Kinetics of the Decarboxylative Elimination of Cinnamic Acid Dibromides

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The decarboxylative elimination of *trans*-cinnamic acid dibromide and of the *p*-methoxy and *p*-nitro analogs was studied in the solvents water, ethanol, and acetone or methyl ethyl ketone. The reactions were first order in the acids in these solvents when the weak bases commonly used to effect this elimination were employed. The solvent and substituent effects are explained in terms of two mechanisms; one a nonstereospecific reaction involving ionization favored in water or when an electron-donating group is present and the other a stereospecific process favored in nonpolar solvents or by an electron-withdrawing group. Arrhenius energies of activation and entropies of activation are reported.

The reaction of β-halo acids with mild base leading to the formation of an olefin, carbon dioxide and halide ion is generally agreed to be first order in the anion of the acid and to proceed at a rate independent of pH.[2]

The reaction of cinnamic acid dibromide has received particular attention and the composition of the olefin mixture arising from this decomposition in water, ethanol and acetone is known. The effect of different bases in altering the ratio of bromostyrene (product of decarboxylative elimination) to α-bromocinnamic acid (product of dehydrobromination) is also known from the work of Sudborough and Thompson,[3] and of Bachman.[4] Decarboxylative elimination in water follows a nonstereospecific course yielding a mixture of *cis*- and *trans*-β-bromostyrene which has a composition approximating that of the equilibrium mixture. As the solvent becomes less polar, the reaction becomes more stereospecific so that in acetone the product is *cis*-β-bromostyrene, the olefin expected of *trans* elimination.[5,6] Two mechanisms were suggested to explain these observations, a concerted process in acetone and a reaction involving ionization of the benzylic carbon-bromine bond in aqueous solution.

The mechanisms are supported by the product analysis and by kinetic data obtained primarily in the study of the decomposition of aliphatic β-bromo acids in water. This paper reports the results of kinetic studies of the reaction of *trans*-cinnamic acid dibromide (*erythro*-α,β-dibromo-β-phenylpropionic acid) and the corresponding *p*-nitro and *p*-methoxy compounds in the solvents water, ethanol, acetone, and methyl ethyl ketone which provide additional information concerning these mechanisms.

The reactions were followed by determining the concentration of unchanged dibromocinnamic acid at convenient intervals. Samples of the reaction mixture were quenched in acetic acid, excess iodide ion was added, and the iodine liberated was titrated.[7] In this way it was possible to study the effect of added bromide ion and to work in solutions of varying degrees of basicity, experiments which are difficult to perform when the reaction is followed by the titration of bromide ion or the evolution of carbon dioxide. However, this method suffers the disadvantage that the total disappearance of dibromo acid is measured rather than the formation of one particular product.

A straight line was fitted by inspection through the points obtained by plotting the logarithm of the concentration of unchanged acid against time. The points gave good straight lines as far as the reactions were followed, 75 to 95% completion. In most cases duplicate runs were made. In Table I the specific rate constants for decomposition of *trans*-cinnamic acid dibromide in water at different pH values and with added salts are listed. In view of the fact that the reaction of dibromo acids in pyridine gives products different from those obtained in aqueous solution,[4] the effect of using pyridine as a base in aqueous solution was tested. The specific rate constant in 0.1 *M* pyridine brought to an ionic strength of 0.3 by adding sodium perchlorate was within 5% of the value obtained with phosphate buffers. From a similar reaction run on a preparative scale, β-bromostyrene was isolated in 55% yield. Apparently in aqueous solution pyridine has no specific effect. A preparative run in pure pyridine yielded such a mixture of products that the reaction seemed unsuited for kinetic study.

At concentrations of base higher than those listed in Table I the rate constant is no longer independent of pH. Studies were made at 40.0° using aqueous sodium hydroxide solutions brought to an ionic strength of 0.5 by adding sodium bromide. The reactions appeared to follow first order kinetics at a given concentration of base, but the apparent k_1 values when plotted against concentration of hydroxide (from 0.07 to 0.42 *M*) gave a straight

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[2] For the last papers in a series of articles see: (a) E. Grovenstein and S. P. Theophilou, *J. Am. Chem. Soc.*, **77**, 3795 (1955). (b) W. R. Vaughan and R. L. Craven, *ibid.*, 4629 (1955); (c) S. J. Cristol and W. P. Norris, *ibid.*, **76**, 3005 (1954), and previous references cited therein.

