sup>8</sup>. More recently Robertson and co-workers<sup>9</sup> have studied this reaction for both cis and trans-cinnamic acids. Hydrogen bromide catalyzed the addition of bromine to trans-cinnamic acid but not for the cis acid. Since the rate of addition of bromine to trans-cinnamic acid in presence of hydrogen bromide approached the faster rate of addition to cis-cinnamic acid, the authors interpreted their results as indicating that hydrogen bromide isomerized trans-cinnamic acid to the cis isomer. None of the workers, however, has reported any isolation of product from brominations in acetic acid.

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(7) C. Liebermann, Ber., 27, 2039 (1894).

(8) D. M. Williams, J. Chem. Soc., 979 (1932).

(9) P. W. Robertson, N. T. Clare, K. J. McNaught, and G. W. Faul, J. Chem. Soc., 335 (1937).

In preliminary experiments in the present work, addition of bromine to cis-cinnamic acid in acetic acid gave by isolation 17 per cent yield of trans-cinnamic acid dibromide and 25 per cent yield of crude cis-cinnamic acid dibromide (m.p. 84-93°). In a similar experiment but in acetic acid which was one molar in hydrogen bromide, 12 per cent yield of trans-cinnamic acid dibromide and 43 per cent yield of crude cis-cinnamic acid dibromide (m.p. 85-93.5°) were isolated. Accordingly, the latter procedure was adopted for the large scale preparations of cis-cinnamic acid dibromide; in six such runs the yield of trans-cinnamic acid dibromide averaged about 20 per cent, while that of crude cis-cinnamic acid dibromide was 60 per cent of product of m.p. 75-94.5° or 50 per cent yield of product of m.p. 87-94.5°. In these experiments the remainder of the product was a dark colored oil which could not be obtained in a crystalline state under any of the conditions tried. Williams<sup>8</sup> in his work upon trans-cinnamic acid reported that the most probable side reaction is substitution either in the aromatic nucleus of cinnamic acid or, perhaps, in the solvent under the influence of the cinnamic acid.

The purity of cis-cinnamic acid dibromide could not be well ascertained by infrared analysis because this compound has an infrared spectrum (in CS<sub>2</sub>) which is closely similar to that of trans-cinnamic acid dibromide. Consequently a thermal method of analysis by use of a melting point curve was devised and probably was able to give compositions within about one per cent accuracy in the vicinity of the eutectic composition. By this method the 50 per cent yield of product of m.p. 87-94.5° (which upon mixing together gave m.p. 88.0-92.5°) is estimated to contain 95.5 ± 1.0 per cent of cis-cinnamic acid dibromide.

Conversion of *cis*-Cinnamic Acid Dibromide to *beta*-Bromostyrene. -- Recent workers have reported the stereochemistry of the conversion of salts of *trans*-cinnamic acid dibromide, (m.p. 200° dec.) to *beta*-bromostyrene in the solvents water<sup>11</sup>, absolute ethyl alcohol,<sup>10,11</sup> and dry acetone<sup>10</sup>. It seemed of interest, therefore, to ascertain the stereochemistry of the conversion of the diastereoisomeric *cis*-cinnamic acid dibromide (m.p. 93.5-95.0°) to *beta*-bromostyrene under comparable conditions. In addition it was deemed desirable to check the composition of the *beta*-bromostyrene from the decomposition of the sodium salt of *trans*-cinnamic acid dibromide in acetone by infrared analysis since Cristol and Morris<sup>9</sup> analyzed their product by a melting point method. These workers reported that this reaction gave an 84 per cent yield of *beta*-bromostyrene of m.p. -11 to -8° and upon distillation gave 64 per cent yield of product of m. p. -8 to -7°, which value is in good agreement with the recorded melting point<sup>12</sup> of -7° for *cis*- *beta*-bromostyrene. In the present work there was obtained a 93.5 per cent yield of distilled *beta*-bromostyrene which by infrared analysis contained 99.5 ± 0.5 per cent of *cis*- *beta*-bromostyrene.

The results of the present investigation upon the conversion of alkali metal salts of *cis*-cinnamic acid dibromide to *beta*-bromostyrene are given in Table 1. Since it was not practicable according to present

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(10) S. J. Cristol and E. P. Morris, J. Am. Chem. Soc., 75, 2645 (1953).

(11) E. Grovenstein, Jr. and D. Lee, J. Am. Chem. Soc., 75, 2639 (1953).

(12) C. Dufraise, Ann. Chim. (Paris), (9) 17, 199 (1922).

techniques to prepare large amounts of the necessary dibromide entirely free of its diastereoisomer, the results must be interpreted in light of the known amount of this isomer present. This is possible since the behavior of trans-cinnamic acid dibromide is known under the present reaction conditions; the available data are shown in Table 2. In the fourth column of Table 1, the amount of cis-beta-bromostyrene in the product due to the trans-cinnamic acid dibromide present is calculated on the assumption that the two diastereoisomeric cinnamic acid dibromides are converted to beta-bromostyrene in the same yield and that the proportion of isomers of beta-bromostyrene from trans-cinnamic acid dibromide is as shown in Table 2. If the maximum yield of beta-bromostyrene in each solvent as shown in Table 1 is used in the previous calculation along with the yields of beta-bromostyrene shown in Table 2 (these are maximum yields), re-estimated values do not differ by more than 0.5 per cent from those recorded in the fourth column of Table 1.

The difference between the amount of cis-beta-bromostyrene found and that calculated to come from trans-cinnamic acid dibromide is shown in the sixth column of Table 1. This column, therefore, represents the cis-beta-bromostyrene which comes solely from the cis-cinnamic acid dibromide under the reaction conditions. In the solvents acetone and absolute ethyl alcohol cis-cinnamic acid dibromide gives beta-bromostyrene which is within the experimental error of being entirely trans-beta-bromostyrene; that is, the decarboxylative elimination is here, quite stereochemically specific both in dry acetone and in absolute ethanol.

Table 1. Olefins from the Alkali Metal Salts of cis-Cinnamic Acid Dibromide

Run	Solvent	Yield of <u>beta</u> - bromostyrene %	Composition of cinnamic acid dibromide % <u>cis</u> -dibromide	Calculated amount of <u>cis</u> - <u>beta</u> -bromostyrene due to <u>trans</u> -dibromide %	Composition of <u>beta</u> - bromostyrene	
					found % <u>cis</u>	calculated due to <u>cis</u> dibromide % <u>cis</u>
I	Acetone	85.0	95.5 ± 1.0	4.5 ± 1.0	4.7	0
II	Acetone	72.8	95.5 ± 1.0	4.5 ± 1.0	4.7	0
I	Abs. ethanol	64.7	95.5 ± 1.0	3.9 ± 0.9	2.8	0
II	Abs. ethanol	54.5	95.5 ± 1.0	3.9 ± 0.9	3.7	0
I	Water (NaOH)	35.6	95.5 ± 1.0	0.99 ± 0.2	0.1	0
II	Water (NaOH)	34.5	95.5 ± 1.0	0.99 ± 0.2	0.05	0
III	Water (NaHCO <sub>3</sub> )	84.0	90.9 ± 1.0	2.00 ± 0.2	4.9	2.9

Table 2. Olefins from the Sodium Salt of trans-Cinnamic Acid Dibromide

Solvent	yield of <u>beta</u> - bromostyrene %	Composition of <u>beta</u> -bromostyrene %		Ref.
		<u>cis</u>	<u>trans</u>	
Abs. ethanol	58 <sup>a</sup>	86.5	13.5	11
Water	60.5	22	78	11
Acetone	93.5	99.5	0.5	Present work

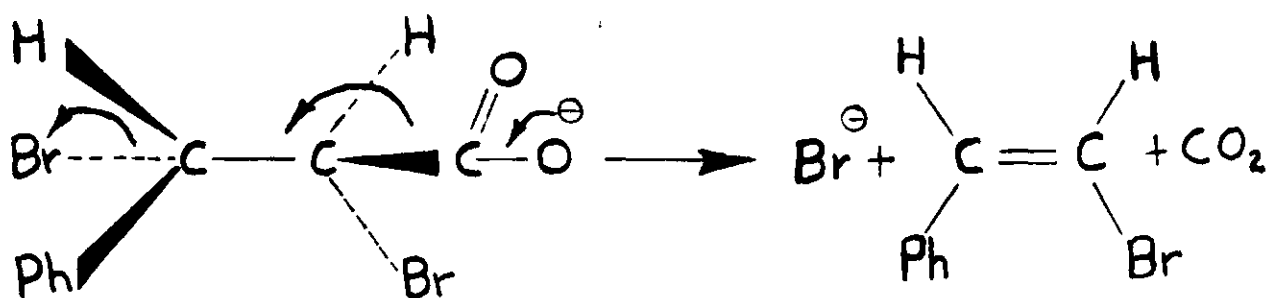
<sup>a</sup> From the data of Cristol and Norris (Ref. 10) for use of sodium acetate as base.

Run I and II in water gave only trans-beta-bromostyrene from cis-cinnamic acid dibromide; however, in these runs a large excess of sodium hydroxide was employed and this alkali might be expected to destroy preferentially any cis-beta-bromostyrene formed. Cristol<sup>13</sup> has reported that the cis- isomer undergoes elimination of HBr with sodium hydroxide in isopropyl alcohol  $2.5 \times 10^5$  times faster than the trans- isomer. Accordingly Run III was made using sodium bicarbonate as base. From this run about 3 per cent of cis-beta-bromostyrene resulted from the salt of cis-cinnamic acid dibromide in water.