[3] J. J. Sudborough and K. J. Thompson, *J. Chem. Soc.*, **83**, 666 (1903).

[4] G. B. Bachman, *J. Am. Chem. Soc.*, **55**, 4279 (1933).

[5] E. Grovenstein and D. E. Lee, *J. Am. Chem. Soc.*, **75**, 2639 (1953).

[6] S. J. Cristol and W. P. Norris, *ibid.*, 2645 (1953).

[7] A. Lespagnol and R. Merville, *Ann. chim. anal.*, **25**, 53 (1943).

TABLE I

RATE OF DECOMPOSITION OF CINNAMIC ACID DIBROMIDE[a]

pH	Added salt	10^5k, sec.$^{-1}$
8.0	None	20.2 ± 0.5
8.0	None	19.0[b]
5.0	None	19.5 ± 0.5
7.9	0.3 *M* NaBr	21.2
7.9	0.3 *M* NaOAc	20.8
8.2	0.3 *M* $NaClO_4$	21.2

[a] Aqueous phosphate buffer, $\mu = 0.3$, initial dibromo acid concentration 0.020 *M;* temp. 40.0 ± 0.1. [b] Initial concentration of dibromo acid = 0.010 *M*.

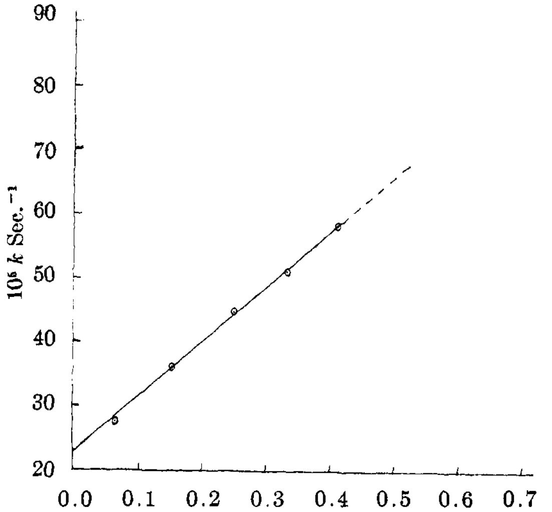

Fig. 1.—Dependence of the apparent first-order rate constant on hydroxide concentration.

line (Fig. 1). The values fitted a relationship of the type $k_{obs} = k_1 + k_2[OH^-]$ where $k_1 = 21.6 \times 10^{-5}$ sec.$^{-1}$ and $k_2 = 8.8 \pm 0.2 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$. The value of k_1 obtained by extrapolation to zero concentration of hydroxide ion is in reasonable agreement with the value observed in the buffered solutions considering that the ionic strength was 0.5 rather than 0.3 in these measurements. At concentrations of hydroxide higher than 0.42 *M* the apparent rate constant increased more rapidly than predicted by the equation above. One preparative reaction was run in 0.43 *M* sodium hydroxide. The reaction yielded 18% of β-bromostyrene which was a mixture of *cis* and *trans* forms. In addition a 45% yield of acidic material with the equivalent weight expected of bromocinnamic acid was obtained. This product melted over a wide range and is presumably a mixture of *cis*- and *trans*-α-bromocinnamic acid.

A solution of dibromocinnamic acid in 75% acetic acid did not undergo decomposition when heated at 100° for thirty minutes indicating that the anion rather than the free acid is involved in the decomposition process.

TABLE II

RATE CONSTANTS FOR THE DECOMPOSITION OF CINNAMIC ACID DIBROMIDES

Acid dibromide	Solvent	Temp. (±0.1°)	10^5k_1 sec.$^{-1}$
Unsubstituted	Water	35.0	8.6 ± 0.5
		40.0	20.2 ± 0.5
		45.0	37.7[a]
		49.7	91.8 ± 0.4
	Absolute ethanol	60.3	6.9 ± 0.6
		70.0	23.8 ± 0.5
		79° (reflux)	70[b]
	Methyl ethyl ketone	35.5	2.53 ± 0.05
		45.3	7.4 ± 0.2
	Acetone	56° (reflux)	73 ± 8
p-Nitro	Water	76.5	25.8 ± 0.1
		91.5	168 ± 1
	Ethanol	76.5	20.8 ± 0.4
		85.0	69.2 ± 1.0
	Acetone	56° (reflux)	188 ± 6
p-Methoxy	Methyl ethyl ketone	30.5	21.8 ± 0.2
		35.5	32.2 ± 0.2

[a] Only one run was made at this temperature. [b] Estimated from ref. 5.

In Table II values of the specific rate constants for the decomposition of cinnamic acid dibromides in aqueous solutions and in the solvents ethanol and acetone or methyl ethyl ketone at different temperatures are listed. The reactions in aqueous solution were run in phosphate buffers at an initial pH of 8 using 0.020 *M* solutions of dibromo acid. The solutions in absolute ethanol were 0.12 *M* in anhydrous sodium acetate and 0.015 *M* in dibromo acid. In methyl ethyl ketone the solutions were 0.020 *M* in dibromo acid, and were stirred in contact with excess solid sodium bicarbonate. The acetone solutions were 0.02 *M* in dibromo acid and 0.30 *M* in triethylamine. In all cases the reactions followed good first order kinetics.

The reaction of *p*-methoxycinnamic acid dibromide both in water and in ethanol was so rapid even at 2° that decomposition was apparently complete in one minute. Kinetic data for this compound were determined only in methyl ethyl ketone.

The composition of the olefinic product produced by decomposition of the substituted cinnamic acid dibromides was studied. *p*-Nitrocinnamic acid dibromide in ethanol gave *cis*-*p*-nitro-β-bromostyrene in 73% yield. In acetone the *cis* olefin was isolated in 48% yield. In water the same acid decomposed in 39% yield to a mixture of olefins which contained 33 ± 3% *trans*- and 67 ± 3% *cis*-*p*-nitro-β-bromostyrene. These results are in general agreement with the observation of Dann, Howard, and Davies,[8] who reported a 50% yield of olefin which was mostly the *cis* isomer by decomposition in water. Since Cristol and Norris[9] isolated only the *cis* olefin when the preparation was carried out in 25% aqueous acetone there was some possibility that the *trans* isomer was not a primary product of reaction but might have been formed by isomerization. However, a sample of pure *cis*-*p*-nitro-β-bromostyrene was recovered in 83% yield when heated with aqueous bicarbonate and sub-

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[8] A. T. Dann, A. Howard, and W. Davies, *J. Chem. Soc.*, 605 (1928).

[9] S. J. Cristol and W. P. Norris, *J. Am. Chem. Soc.*, **75**, 632 (1953).

jected to the conditions used to isolate olefins from the reaction mixture. The presence of 2–3% of *trans* isomer would have been observed in the infrared spectrum of the olefin.

p-Methoxycinnamic acid dibromide in water gave an 86% yield of a solid olefin which had the infrared spectrum expected of a *trans*-β-bromostyrene. In methyl ethyl ketone the same olefin was isolated in 78% yield. The infrared spectra of the crude neutral fractions in these reactions were identical with the spectrum of the recrystallized solid olefin. Accordingly, we feel that no more than 2–3% of the *cis* isomer could have been present.

The stereochemical course of these reactions and of the unsubstituted cinnamic acid dibromide is summarized in Table III.

Table III

Olefins Prepared from Cinnamic Acid Dibromides

Cinnamic acid dibromide	Solvent	% Olefin	Composition
Unsubstituted	Water	61[2a]	22% *cis*, 78% *trans*
	Ethanol	58[2a]	86.5% *cis*, 13.5% *trans*
	Acetone	94[2a]	99.5% *cis*
p-Nitro	Water	50,[8] 39	67% *cis*, 33% *trans*
	Ethanol	73	Pure *cis*
p-Methoxy	Water	80	Pure *trans*
	Methyl ethyl ketone	78	Pure *trans*

It has been assumed that the *trans* olefins are produced from these *erythro* dibromo acids only by the ionization mechanism (similar to E_1), while the *cis* isomers are formed mostly by the concerted mechanism (similar to E_2), although a few per cent is expected to be produced by the nonstereospecific ionization process as well. From the composition of the products it is possible to estimate the mechanisms of the decomposition, although in those cases where mixtures are obtained and the two mechanisms are assumed to operate simultaneously the estimate of the contribution of each mechanism is rough. Table IV lists these mechanisms using the symbols I for ionization and C for concerted as well as the Arrhenius energies of activation and the entropies of activation calculated from the data in Table II. The specific rate constants in Table II refer to the total disappearance of dibromo acid and the activation parameters listed in Table IV actually refer to this process rather than to the elimination process alone.