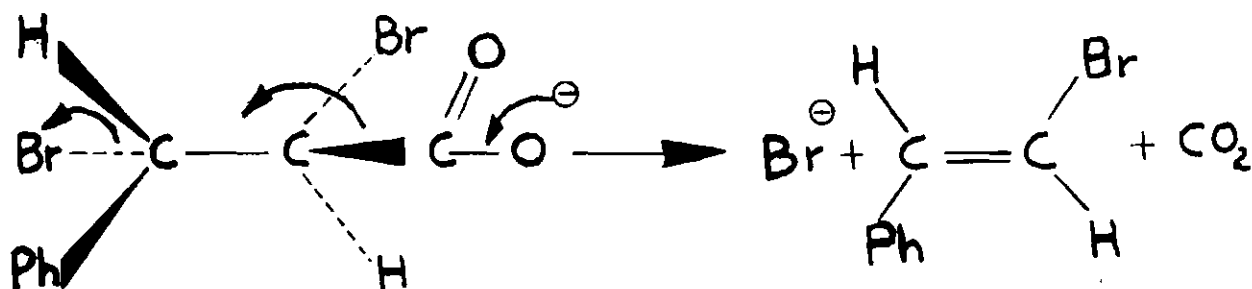
Comparison of the present work upon cis-cinnamic acid dibromide with previous work upon trans-cinnamic acid dibromide (see Table 2) shows that while both diastereoisomers undergo decarboxylative elimination in a stereospecific trans manner in dry acetone, the cis dibromide reacts more stereospecifically in absolute ethanol and in water than the trans dibromide. The apparent explanation is that for the concerted stereospecific trans mechanism of elimination,<sup>10,11</sup> cis-cinnamic acid dibromide has a more favorable transition state for elimination than its diastereoisomer because of less steric hindrance in its transition state (the alpha-bromine and beta-phenyl groups are further apart). See Figure 2 in which one enantiomorph only is shown for each diastereoisomer. The prediction could be made that cis-cinnamic acid dibromide undergoes decarboxylative elimination in acetone, ethanol, and probably water faster than does its diastereoisomer.

---

(13) S. J. Cristol, lecture at the Fourth Conference on Reaction Mechanisms, Bryn Mawr College, Sept. 10, 1952.



trans-Cinnamic Acid  
Dibromide



cis-Cinnamic Acid  
Dibromide

Figure 2. The Stereospecific trans Decarboxylative Elimination of cis- and trans-Cinnamic Acid Dibromides to beta-Bromostyrenes.

## CHAPTER II

EXPERIMENTAL DETAILS<sup>a</sup>

## Materials Used and Methods of Purification

Benzene: Commercial grade was washed three times with concentrated  $H_2SO_4$  and three times with water and distilled, b.p. 79.5-80.5° (atm.press.).

trans-Cinnamic acid: Eastman Kodak Co., was recrystallized from benzene to give white crystals of m.p. 132.5-134.0°. A crystallization from  $CCl_4$  gave similar results.

n-Hexane: Commercial grade, from Matheson Co., Inc.

Cyclohexane: Commercial grade, from Matheson Co., Inc.

n-Pentane: Pure grade, 99 mol. per cent minimum, from Phillips Petroleum Co.

n-Pentane: Commercial grade, from Phillips Petroleum Co. The term n-pentane in this thesis refers to this commercial grade unless the designation "pure" n-pentane is given.

Aniline: Reagent grade, Merck Co., Inc., was distilled from zinc dust, b.p. 181.5-182.5° (atm.press.).

Bromine: Baker's "Analyzed Reagent", J. T. Baker Chemical Co.

Acetic Acid: Glacial commercial grade was refluxed over and distilled from chromium tri-oxide, b.p. 117-118° (atm. press.).

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<sup>a</sup> All melting points are uncorrected and were determined upon samples in capillary tubes with a 360° melting point thermometer in a stirred silicone oil bath.

**Diethyl Ether:** Commercial anhydrous diethyl ether was washed with acidic ( $\text{H}_2\text{SO}_4$ ) solution of ferrous sulfate, dried over anhydrous magnesium sulfate, then distilled, b.p.  $34^\circ$  (atm. press.).

**Hydrogen Bromide:** Anhydrous grade from Matheson Co., Inc.

**Carbon Disulfide:** Commercial grade. For infrared analysis the carbon disulfide was distilled, b.p.  $46^\circ$  (atm. press.).

**Absolute Ethanol:** Commercial absolute ethanol was purified by the method described by Fieser<sup>14</sup> and stored in a brown screw-cap bottle whose cap was lined with tinfoil.

**Acetone:** Commercial grade was dried over anhydrous  $\text{MgSO}_4$ .

**trans-Cinnamic Acid Dibromide:** Half of the amount used came from D. E. Lee's<sup>11</sup> preparation and the rest from the bromination of cis-cinnamic acid. It was recrystallized from chloroform to give white crystals of m.p.  $196-197^\circ$  (dec.).

**Sodium Bicarbonate:** Arm and Hammer, Church & Co.

**Potassium Acetate:** Reagent grade, Merck and Co., Inc. was dried for one hour in vacuum oven at  $70^\circ$ .

**Sodium Hydroxide:** Commercial grade was dissolved in small amount of water, filtered to remove sodium carbonate, and then diluted with distilled water.

**<sup>H</sup>Isooctane:** Practical grade, 99.5+ per cent pure, from Eastman Kodak Co., was washed two times with concentrated  $\text{H}_2\text{SO}_4$  and three times with water, distilled b.p.  $96.0-98.5^\circ$  (atm. press.) and stored over sodium wire.

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(14) L. F. Fieser, "Experiments in Organic Chemistry", 2nd. ed., D. C. Heath and Co., Inc., New York, 1941. p. 359.

Methanol: Commercial grade from Merck Co., Inc.

#### Apparatus for Irradiations

The apparatus used for the irradiations was made by the Hanovia Chemical and Mfg. Co. of Newark, N. J. It consisted of a high pressure quartz mercury arc lamp (type LL) which had an arc length of 30 cm. and a diameter of 2 cm. The lamp operated on about 1000 watts and was run at such a temperature that the current was between 3.8 to 4.2 amperes. Proper cooling was demanded to keep the current in the desired range. This was accomplished in part by having the lamp in an air-conditioned room (for summer operation) with a stream of air blowing over the quartz arc. Additional cooling and protection of the sample being irradiated was effected by running water through the inner cell compartment. A drawing of the quartz cell is shown in Figure 3. The solution of sample was placed in the outer cell compartment which held 325 ml. of solution. The characteristics of the mercury arc and the light obtained therefrom are given in Table 3, the data being supplied by the manufacturer.

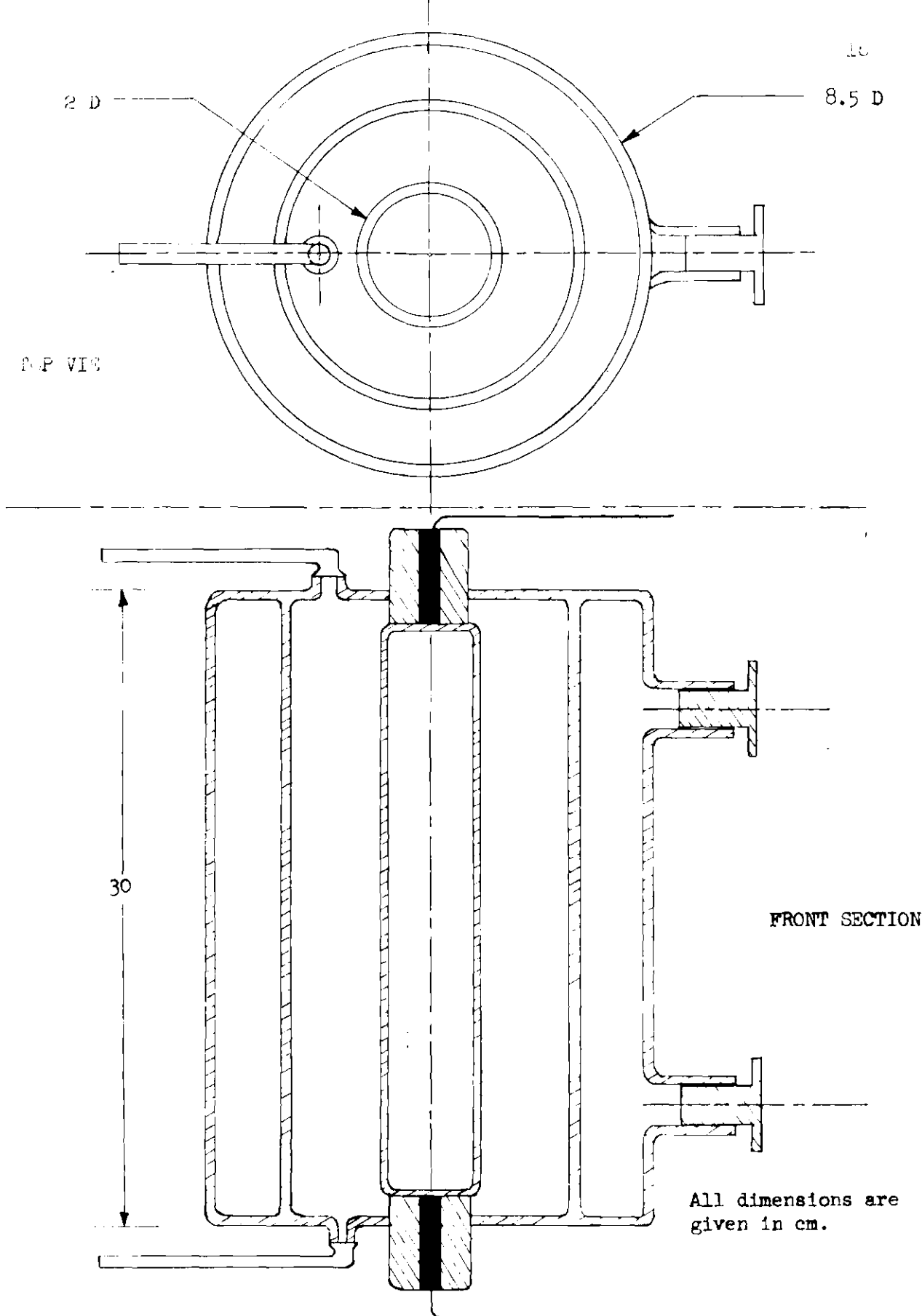


Figure 5. Schematic Diagram of Quartz Cell with Mercury Lamp.