Table IV

Activation Parameters and Mechanisms for the Decomposition of Cinnamic Acid Dibromides

Cinnamic acid dibromide	Solvent	E_a kcal.	ΔS^* e.u.	Mechanism
Unsubstituted	Water	32.0	+23.1	I
	Ethanol	29.0	+ 7.1	3 C:1 I
	Methyl ethyl ketone	22.3	− 9.5	C
p-Nitro	Water	31.7	+13.4	1.5 C:1 I
	Ethanol	35.2	+22.9	C
p-Methoxy	Water	[a]	[a]	I
	Methyl ethyl ketone	14.9	−28.3	I

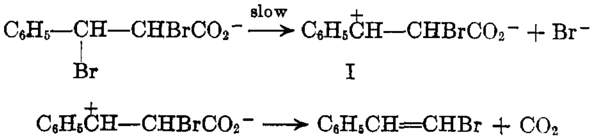
[a] Too fast for convenient measurement.

threo-α,β-Dibromo-β-phenylpropionic acid was prepared by the addition of bromine to *cis*-cinnamic acid. However, this compound decomposed so rapidly with base both in water and in ethanol that 0.02 M solutions prepared at 35° were almost completely reacted when the first sample was removed at one minute. A kinetic study of this rapid reaction was not undertaken. The product of these reactions is known to be *trans*-β-bromostyrene.[2a]

In subsequent work[10] the reaction of *cis*-cinnamic acid dibromide with iodide ion was studied. The *cis* dibromide reacts more slowly than does the *trans* dibromide and liberates only about 50% of the theoretical quantity of iodine. The reaction with iodide ion then is not a good analytical procedure for *cis*-cinnamic acid dibromide. However, only 7% of the theoretical quantity of iodine was liberated from a sample of *cis* dibromide after treatment with base for one minute and this titer did not decrease during the next forty minutes. *cis*-Cinnamic acid dibromide as prepared always contains a small amount of the *trans* dibromide and we believe that most of the iodine titrated was produced by this impurity and that the *cis* dibromide had reacted essentially completely in one minute.

Discussion

The decomposition of the anion of *trans*-cinnamic acid dibromide in aqueous solution is first order, with a rate which is independent of pH in the range pH 5–8. The reaction shows a slight positive salt effect, no mass law effect with bromide ion and is nonstereospecific. The entropy of activation is positive. These results are consistent with a mechanism in which the β-bromine atom is lost from the anion in the rate-determining step. The dipolar ion produced then loses carbon dioxide and collapses to a mixture of *cis*- and *trans*-β-bromostyrene in which the more stable *trans* isomer predominates. There is an increase in charge in going to the transition state which explains the positive salt effect.



$$C_6H_5\text{—}\underset{\underset{\textstyle Br}{|}}{C}H\text{—}CHBrCO_2^- \xrightarrow{\text{slow}} \underset{\textstyle I}{C_6H_5\overset{+}{C}H\text{—}CHBrCO_2^-} + Br^-$$

$$C_6H_5\overset{+}{C}H\text{—}CHBrCO_2^- \longrightarrow C_6H_5CH{=}CHBr + CO_2$$

We have little direct evidence concerning the degree of separation of the bromide ion from the dipolar ion in the transition state. Olson and Miller[11]

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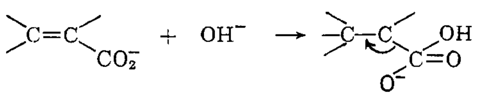
(10) K. M. Ibne-Rasa, Ph.D. thesis, Brown University, 1959.

(11) A. R. Olson and R. J. Miller, *J. Am. Chem. Soc.*, **60**, 2687 (1938).

observed that the titrimetric and polarimetric rate constants for the decomposition of β-bromobutyrate ion in water were equal. If these results can be extrapolated to the dibromocinnamate ion, internal return or isomerization before decomposition cannot be accepted as an explanation for the nonstereospecific nature of the elimination process. The fact that bromide ion exerts no mass-law effect argues against external return. The postulate that an intermediate dipolar ion collapses by loss of carbon dioxide to give the *cis* and *trans* olefins explains the result most simply.

The expression for the rate of decomposition of dibromocinnamate ion in solutions containing a considerable excess of hydroxide ion contains two terms, one of which is the first order factor observed in the pH range 5–8 and the second of which is a second order term involving hydroxide ion. Because of the values of the constants in these two terms at 40°, the second order process would account for less than 1% of the total reaction until the hydroxide ion concentration exceeds 2.5×10^{-4}. Accordingly, the rate of reaction would appear independent of pH to a value somewhat above pH 10. The nature of the second order reaction is not clear. To a large extent it must represent the dehydrobromination of dibromocinnamate ion to the α-bromocinnamic acids. Sudborough and Thompson[8] isolated these acids in 85% yield from a solution which was approximately 1 *M* in excess potassium hydroxide. We have obtained a 45% yield of bromocinnamic acids in 0.4 *M* sodium hydroxide. However, the yield of β-bromostyrene under these conditions (18%) was greater by a factor of three than can be explained using our expression for simultaneous first order and second order reactions if it is assumed that only the first order term represents decarboxylative elimination.

Vaughan and Craven[2b] report a case in which the amount of decarboxylative elimination is increased by using excess potassium hydroxide in place of sodium bicarbonate and have suggested a bimolecular process in which hydroxide ion assists in the release of electrons from the carboxylate group by attack at that carbon atom. This mechanism may represent part of our second order term. As far as we could determine by infrared analysis of the products, the β-bromostyrene isolated from the sodium hydroxide reaction had the same composition as did that isolated from a sodium bicarbonate induced reaction. It would appear that the bimolecular process in this case is not stereospecific. Sudborough and Thompson have shown, however, that the reaction leading to the α-bromocinnamic acids gives an excess (3:1) of the less stable "allo" form in which the phenyl and carboxyl groups are *cis*. Apparently, the dehydrobromination occurs predominantly by a stereospecific path involving *trans* elimination.



In the solvent absolute ethanol the decomposition of dibromocinnamate ion is still first order but proceeds much more slowly than in water. The yield of olefin is about the same but it consists largely of the *cis* isomer. It is assumed that the small amount of *trans* isomer obtained is produced by the same ionization mechanism that prevails in water and that the *cis* form arises from a stereospecific mechanism not observed in water.[5] The nature of the stereospecific elimination presumably involves a transition state in which the leaving bromide ion and carbon dioxide are *trans* and the charge of the anion is dispersed. The geometry of the reactant is more restricted in the transition state than in the ground state, but solvent molecules may be released, since the degree of solvation of the ion with dispersed charge is expected to be less. The effect of these factors on the entropy of activation is opposite and tends to cancel in a solvent such as ethanol so that the entropy of activation is small.

In methyl ethyl ketone the reaction of the unsubstituted acid dibromide occurs more rapidly than in ethanol and almost as rapidly as in water. Since the reaction system is heterogeneous in this solvent, some justification for believing that the reaction measured is the decomposition of dibromocinnamate ion was sought. Two runs were made at 45° using triethylamine as base and the value of the specific rate constant was $7.4 \pm 0.6 \times 10^{-5}$ sec.$^{-1}$, in agreement with the value found using sodium bicarbonate. Accordingly, we feel that the dibromocinnamic acid is rapidly converted to the anion by reaction with sodium bicarbonate and the anion remains in solution until it decomposes to olefin. However, reactions with sodium bicarbonate in boiling acetone or boiling methyl ethyl ketone did not follow first order kinetics and in these cases formation of the anion may be slow enough in comparison with the rate of decomposition to affect the order of the reaction.

The decomposition of *trans*-cinnamic acid dibromide is almost entirely stereospecific in acetone[2a] and is assumed to retain this characteristic in methyl ethyl ketone. The increase in rate in going from ethanol to the ketone as solvent is considered to be due to decreased stability of the anion in methyl ethyl ketone which is expected to be a poor solvating agent for a negative ion. This influence would be of less significance in the transition state for concerted elimination where the charge is dispersed than in the reactant anion where it is on the carboxyl group.

The *cis* effect in decarboxylative elimination has been reported to be large[12] and our observations of

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[12] D. Y. Curtin, *Rec. Chem. Progr.* (Kresge-Hooker Sci. Lib.), **15**, 111 (1954).

the reaction of *cis*-cinnamic acid dibromide are in qualitative agreement with this expectation.