Table 3. Radiation Data\* and Characteristics of Lamp Type LL.

<u>Characteristics:</u>		
Burner tube		range 900-1200 watts
Radiation data applies to		1050 watts
Temperature: quartz tube		380°C
Total radiation (all wave lengths)		790 watts
<u>Spectral energy distribution</u>		
Values given on a per cent basis with total radiation equal to 100 per cent. To find energy at any wave length, take per cent of total radiation above.		
Infrared (bands and continuum)		53.9
Visible	red - 6234 A	0.4
	yellow - 5700 A	6.7
	green - 5460 A	4.8
	blue - 4960 & 4358 A	4.4
Total visible		<u>16.3</u>
Ultraviolet	4045 & 3905 A	3.68
	3660 A	7.80
	3341 A	0.82
	3130 A	5.38
	3025 A	2.92
	2967 A	1.16
2925, 2893 & 2803 A		1.10
2752 & 2700 A		.65
	2652 A	1.85
	2571 A	.65
	2537 A	1.86
2482, 2400, 2360, 2300 A		1.75
1942, 1849 A		.18
Total ultraviolet		<u>29.80</u>
Accuracy of data:	Infrared $\pm$ 1 per cent; visible $\pm$ 5 per cent; ultraviolet: strong bands $\pm$ 8 per cent; weak bands $\pm$ 15 per cent. Data was evened to total to 100 per cent.	

\* The data were supplied by the Research Laboratory of Hanovia Chemical and Mfg. Co. of Newark, N. J.

### Purification of trans-Cinnamic Acid

Eastman Kodak white-label grade trans-cinnamic acid 400 g. (2.7 moles) was refluxed for one hour with four liters of pure dry benzene and then was cooled in an ice-water bath for two hours. A yield of 362 g. (2.45 moles or 90.5 per cent yield) of well-formed white crystals m.p. 132.5-134.0° were recovered after filtration.

### Preliminary Irradiation Experiments

Experiment 1. -- Purified trans-cinnamic acid, 50 g. (0.338 mole), m.p. 132.5-134.0°, in 300 ml. of ethanol was irradiated for 10 hours. Evaporation of the solvent was carried out in an evaporating dish on a water bath with the aid of an inverted funnel, connected to a water-aspirator, over the dish. This experiment was repeated for 54.5 g. (0.368 mole) of cinnamic acid in 325 ml. ethanol for 20 hours. See Figure 1 for the product analysis.

Experiment 2. -- Irradiation of purified trans-cinnamic acid, 72.5 g. (0.480 mole), m.p. 134.5-134.0°, in 325 ml. methanol was conducted for 20 hours. Similar experiments were repeated for 10-hour, 6-hour, and 3-hour periods of irradiation. Evaporation of methanol was performed as mentioned before. From the infrared analysis of the resulting crude products, the per cent of the cis-isomer in the irradiated mixture was plotted against the irradiation time (see Figure 1, p. 4).

An irradiation period of six hours, yielded a 19 per cent transformation while an irradiation period of ten hours yielded a transformation

of 51.5 per cent and that for 20 hours 51.7 per cent (these yields being based upon the amount of starting acid). As a result of these data and in order to economize on time, an irradiation period of six hours in solvent methanol was chosen for preparative purposes.

#### Preparation of cis-Cinnamic Acid.

cis-Cinnamic acid was made by irradiation of a methanolic solution of trans-cinnamic acid with ultraviolet light. From the irradiated mixture of cis- and trans-cinnamic acids, the separation of cis-isomer was effected by several extractions of the mixture with n-hexane (or cyclohexane) and then preparation of the aniline salt of the crude cis-cinnamic acid. Elimination of the cis- acid from its aniline salt was brought about by extraction of the ethereal solution of the salt with hydrochloric acid solution. The detailed procedure is given below.

#### General Procedure for Preparation of cis-Cinnamic Acid

##### 1. Irradiation

Recrystallized trans-cinnamic acid was completely dissolved in 350 ml. of methanol and 5 ml. of this solution titrated with 13.9 ml. of 0.492 N sodium hydroxide to a phenolphthalein endpoint. A 325 ml. portion (calculated from the titration to contain 60 g. trans-cinnamic acid) was irradiated for six hours in the above described ultraviolet light apparatus. Then the methanol was evaporated from a dish on a water bath with an inverted funnel connected to a water-aspirator over the evaporating dish.

##### 2. Isolation

The isolation of cis-cinnamic acid from the irradiated mixtures

was effected by selective extraction of the cis-isomer with n-hexane and by fractional crystallization of the resulting hexane solution. Procedure: After evaporation of methanol from the irradiated mixture of acids, a 485 g. (3.28 moles) portion was extracted with three one-liter portions of n-hexane (at room temperature). The solvent was recovered by distillation and the last 100 ml. of it was evaporated over a water bath; 48 g. (0.324 mole) of yellow colored crystals with a melting point of 53-65° was obtained.

The unextracted crystals were refluxed for two hours with 1.5 liters of n-hexane and the portion of the crystals (224 g. of m.p. 75-120°) which remained undissolved was separated by decantation. The solution upon cooling to room temperature deposited 110 g. of crystals of m.p. 65-95°. From complete evaporation of the mother liquors, 100 g. of yellow crystals of m.p. 48-55° were obtained.

The 224 g. of crystals which remained unextracted in the previous procedure was again refluxed with n-hexane (1 liter) for two hours. There were obtained 145 g. of crystals (m.p. 110-130°) which were undissolved in the hot hexane, 43 g. of crystals (m.p. 80-105°) which crystallized at room temperature from the hexane, and 29 g. (m.p. 48-50°) which were recovered by evaporation of the solvent.

The crystals which were obtained by crystallization of the above two hot n-hexane extracts at room temperature were combined to give 153 g. (110 + 43 g.) of crystals of m.p. 65-105°. These crystals were refluxed for one hour with one liter of n-hexane to give 9 g., m.p. 110-125°, of undissolved crystals, 91 g. of crystals of m. p. 78-110° obtained from cooling the hexane solution to room temperature, and 43 g. of crystals

of m.p. 48-60° recovered by evaporation of the solvent. The 91 g. batch of crystals so obtained was extracted with 800 ml. of boiling n-hexane to give 24 g. of undissolved crystals of m.p. 110-120°, 46.5 g. of crystals of m.p. 82-110° obtained by cooling the solvent to room temperature, and 18 g. of crystals, m.p. 50-60°, from evaporation of the solvent.

The 46.5 g. batch of crystals so obtained was finally extracted with 500 ml. of boiling n-hexane to give 7 g. of undissolved crystals of m.p. 115-125°, 28 g. of crystals (m.p. 90-120°) deposited upon cooling to room temperature, and 11.5 g. of crystals (m.p. 50-65°) from evaporation of the solvent. The 28 g. portion of crystals was combined with crude crystals from another irradiation.

As final results from the 485 g. of starting material there were collected the following products which are shown together with their infrared analyses where determined:

- (1) 249.5 g. of m.p. 48-68°, (76.5 per cent cis- and  
(20.9 per cent trans-cinnamic acid
- (2) 28.0 g. of m.p. 90-120°
- (3) 185.0 g. of m.p. 110-130°, (14.7 per cent cis- and  
(85.2 per cent trans-cinnamic acid.

The infrared analysis of a batch of crystals of m.p. 70-90° gave 55.1 per cent cis- and 44.4 per cent trans-cinnamic acid.

### 3. Purification

The purification of isolated cis-cinnamic acid was successfully accomplished by the formation of its aniline salt<sup>15,16</sup> followed by

(15) The formation of the aniline salt of trans-cinnamic acid fails under the same conditions.  
C. Liebermann, Ber., 23, 2515 (1890).

(16) F. Eisenlohr and W. Hass, Z. Physik Chem., (A) 173, 252 (1935).

decomposition of the salt with hydrochloric acid.

Procedure: In a 4-liter round-bottom flask a portion of 125 g. (0.845 mole) from the above 249.5 g. of crude cis-cinnamic acid (m.p. 48-68°) was dissolved in 600 ml. pure benzene and 100 g. (1.075 moles), of freshly distilled aniline was added. The flask was shaken for a period of 10 minutes; a yellow-colored cotton-like salt was formed. After filtration, the salt was washed with one liter of n-pentane; 82 g. of white salt was obtained with a melting point of 82.5-84.0°. The white aniline salt was dissolved in 500 ml. ether, 40 ml. of concentrated hydrochloric acid with 120 ml. water was added, and the mixture was shaken in a large separatory funnel. The ether layer was separated and washed with two 100 ml. portions of 5 per cent hydrochloric acid and two times with 100 ml. portions of water. The combined aqueous layers were washed with 100 ml. of ether; the ether layer was combined with the first ether extract. The ether solution was dried over anhydrous  $\text{MgSO}_4$  overnight. After filtration, the ether solution was evaporated on a water bath to give 61 g. (0.412 mole) of crystals of m.p. 60-64°. The same procedure applied to a second batch of 130 g. (0.88 mole) of crude cis-cinnamic acid (m.p. 46-68°) gave 75 g. of crystals of m.p. 50-62°. Infrared analysis of a mixture of these crystals (m.p. 58-64°) gave 99 per cent cis- and 1 per cent trans-cinnamic acid.

Purification of Samples of cis- and trans-Cinnamic Acids  
for Infrared Analysis

A portion (18 g.) of cis-cinnamic acid crystals (m.p. 60-64°) purified by the above aniline salt procedure was dissolved in 150 ml. diethyl ether in a 500 ml. separatory funnel. The ether solution was

washed with three 60 ml. portions of 3 N HCl solution and then with two 50 ml. portions of water.  $\text{CaSO}_4$  was used to dry the ether layer. After filtration, the ether was evaporated on a water bath at  $50^\circ$ . Pale brown-colored crystals were obtained.

These crystals were dissolved in 50 ml. boiling n-hexane, an oil remaining undissolved in the solvent; therefore, 100 ml. more of boiling n-hexane were added, but the oil did not dissolve. This solution was then refluxed for half an hour with one teaspoonful of charcoal, filtered hot through a heated sintered-glass funnel, and the charcoal washed with 30 ml. of hot n-hexane. The combined hexane solutions were transferred to an Erlenmeyer flask and cooled in an icebox for 20 minutes. Light yellow crystals were formed and were collected by filtration.

In a further attempt at purification these crystals were dissolved in 40 ml. of ethanol and 55 ml. of distilled water and refluxed with one spoonful of charcoal. Filtration and washing of the charcoal was carried out in a heated sintered-glass funnel. After the solution was cooled in the ice-box, it was filtered to recover crystals. These crystals were covered with a yellow oil which passed through the funnel upon pressing the crystals with a spatula. These crystals were recrystallized once more from 150 ml. boiling n-hexane to yield 5.5 g. very white crystals of cis-cinnamic acid (m.p.  $67-68^\circ$ ).

Once recrystallized trans-cinnamic acid (10 g. of m.p.  $132.5-134.0^\circ$ ) was recrystallized two more times from 100 ml. of boiling pure benzene. Five grams of very white crystals of trans-cinnamic acid, m.p.  $132-133^\circ$ , were recovered.

### Infrared Analysis of cis- and trans-Cinnamic Acids

The infrared spectrophotometer used in the present work was the Perkin-Elmer, Model 21, Recording Infrared Spectrophotometer, a double beam instrument with rock salt prisms. The cells used were 3 mm. cells with NaCl windows. For qualitative and quantitative analysis the machine was zeroed and set at 100 per cent transmission with both cells filled with solvent.

Spectrum in Carbon Disulfide.-- The recrystallized and dried (in vacuum oven at 50° for one hour) trans-cinnamic acid (1.3894 g. m.p. 132-133°) was dissolved in 100 ml. of distilled carbon disulfide in a 100 ml. volumetric flask; likewise 0.6947 g. of purified and dried (in vacuum oven at 35° for an hour) cis-cinnamic acid (m.p. 67-68°) was dissolved in 50 ml. of distilled carbon disulfide in a 50 ml. volumetric flask. The concentration of both solutions was accordingly the same.

Since the solutions proved too concentrated for the 3 mm. cell, 8 ml. of each solution was diluted to 100 ml. with carbon disulfide. The corresponding spectra are given in Figure 4.

Quantitative Analysis.-- On the basis of the above spectra of cis- and trans-cinnamic acid, carbon disulfide was selected as solvent and the absorption maxima at 10.129 and 14.125 microns were selected for the trans isomer and the maxima at 12.080 and 14.435 microns for the cis isomer. The optical densities of solutions of cis- and trans-cinnamic acid at various known concentrations were determined at the above wave lengths, the optical densities being read directly from the recording paper.

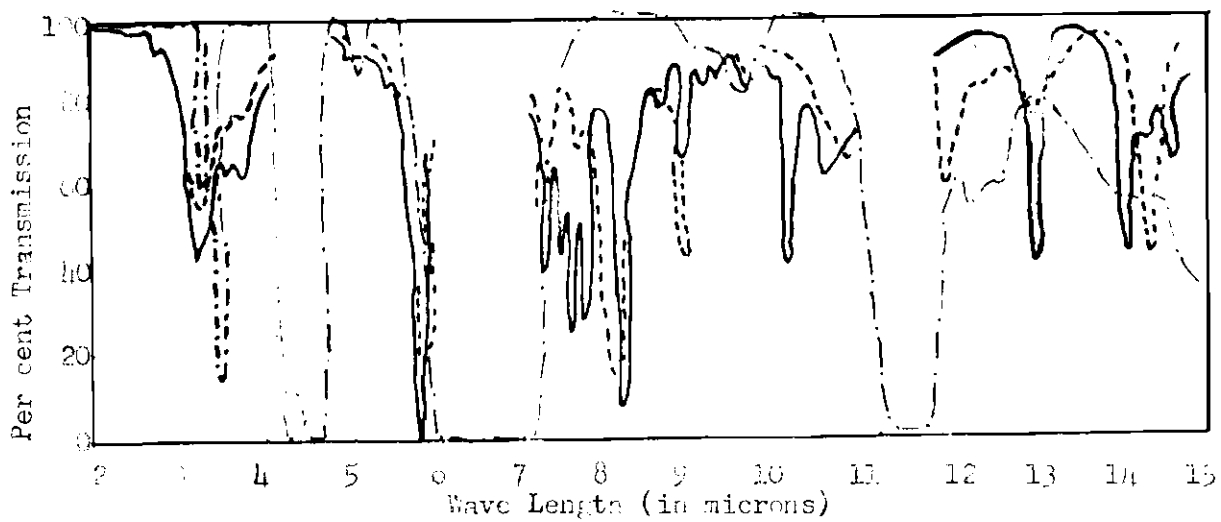


Figure 4. Infrared Spectra: cis-cinnamic acid -----  
trans-cinnamic acid \_\_\_\_\_ carbon disulfide .....  
 Concentration of the solutions was 0.111 g./l. in carbon  
 disulfide with 3 mm. rock salt cell.

From the data of optical densities,  $D$ , the apparent extinction coefficient,  $E$ , was calculated according to the equation:

$$E = D/C$$

where  $C$  = concentration of solutions in g./l.

The data for the extinction coefficients and optical densities are given in Table 4. From this table, it is seen that the extinction coefficients are satisfactorily constant over the range of concentrations studied. Average values of  $E$  were used in the analysis of the unknown samples.

If  $D$  is the total optical density and if  $E_t$  and  $E_c$  represent the extinction coefficients of trans- and cis-cinnamic acids respectively, then at wave lengths  $\lambda$  and  $\lambda'$  the following relationships hold:

$$D = (C_t) (E_t) + (C_c) (E_c) \quad \text{at wavelength } \lambda$$

$$D' = (C_t) (E'_t) + (C_c) (E'_c) \quad \text{at wavelength } \lambda'$$

From these two equations the unknown concentrations  $C_t$  and  $C_c$  may be calculated as follows:

$$C_t = \frac{(E'_c) (D) - (E_c) (D')}{(E_t) (E'_c) - (E_c) (E'_t)} \quad (a)$$

and

$$C_c = \frac{(E_t) (D') - (E'_t) (D)}{(E_t) (E'_c) - (E_c) (E'_t)} \quad (b)$$

The wave lengths  $\lambda$  and  $\lambda'$  must be those at which the cis and trans isomers have different extinction coefficients (at least at one of the wave lengths); accordingly they were chosen at a maximum for the cis acid and at a maximum for the trans acid. Two pairs of wave lengths were used in the present work, namely, 10.129 and 12.980 microns for one

pair and 14.125 and 14.435 microns for the other pair. Data calculated with these pairs are given in Table 5.

Known synthetic mixtures were somewhat more accurately analyzed at the two lower wave lengths and accordingly, this pair of wave lengths only was used for other analyses reported in this thesis. The infrared technique used here for analysis probably was accurate within three or four per cent.

Table 4. Infrared Data of cis- and trans-Cinnamic Acid Solutions for Various Concentrations at the Four Selected Maxima, in 3 mm. Cell.

Wave Lengths (in microns)	Concentration in g./l.	<u>cis</u> - Isomer		<u>trans</u> - Isomer	
		D	E	D	E
10.129	5.5300	0.198	0.0358		
	2.6612	0.095	0.0357		
	1.6608	0.059	0.0355	0.572	0.344
	1.1072			0.380	0.343
	0.6653			0.222	0.330
12.080	5.5360			0.185	0.0334
	2.6612	0.574	0.2157	0.090	0.0338
	1.6608	0.347	0.2089	0.055	0.0331
	1.1072	0.236	0.2131		
	0.6653	0.132	(0.198)		
14.125	5.5360	0.237	(0.0438)		
	2.6612	0.104	0.0391	0.861	0.323
	1.6608	0.064	0.0385	0.530	0.319
	1.1072	0.040	0.0361	0.350	0.316
	0.6653	0.025	0.0375	0.194	(0.292)
14.435	5.5360			0.790	0.143
	2.6612	0.864	0.325	0.384	0.144
	1.6608	0.552	0.332	0.234	0.141
	1.1072	0.384	0.347	0.163	0.147
	0.6653	0.213	0.320	0.085	(0.128)

Table 5. Per Cent Yield of cis- and trans-Cinnamic Acids Obtained from Irradiation Experiments in Methanol and Ethanol for Various Times of Exposure.

Time (in hours)	Solvent	Per Cent <sup>a</sup>		
		<u>cis</u>	<u>trans</u>	Average <u>cis</u>
3	Methanol	27.0	09.9	30.3
		33.0	60.2	
6	"	45.8	48.5	49.3
		52.8	45.1	
10	"	51.1	40.9	51.5
		52.0	39.3	
10	"	52.0	39.9	48.0
		45.2	42.6	
20	"	50.2	41.8	51.7
		53.1	35.2	
10	Ethanol	48.8	42.0	53.4
		58.0	40.0	
10	"	49.0	40.9	50.1
		50.7	44.1	
20	"	47.0	38.8	53
		58.7	37.2	
20	"	48.4	37.8	50
		51.6	44.1	

<sup>a</sup> For each time shown two sets of analyses are given, the first refers to analysis at 10.129 and 12.080 microns, and the second to analysis at 14.125 and 14.435 microns.