The effect of a substituent in the *para* position is expected to be the greatest in reactions which proceed by the ionization mechanism where a positive charge is developed at the benzylic carbon atom. The methoxyl group should greatly increase the rate of this nonstereospecific mechanism for elimination whereas the nitro group should retard it. For the concerted reaction path the effect of both groups would be smaller because the development of charge in the transition state should be much less. In this system the interpretation of the substituent effect is complicated by the fact that the mechanism changes both with solvent and with substituent. In none of the cases reported here do the three compounds react by the same mechanism in any of the solvents. The effect of the *p*-methoxyl group on the reaction in water or ethanol, solvents in which the ionization mechanism is at least partly operative with the unsubstituted acid, is to enhance the rate greatly. In methyl ethyl ketone the reaction is slower but the nature of the product indicates that the ionization mechanism is still favored. The *p*-methoxy compound reacts (by the ionization mechanism) about twelve times as rapidly as does the unsubstituted dibromo acid (by the concerted mechanism) in methyl ethyl ketone at 35°. The substituent effect thus appears to be less in this solvent than in ethanol or water, but the reaction mechanism for the unsubstituted acid has changed. If the difference in rate of both compounds reacting by the ionization mechanism in methyl ethyl ketone could be obtained, it would necessarily be greater than the difference observed. On the other hand the reaction of *p*-nitrocinnamic acid dibromide occurs principally by the concerted path even in water and completely by the concerted path in ethanol. The unsubstituted acid reacts by the ionization mechanism in water and decomposes much more rapidly than does the *p*-nitro acid in this medium. The hypothetical reaction of the *p*-nitro acid in water by the ionization mechanism alone must be slower than the observed rate so that again the substituent effect on the ionization mechanism is seen to be large. In ethanol, however, both compounds react principally by the concerted mechanism and the difference in rate is not great; at 70° the specific rate constant for the unsubstituted acid is approximately the same as that of the *p*-nitro acid at 76.5°.

In refluxing acetone the reactions of the unsubstituted acid and of the *p*-nitro acid are stereospecific. Both compounds react more rapidly than in ethanol and the *p*-nitro acid is now faster than the unsubstituted acid. These results are consistent with the assumption that the ketones are poor solvating agents for anions so that for the concerted reaction in acetone, electronic factors which aid in formation of the double bond are more important than those which would favor breaking the benzylic bromide bond. The situation is analogous to that of the reaction of benzyl chlorides with iodide ion in acetone.[13]

This reaction series presents an interesting example in which the rates of two competing reactions are almost balanced in the decomposition of the unsubstituted dibromo acid in water. Changes in the solvent or the introduction of substituents suffice to direct the course of the decomposition into one or the other of the possible mechanisms in easily predictable ways. The solvent and substituent effects, the kinetic order of the reactions, and the activation parameters are consistent with the mechanisms previously proposed for this decomposition,[2] and the evidence taken as a whole provides a strong case for these mechanisms.

Experimental

Kinetic Method.—A sample of cinnamic acid dibromide was dissolved in 20 ml. of diethylene glycol and allowed to equilibrate with the constant temperature bath. This solution was poured into 180 ml. of the aqueous buffer or base solution which had also been brought to temperature. At intervals 10-ml. samples were withdrawn and run into 25 ml. of glacial acetic acid. Five milliliters of a freshly prepared 10% solution of potassium iodide was added and the flask was stoppered and heated in boiling water for 30 min. The solution was cooled, 100 ml. of water was added, and the iodine was titrated with thiosulfate. Blanks were run to correct for iodine liberated by chance oxidation of the iodide, but these were low.

The reactions in ethanol were followed similarly except that the solutions of dibromo acid and sodium acetate in absolute alcohol were mixed at room temperature and measured into tubes which were then cooled and sealed. The tubes were inserted into the thermostat and removed one at a time for analysis. Reactions in methyl ethyl ketone were run in a three-necked flask with continual stirring to keep the solvent saturated with sodium bicarbonate.