Preparation of cis-Cinnamic Acid Dibromide

## Preliminary Bromination Experiments.

Experiment 1. Bromination in Carbon Disulfide as solvent? -- Purified cis-cinnamic acid, 8 g. (0.054 moles), m.p. 66-68°, was dissolved in 64 g. (51.2 ml.) of freshly distilled carbon disulfide. Pure bromine, 23.5 g. (0.147 moles), was dissolved in 50 g. (40 ml.) of carbon disulfide. The solution of cis-cinnamic acid in carbon disulfide was added to the bromine solution dropwise through a dropping funnel into a three-neck flask. The second neck of the three-neck flask was connected to a condenser and the third to a mechanical stirrer. The reaction was carried out in the dark for an hour and 45 minutes. The mixture was transferred to a thick-walled bottle. Crystals had formed. The bottle, wrapped in a towel, was shaken on a shaking machine for three hours then was left over night. It was again shaken for one hour the next morning. In order to remove the carbon disulfide and the bromine vapors<sup>17</sup> nitrogen gas was bubbled for four hours through the bottle which was connected with an aspirator. The residue was extracted with 150 ml. of carbon disulfide and filtered; 10 g. (0.0325 moles) of crystals m.p. 195° (dec.), was collected. A reddish oil was obtained from the filtrate. It was dissolved in 50 ml. of benzene and 300 ml. of n-hexane was added. A powder, 2 g. (0.0065 moles), of m.p. 120-125° was collected after the filtration. On evaporation of the n-hexane 2.5 g. (0.0091 moles) of powder, m.p. 62-65°, was collected.

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(17) J. Wislicenus, Ann., 272, 17 (1892).

These crystals upon fusion with sodium gave a positive test for bromine.<sup>18</sup>

A second identical run gave about the same amount of trans-cinnamic acid dibromide, 11 g. or 66 per cent yield of product (m.p. 185-191°), and 4 g. or 24 per cent of product, m.p. 55-80°.

Experiment 2. Bromination in Glacial Acetic Acid. -- cis-Cinnamic acid, 10 g. (0.0675 moles), m.p. 60-68°, was dissolved in 30 ml. acetic acid and a solution of bromine (15 g., 0.094 mole.) in 30 ml. of acetic acid was prepared. The bromine solution was added in three portions to the first solution within a fifteen minute period. The temperature during the addition of bromine rose spontaneously to a maximum of 51°. The reaction was stirred for 30 minutes and was then left over night. This reaction was carried out in the dark. Acetic acid and bromine vapors were evaporated with the help of an aspirator connected to a filtration flask heated by a water bath. The remaining brown oil was extracted with 50 ml. carbon disulfide; 2 g. (0.0065 moles) of a product with a m.p. of 192-195° (dec.) remained undissolved in carbon disulfide. The evaporation of the carbon disulfide was carried out in the same manner as the evaporation of the acetic acid. The residue remaining after the evaporation of the carbon disulfide was extracted again with 40 ml. more of carbon disulfide; 1 g. of material m.p. 190-195° (dec.), remained undissolved. After evaporation of solvent and a third extraction with carbon disulfide, 0.5 g. m.p. 190-195° remained undissolved. After complete evaporation of carbon disulfide, an oil remained which was extracted with 50 ml. of hot n-hexane. Some undissolved oil was isolated by

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(18) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," J. Wiley and Sons Inc., New York, (1946) 3rd ed., p. 52.

mechanical separation from the solvent. This oil was re-extracted with 50 ml. hot n-hexane and the solvent was again separated from the undissolved oil. The two 50 ml. portions of n-hexane were combined and cooled in an ice bath. Upon rubbing the walls of the vessel with a glass rod, white gummy mass precipitated. An attempt was made to collect this mass by suction filtration. In the filtration flask 1 g., m.p. 90.0-92.5°, of white crystals were formed. The gummy mass had a strong acetic acid like odor and was left over night in the desk in an evaporating dish for complete evaporation of acetic acid. The next morning it was dry, and was extracted with 40 ml. n-hexane. The solution was cooled slowly; 4 g. of crystals, m.p. 84-87°, was collected. After complete evaporation of the n-hexane, 0.4 g., of crystals, m.p. 70-84, was obtained. From the re-extraction of the 4 g., m.p. 84-87°, with 30 ml. of hot n-hexane, 3.2 g. of white crystals, m.p. 88-93°, was isolated.

Results from this experiment:

3.5 g. (17%), m.p. 190-5° dec.

1 g. { 25% }, m.p. 90.5-92.5°

3.2 g. { 25% }, m.p. 84-90°

1 g. { 25% }, m.p. 91-93°

plus an oil.

Experiment 3. Bromination in Glacial Acetic Acid in the Presence of HBr. -- cis-Cinnamic acid, 10 g. (0.0675 moles), m.p. 66-68°, was dissolved in 25 ml. of acetic acid. In another 25 ml. portion of acetic acid, 4 g. (0.0495 moles) of HBr gas was bubbled through and 18 g. (0.112 moles) of bromine was added. The same procedure was followed as in Experiment 2 in acetic acid.

## Results of Experiment 3:

2.5 g. (12%), m.p. 191-3° (dec.)

5.5 g. (27%), m.p. 91.0-93.5°

3.5 g. (10%), m.p. 85-90°.

General Method of Bromination of cis-Cinnamic Acid.

Procedure. -- cis-Cinnamic acid, 100 g. (0.675 moles), m.p. 66-68°, was dissolved in 250 ml. of purified acetic acid. In another 300 ml. portion of acetic acid 36 g. (0.445 moles) of HBr and 190 g. (1.19 moles) of bromine were dissolved. The second solution was added in three portions to the first solution within a period of 10 minutes. The maximum temperature of the reacting mixture was found to be 75°. The reaction was continued for 8 hours in a red-colored flask made of low-actinic glassware. After this 8 hour period the contents of the flask were added to a 5-liter separatory funnel containing 3 liters of ice water with an excess of ice. It was extracted with three 400 ml. portions of diethyl ether. The ether layer was then washed with 600 ml. of a solution of  $\text{NaHSO}_3^a$  in order to destroy the excess bromine. The ether layer was next washed two times with water and then stored overnight over anhydrous magnesium sulfate. The ether layer, after filtration, was evaporated and the remaining residue was extracted three times with carbon disulfide. The carbon disulfide was removed by evaporation and the residue was extracted with n-hexane.

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(a) Anhydrous  $\text{Na}_2\text{SO}_3$  (80 g.) was dissolved in 600 ml. water. To this, 55.5 ml. (1 mole) of 36 N  $\text{H}_2\text{SO}_4$  were slowly added. A strong odor of  $\text{SO}_2$  developed.

The crystallization of the crude dibromide obtained from the evaporation of carbon disulfide was effected by a selective extraction of the cis isomer from the oily by-product with boiling n-hexane. The residue of the evaporation of carbon disulfide was extracted with two portions of 600 ml. boiling n-hexane. An oil remained undissolved in the solvent which was separated by decantation. The solution upon cooling in an icebox deposited white crystals. It was later found that slow evaporation of the solvent at room temperature was a better process for crystallization. Filtration of the formed crystals and concentration of the solvent, followed by cooling in an icebox, gave more crystals.

The results of this experiment are as follows:

41 g. (0.133 mole),	19.7 %,	m.p. 193-195°
34 g. (0.11 mole),	16.35%,	m.p. 93.5-94.5°
3 g. (0.00975 mole),	1.43%,	m.p. 90-94°
66 g. (0.211 mole),	31.7 %,	m.p. 87-93°
20 g. (0.065 mole),	9.62%,	m.p. 75-91°

Total 123 g. 59.3 %, of crystals of m.p. 75.0-94.5°

Completeness of Bromination at the end of 6 hours. -- The theoretical excess of bromine in the above reaction was 82 g. The volume of the solution was 650 ml. Crystals of potassium iodate, 1.43 g., (three times the theoretical amount) were dissolved in 30 ml. of distilled water. Two milliliters of solution was removed from the bromination reaction with a pipette and was added to the potassium iodate solution. The resulting solution was titrated with 29.0 ml. of 0.115 N sodium thiosulfate in presence of starch as indicator. This titration shows that the reaction was 9/4 per cent complete at the end of 6.0 hours.

From the intergrated form of the second order reaction law:

$$k = \frac{2.303}{(b-a)t} \log \frac{a}{b} \frac{(b-x)}{(a-x)}$$

the percent of bromination at the end of 8 hours was calculated to be 97.2 per cent.

The per cent of trans-cinnamic acid dibromide recovered in five similar runs was  $20 \pm 1$  per cent and that of the crude cis-cinnamic acid dibromide was  $60 \pm 2$  per cent.

#### Analysis of cis-Cinnamic Acid Dibromide

Infrared Spectra. -- Selected whiter and higher melting crystals of the cis-cinnamic acid dibromide sample was dissolved in carbon disulfide and recrystallized by slow evaporation of carbon disulfide. Very pure hexagonal crystals, m.p.  $93.5-94.5^\circ$ , were obtained. The trans-cinnamic acid dibromide sample was recrystallized from boiling chloroform. The crystals, m.p.  $198.5-200.0^\circ$  (dec.), were white in color. The infrared spectra of the above samples in very dilute solutions of carbon disulfide were determined (Figure 5). The two spectra were very similar; therefore it was decided to analyze the samples in another way.

Mixed Melting Point Curve. -- Several mixtures (ca. 0.15 grams) of pure cis- and trans-cinnamic acid dibromide were weighed in small bottles and were then melted for 10 minutes in the oven at  $130^\circ$ . They were allowed to recrystallize at room temperature. Melting points for different mixtures are shown in Table 6. From these data, melting points were plotted against the per cent of cis-cinnamic acid dibromide (Figure 6). The two dibromides form a eutectic of m.p. near  $90^\circ$  containing about 92 per cent cis-cinnamic acid dibromides.

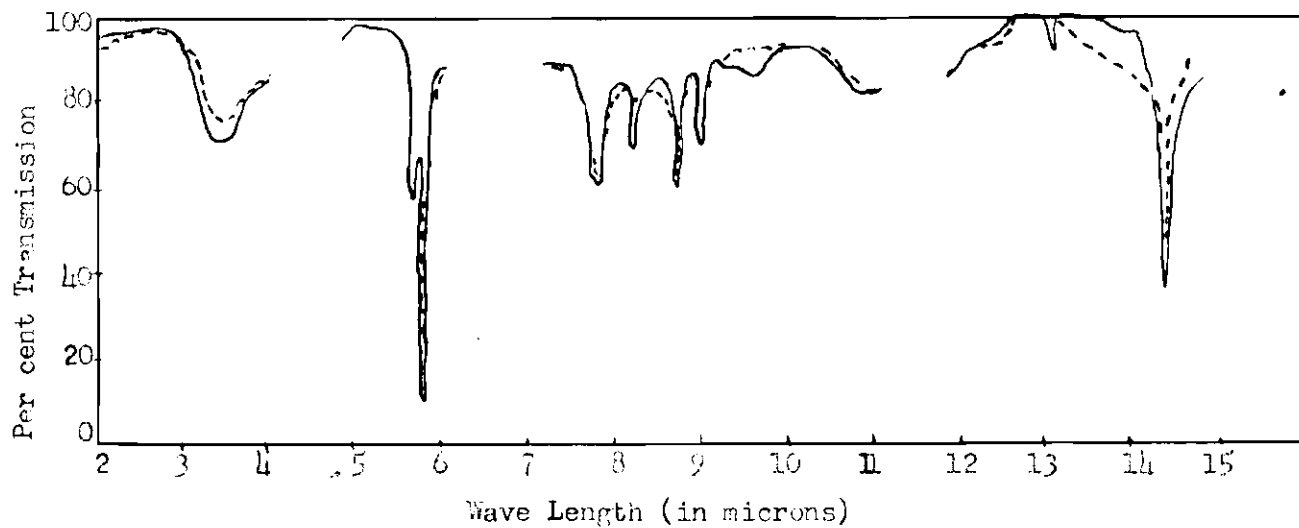


Figure 5. Infrared spectra: *cis*-cinnamic acid dibromide ----- and *trans*-cinnamic and dibromide ----- at concentration of 1.552 g./l. in carbon disulfide with 3 mm. rock salt cell.

Table 6. Melting Points<sup>a</sup> of cis- trans-Cinnamic Acid Dibromide Mixtures  
in Various Proportions

Per cent <u>cis</u> -Isomer	Melting Points Initial - Final
100.00	93.5-95.0°
98.60	91.5-94.5°
97.50	91.0-94.0°
95.56	89.0-92.5°
94.40	89.0-92.5°
93.35	88.0-91.5°
91.68	88.0-92.0°
87.50	89.0-108.0°
75.00	89.0-162.0°
50.00	90.5-176.0°
0.00	196.0-198.0°

<sup>a</sup>The melting points are uncorrected and were determined with a 360° immersion thermometer which read 0.5° lower than a Bureau of Standards thermometer at 20°C. The melting points were run in capillary tubes in a stirred silicone oil bath at a rate of 1 to 2°/min. for samples which melted at 108° or lower and at higher rates of heating (up to 5°/min. for pure trans-cinnamic acid dibromide) for the higher melting samples since these melted with decomposition.

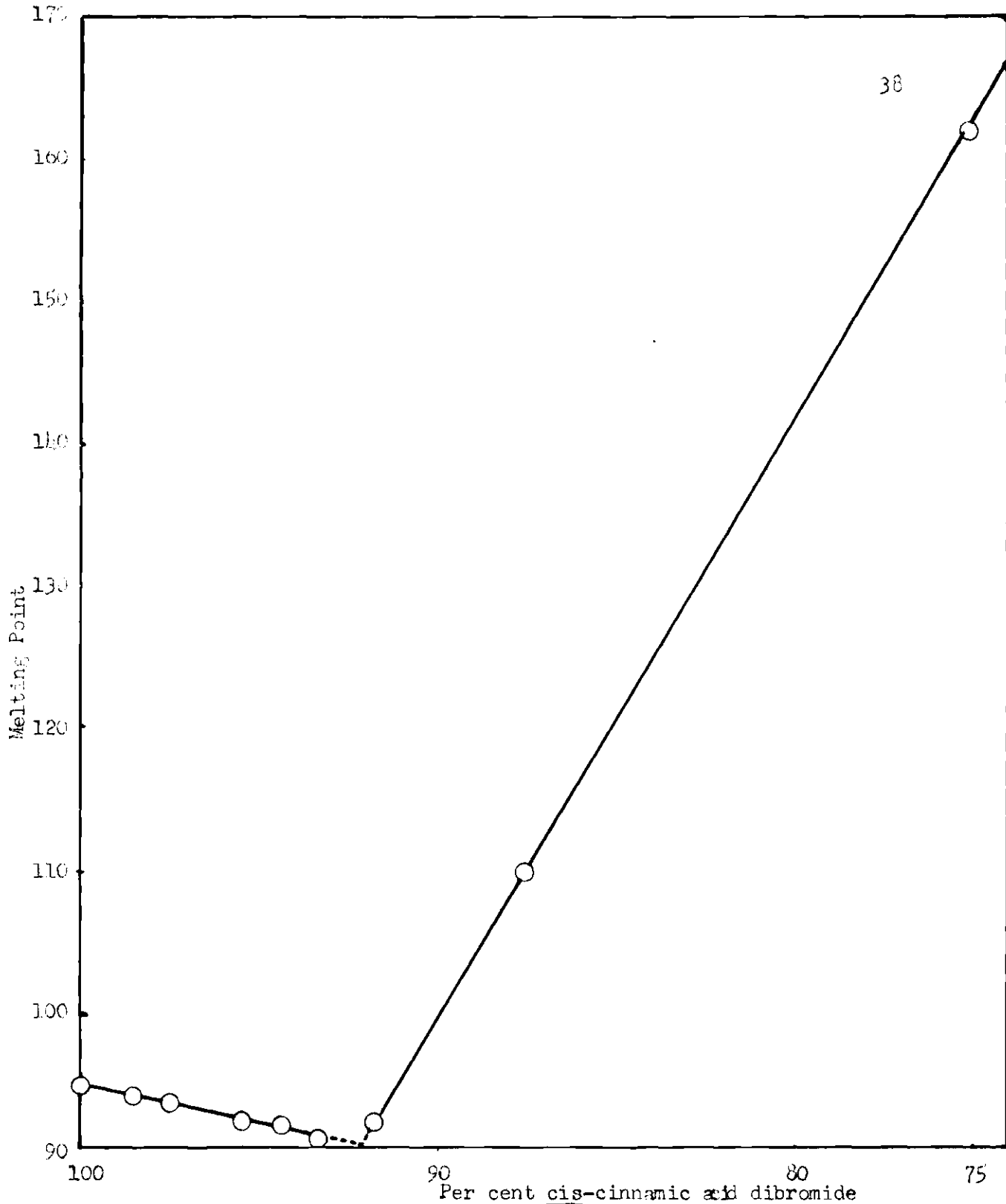


Figure 6. Mixed melting point curve upon Synthetic mixtures of cis- and trans-Cinnamic Acid Dibromides.

Purity of *cis*-Cinnamic Acid Dibromide Used for the Transformations to *beta*-Bromostyrene. -- The 540 g. of *cis*-cinnamic acid dibromide, from individual batches of m.p. 87.0-94.5°, was completely granulated to form a homogeneous mixture. This sample was dried in a vacuum oven for one and one-half hours at a temperature of 55°. The melting point of this mixture was checked as mentioned before at 88.0-92.5°. This melting point could represent either 95.5 per cent of *cis*-cinnamic acid dibromide or 91.7 per cent *cis*-isomer. In order to ascertain which side of the eutectic the unknown sample lies a mixture of 1.0 part of pure *cis* and 10.0 parts of the unknown sample was made and the melting point with the same procedure was found to be 88-93°.

In 1 g. of prepared (1 to 10 parts) mixture:

the *cis* isomer is  $0.955 + 0.1 = 1.055$  g.

the *trans* isomer is  $\quad\quad\quad = 0.045$  g.

Total  $\quad\quad\quad 1.1$  g.

and the *cis* isomer in the mixture is  $\frac{1.055}{1.1} \times 100 = 96\%$ .

From the plotted curve the melting point of 96 per cent *cis*-isomer is 92.8° for complete melting. By similar calculations a sample prepared from 10 parts of 91.7 per cent *cis* with 1 part of pure *cis* would contain 92.3 per cent *cis*-isomer would be the eutectic point (90.5°), and so the prepared *cis*-cinnamic dibromide seems to be 95.5 ± 1 per cent pure *cis*.

Conversion of *cis*-Cinnamic Acid Dibromide to *beta*-Bromostyrene  
*beta*-bromostyrene from *cis*-Cinnamic Acid Dibromide in Acetone. -- In a 2 liter, 3 necked flask equipped with a stirrer, a dropping funnel, and a reflux condenser was placed 90 g. (0.292 mole) of *cis*-cinnamic acid

dibromide (m.p. 90.0-92.5° and remelted gave 88.0-92.5°) 80 g. (0.955 mole) of sodium bicarbonate, and 1000 ml. of acetone (dried over anhydrous magnesium sulfate). The mixture was stirred and heated at reflux for 3 hours. The acetone was then removed under reduced pressure using a water pump. The residue containing about 30 ml. of acetone was added to a large separatory funnel containing 2.5 liters of water. The resulting oil was extracted with three 200-ml. portions of "pure" n-pentane. The pentane extracts were washed three times with 200-ml. portions of 0.5 M sodium thiosulfate, and finally with one 500-ml. portion of water. The pentane layer after drying overnight over anhydrous calcium chloride was distilled through an eight inch column packed with glass helices. Finally the remaining oil was distilled in vacuo through a Claisen flask with an indented side arm. Care was taken not to heat the flask above 80° while the beta-bromostyrene remained undistilled. There was obtained 45.5 g. (85.0 per cent) pale yellow beta-bromostyrene, b.p. 54-58° (1.3 mm.)  $n_D^{25}$  1.6070. In a second run under the same conditions the yield of beta-bromostyrene was 72.8 per cent,  $n_D^{25}$  1.6070.

During all steps of the reaction the solution containing beta-bromostyrene was kept in darkness.

beta-Bromostyrene from cis-Cinnamic Acid Dibromide in Ethanol. -- In 1000 ml. of absolute ethanol, 90 g. (0.292 mole) of cis-cinnamic acid dibromide (m.p. 90.0-92.5° and remelted gave m.p. 88.0-92.5°) were dissolved; 140 g. (1.42 moles) of dry potassium acetate (dried in vacuum oven for one hour at a temperature of 70°) was added. The mixture was stirred and refluxed for 3 hours. The ethanol was distilled at atmospheric

pressure; the time required for the distillation was one and one-half hours. The last 40 ml. of ethanol and the pale yellow oil were transferred to a large separatory funnel containing 2.5 liters of water. The resulting oil was extracted with three 250-ml. portions of "pure" n-pentane. The pentane extracts were washed two times with 200-ml. portions of 0.5% sodium thiosulfate, and finally with three 400-ml. portions of water. The pentane after drying over night over anhydrous calcium chloride was distilled through the short, helices-packed column. Finally the remaining oil was distilled in vacuo through a Claisen flask with indented side-arm. Care was taken not to heat the flask above 80° while the beta-bromostyrene remained undistilled. There was obtained 34.03 g. (64.73 per cent) of beta-bromostyrene b.p. 53-68° (1.7 mm.),  $n_D^{25}$  1.6066. In a second run under the same conditions the yield of beta-bromostyrene was 54.5 per cent,  $n_D^{25}$  1.6057.

beta-Bromostyrene from cis-Cinnamic Acid Dibromide in Water. -- cis-Cinnamic acid dibromide, 90 g. (0.299 mole), m.p. 90.0-92.5° and remelted gave m.p. 88.0-92.5°, was treated as described above except that water and sodium hydroxide were used in place of ethanol and potassium acetate. In all 1000 ml. (1.233 moles) of 1.233 N sodium hydroxide were used. The addition of sodium hydroxide was made slowly during the heating of the solution, one and one-half hours were required to bring the solution up to 78 - 2° and the solution was maintained at this temperature for 30 minutes. Upon cooling, the solution was extracted directly with "pure" n-pentane and worked up as previously described for the reactions in ethanol and acetone. After the vacuo distillation there was obtained 19.03 g. (35.0 per cent) of beta-bromostyrene, b.p. 43-50° (0.3 mm.),

$n_D^{25}$  1.0071. In the second run under the same procedure the yield of beta-bromostyrene was 34.5 per cent,  $n_D^{25}$  1.0072.

From the determination of the refractive indices and infrared spectrum of the products from the reaction in water it was found that the beta-bromostyrene was pure trans-isomer. The loss of the cis-isomer is probably to be attributed to addition of excess alkali. This addition of the excess alkali was done as follows: At the start of the reaction 400 ml. of the above sodium hydroxide solution was added. The characteristic pink color of the phenolphthalein immediately disappeared. The addition of alkali was continued until 1000 ml. in all had been added; the solution was still colorless at this time. Upon heating the solution at  $78 \pm 2^\circ$  for 30 minutes the pink color returned. Phenolphthalein seems to be an unreliable indicator under the reaction conditions.

For a third run in water 95 g. (0.306 mole) of cis-cinnamic acid dibromide (m.p.  $86-96^\circ$ )<sup>a</sup> was suspended in 400 ml. distilled water. Sodium bicarbonate, 84 g. (1.0 mole), was dissolved in 600 ml. distilled water and added in a period of thirty minutes to the slowly heated and stirred suspension of dibromide. The reaction was heated to  $75 \pm 2^\circ$  in 1.15 hours and kept at this temperature for 20 minutes. The extraction with pure n-pentane and the vacuo distillation (b.p. 48.5-57.5 at 0.3-0.8 mm.) were performed as described on page 41. A yield of 84 per cent

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<sup>a</sup> This cinnamic acid dibromide is of different purity from that used in the other runs. A sample of 0.42 g. of this dibromide of m.p.  $86-96^\circ$  upon fusion with 0.040 g. of pure cis-cinnamic acid dibromide gave a melting point of  $88.0-93.5^\circ$ . According to the mixed-melting point curve of Figure 6, page 38, the impure cis dibromide should contain 90.9 per cent cis-cinnamic acid dibromide and upon dilution with the pure cis dibromide should contain 91.7 per cent cis and be completely molten at  $92.5^\circ$ .

(40.5 g.) of beta-bromostyrene was obtained. The refractive index of this product was  $n_D^{25}$  1.6007.

beta-bromostyrene from trans-Cinnamic Acid Dibromide in Acetone<sup>10</sup> -- To two liters of dry acetone (dried over anhydrous magnesium sulfate) was added 100 g. (0.325 mole) of trans-cinnamic acid dibromide m.p. 190° (dec.) and 90 g. (1.07 moles) of sodium bicarbonate. The mixture was stirred and refluxed for 8 hours. The acetone was distilled under reduced pressure. The remaining oil containing about 50 ml. of acetone was added to 3500 ml. of water. The solution was extracted with three 200-ml. portions of "pure" n-pentane. The pentane extracts were washed with two 250-ml. portions of 0.5 M sodium thiosulfate, and finally with one 500-ml. portion of water. The pentane layer, after drying overnight with anhydrous calcium chloride, was distilled through the short, helices-packed column. From the vacuum distillation 55.61 g. (93.5 per cent) of beta-bromostyrene, b.p. 53-56° (1.5 mm.),  $n_D^{25}$  1.5960-1.5982, was collected. During all steps of the reaction the solution containing cis-beta-bromostyrene was kept in darkness.

#### Infrared Analysis for cis-trans-Isomers of beta-Bromostyrene

Pure trans-beta-bromostyrene was prepared by crystallization of a sample of beta-bromostyrene prepared from cis-cinnamic acid dibromide in acetone. The crystallization was made in the apparatus shown in Figure 7. Nitrogen gas was supplied at such pressure as to prevent the passage of the solution through the fritted glass while crystallization was taking place. Connection to a water aspirator by turning the three-way stopcock permitted filtration to be effected.

In this apparatus 8 ml. of trans-beta-bromostyrene was dissolved in 25 ml. pure methanol. For 10 minutes the tube was cooled at  $-30^{\circ} \pm 2^{\circ}$  whereupon a white powder formed. The solvent was removed by application of the vacuum of a water aspirator and the powder was recrystallized from 15 ml. of methanol. The crystallization was repeated for another 8 ml. of trans-beta-bromostyrene. The two recrystallized samples were combined to give 10-12 ml. of product. Using the vacuum of an oil pump, the trans-beta-bromostyrene was dried for 3 hours at  $0^{\circ}$  to give a product of  $n_D^{25}$  1.6074.

The same general procedure for the crystallization of trans-beta-bromostyrene was applied to the cis-beta-bromostyrene prepared from trans-cinnamic acid dibromide in acetone. The crystallization was initiated at  $70^{\circ}$  and continued at  $-45^{\circ}$  for 30 min. using for solvent "pure" n-pentane. One recrystallization only was made. The crystals were dried at  $0^{\circ}$  with an oil pump for 3 hours  $n_D^{25}$  1.5962.

The results of the refractive indices for the cis- and trans-isomers seem to be higher than those, 1.5960 and 1.6071 respectively, reported<sup>11</sup> in the literature. For this reason the refractive index of redistilled water was checked. The result was  $n_D^{40}$  1.3309 but the reported value<sup>19</sup> is  $n_D^{40}$  1.3306. If this correction of -0.0003 is applied to our values for the beta-bromostyrenes, the resulting indices are in agreement with the reported values.

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(19) E. S. Washburn, International Critical Tables, McGraw-Hill Co., Inc., New York (1930), Vol. VII. p. 52.

The infrared spectra were determined with the same spectrophotometer described in the cis-trans-cinnamic acid analysis and with 0.1-mm. rock salt cells and solutions which contained 0.400 g. of beta-bromostyrene per 2.00 ml. of pure iso<sup>o</sup>ctane. These spectra agreed with those which are reported.<sup>10</sup> For quantitative analysis 0.400 g. samples of beta-bromostyrene were dissolved in 6.00 ml. of pure iso<sup>o</sup>ctane. Empirical calibration curves were prepared (Figure 7) based upon synthetic mixtures (Table 7) of the above pure cis- and trans-beta-bromostyrene. Plots of optical density versus percentage composition were almost linear for the two cis- bands and were linear up to an optical density of 0.6 for the two trans bands. The absorption maxima at 10.048 and 13.088 microns for trans-beta-bromostyrene, and at 12.068 and 13.012 microns for the cis- isomer were used in the analysis. The optical densities at these wave lengths for all of the samples of beta-bromostyrenes prepared by the decarboxylative elimination reactions in the different solvents are reported in Table 8. and the corresponding per cent compositions in Table 9. The average deviation of the individual values from the average value of the four values was 0.8 per cent or less, the maximum deviation of any of the individual values was 1.5 per cent.

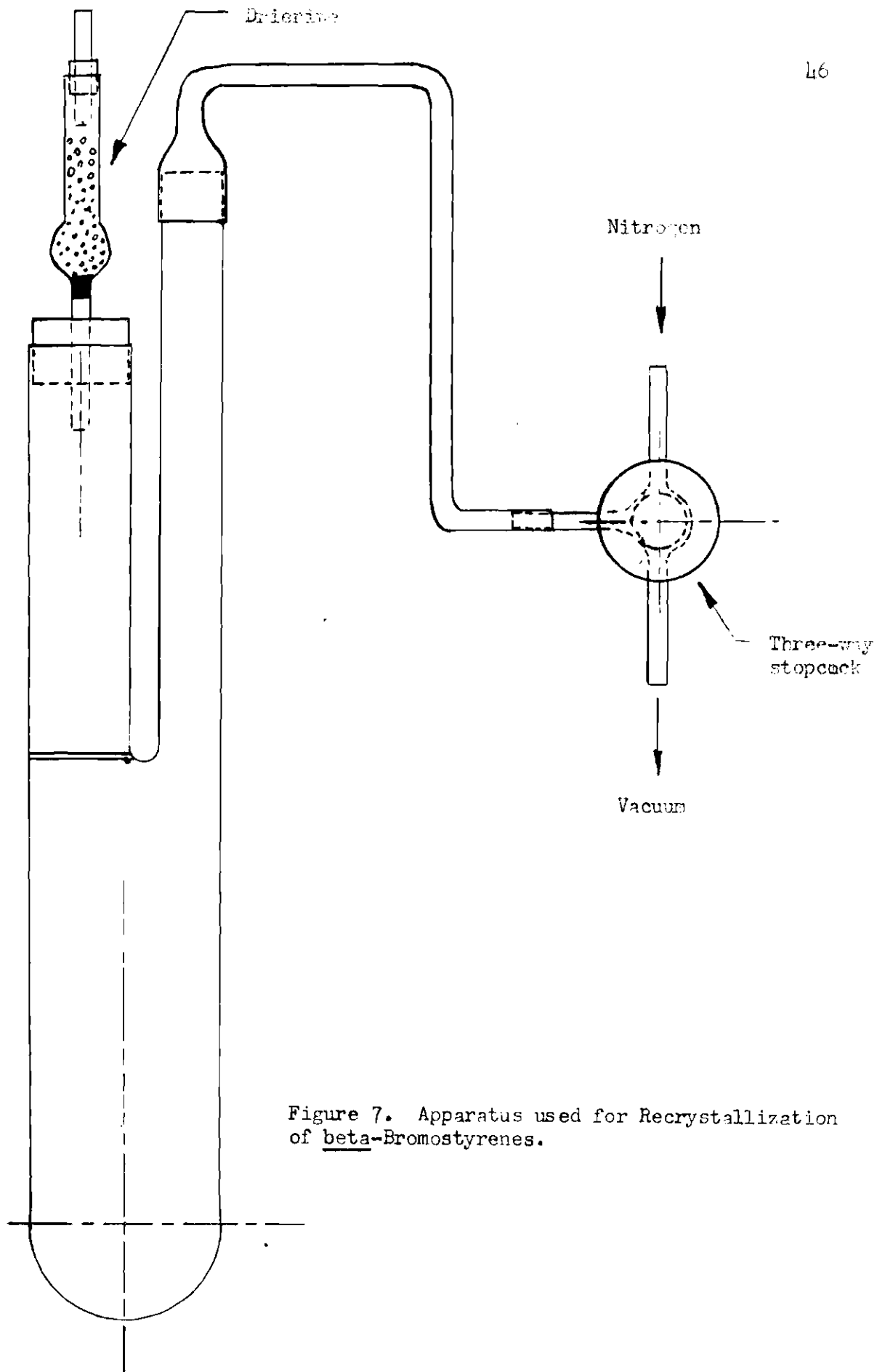


Figure 7. Apparatus used for Recrystallization of beta-Bromostyrenes.

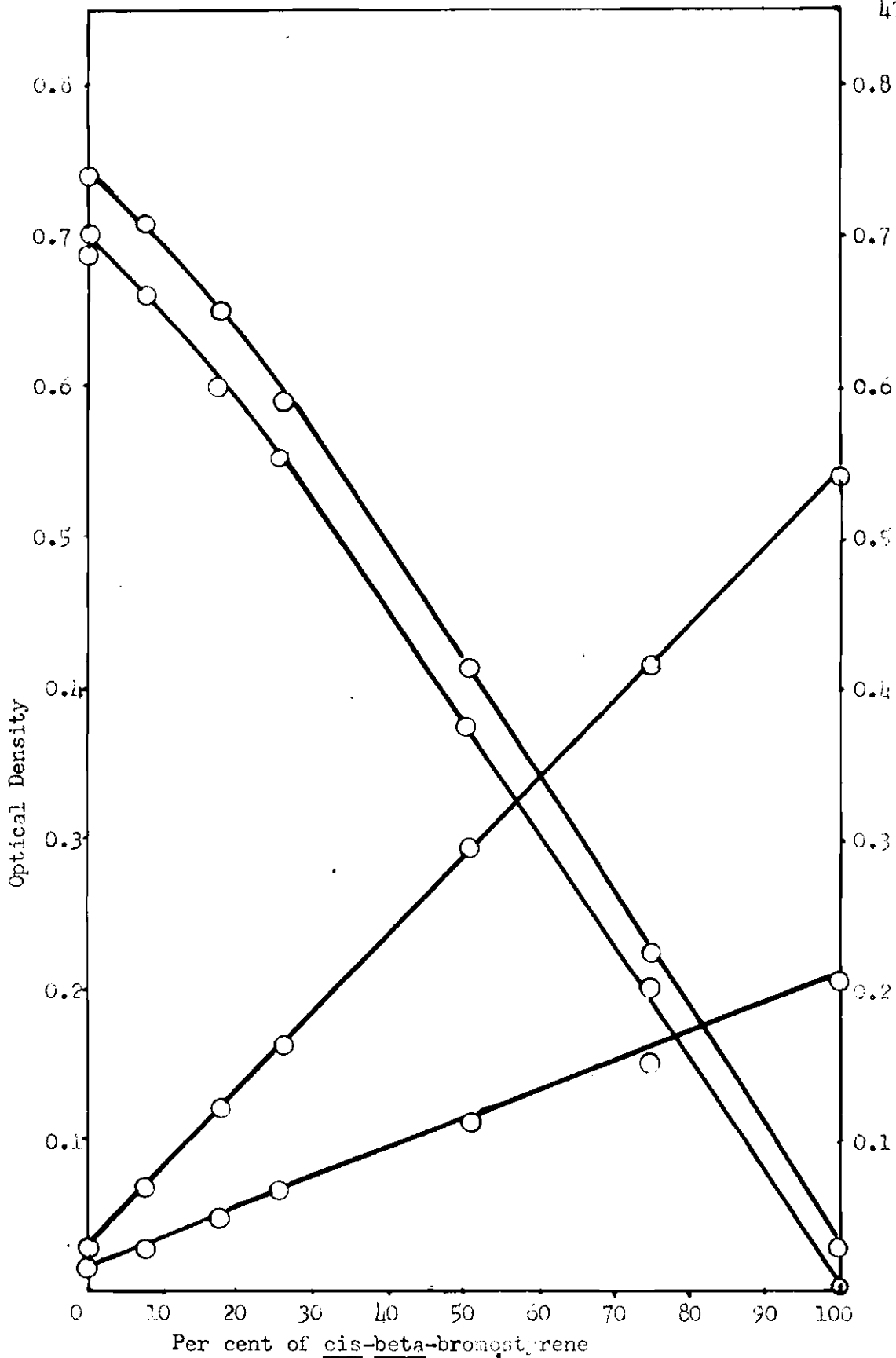


Figure 8. Empirical calibration curves for infrared analysis of synthetic mixtures of cis- and trans-beta-bromostyrenes versus the optical densities.

Table 7. Optical Densities for Various Compositions of cis- and trans-  
beta-Bromostyrenes at Four wave Lengths (0.44 g. Samples/6.00  
ml. of Iso<sup>o</sup>ctane) in 0.1 mm. Cells

Per cent of <u>cis</u> -Isomer	wave lengths in microns			
	10.648	12.068	13.012	13.688
100.00	0.003	0.208	0.543	0.028
74.90	0.201	0.151	0.418	0.227
50.40	0.375	0.1145	0.296	0.415
25.32	0.554	0.068	0.165	0.590
17.25	0.602	0.050	0.123	0.652
7.80	0.661	0.030	0.070	0.709
0.00	0.702	0.016	0.029	0.740

Table 8. Optical Densities for the Prepared beta-Bromostyrenes at Four  
Wave Lengths

Run No.	Solvent Used for Preparation	Wave length in microns			
		10.648	12.068	13.012	13.688
I	Acetone	0.677	0.025	0.055	0.726
II	Acetone	0.676	0.024	0.054	0.730
I	Absolute Ethanol	0.692	0.021	0.044	0.738
II	Absolute Ethanol	0.679	0.022	0.046	0.735
I	Water	0.702	0.017	0.030	0.752
II	Water	0.703	0.017	0.032	0.753
III	Water <sup>B</sup>	0.678	0.024	0.048	0.722
	Acetone <sup>A</sup>	0.010	0.207	0.551	0.027

<sup>A</sup> From trans-cinnamic acid dibromide.

<sup>B</sup> Third run with sodium bicarbonate.

Table 9. Per Cent of cis-beta-Bromostyrene in the beta-Bromostyrenes from the Sodium or Potassium Salts of cis- and trans-Cinnamic Acid Dibromides

Run No.	Solvent Used for Preparation	Wave lengths in microns				Average
		10.048	12.068	13.012	13.688	
I	Abs. Ethanol	2.5	2.8	2.7	3.0	2.75
II	Abs. Ethanol	4.5	3.5	3.2	3.5	3.70
I	Acetone	5.0	4.5	4.5	4.8	4.70
II	Acetone	5.0	5.0	4.5	4.2	4.70
I	Water	0.0	0.15	0.0	0.25	0.10
II	Water	0.0	0.0	0.0	0.20	0.05
III	Water	5.5	5.0	3.3	5.5	4.83
	Acetone <sup>A</sup>	99.0	100.0	99.0	100.0	99.50

<sup>A</sup> From the trans-cinnamic acid dibromide reaction.

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## BIOGRAPHICAL SKETCH

The author was born February 18, 1925 in Athens, Greece. In 1931 he went to Constantinople, Turkey where he attended public schools. In 1939 he came back to Athens and graduated from Annunciation High School in June 1946. He attended the University of Athens for two years before enlisting in the Air Force in 1948 for service in the Civil War. After being discharged from the Air Force, he returned to the University of Athens where he received his Diploma in Chemistry in June 1952.

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