Isolation of Products from Reaction of Cinnamic Acid Dibromide with Sodium Hydroxide.—A sample of 5.00 g. (0.0163 mole) of *trans*-cinnamic acid dibromide was dissolved in 200 ml. of 0.509 *M* sodium hydroxide and heated at 40.0 ± 0.2° for 3 hr. The solution was cooled and extracted with five 20-ml. portions of carbon tetrachloride. These portions were combined and concentrated at room temperature under reduced pressure. The residue weighed 0.53 g. (18%). The infrared spectrum of this material was identical with that of mixtures of *cis*- and *trans*-β-bromostyrene obtained by decomposition using aqueous sodium bicarbonate as the base. The aqueous portion from which the bromostyrene had been extracted was acidified. A solid separated and was collected. This material weighed 1.67 g. when dry (45%) and had m.p. 86–110°. The neutralization equivalent was 230.0 (theoretical 227.1).

***cis*-Cinnamic Acid.**—Twenty grams of phenylpropiolic acid (m.p. 137–138°) was dissolved in 250 ml. of dry pyridine. Three grams of 5% palladium on calcium carbonate was added and washed in with 100 ml. of pyridine. The mixture was reduced with hydrogen at 1 atm. until an uptake of 1.0 mole of hydrogen per mole of acid was obtained. The catalyst was removed by filtration and the pyridine distilled from the filtrate under reduced pressure. The residue was washed with 50 ml. of 10% hydrochloric acid and the acid washings were extracted with three 100-ml. portions of pentane. Material which had not dissolved in the aqueous acid

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[13] G. M. Bennett and B. Jones, *J. Chem. Soc.*, 1815 (1935).

was taken up in boiling pentane and the pentane solution decanted from insoluble oil. The clear pentane extracts from the solid and from the aqueous acid washings deposited crystals of *cis*-cinnamic acid when the pentane was cooled. The acid was recrystallized from pentane to give 12.5 g. (63%) of material, m.p. 66–68° (lit.[2a] m.p. 66–68°).

***threo*-α,β-Dibromo-β-phenylpropionic Acid.**—*cis*-Cinnamic acid was converted to the dibromide by the procedure of Grovenstein and Theophilou.[2a] The first crystals which separated from hexane were discarded and later crops gave *cis*-cinnamic acid dibromide, m.p. 93.5–95.0°, 39% yield (lit.[2a] m.p. 88–92.5°).

***erythro*-α,β-Dibromo-β-(*p*-nitrophenyl)propionic Acid.**—The addition of bromine to *trans*-*p*-nitrocinnamic acid was carried out in acetic acid.[8] A solution of 12.9 g. (0.067 mole) of the acid in 160 ml. of glacial acetic acid was treated with a solution of 10.7 g. (0.067 mole) of bromine in 15 ml. of acetic acid. The mixture was heated at 100° for 6 hr. with stirring. About half of the solvent was removed by distillation under reduced pressure and the remainder poured into 400 ml. of ice water. The product was collected on a filter, dried, and recrystallized from a mixture of acetic acid and ether. The yield was 20.2 g. (86%) of material m.p. 216–217° (lit.[14] m.p. 216–217°)

***erythro*-α,β-Dibromo-β-(*p*-methoxyphenyl)propionic Acid.**—A solution of 7.10 g. (0.040 mole) of *trans*-*p*-methoxycinnamic acid prepared according to Borsche and Walter[15] in 25 ml. of glacial acetic acid was placed in a flask covered with aluminum foil. A solution of 6.40 g. (0.040 mole) of bromine in 15 ml. of acetic acid was added with stirring at room temperature over 90 min. and the mixture was stirred for an additional hour. The acetic acid was decanted from the solid which formed during this time and the solid was taken up in a small quantity of ether. Hexane was added and the ether removed to give 8.3 g. of crystalline material. An additional 1.8 g. was obtained from the mother liquor to yield 10.1 g. (75%), m.p. 156–157° (lit. m.p. 160°,[16] 140–145°[17]). The product contained 99.4% of the theoretical amount of bromine as shown by treatment with potassium iodide.[1] *trans*-*p*-Methoxycinnamic acid dibromide decomposes slowly and is especially unstable when stored under reduced pressure.

Isolation of Olefins from Decarboxylative Elimination Reactions. *trans*-*p*-Nitrocinnamic Acid Dibromide. a. In Ethanol.—Treatment of *trans*-*p*-nitrocinnamic acid dibromide with sodium acetate in anhydrous ethanol gave *cis*-*p*-nitro-β-bromostyrene in 73% yield, m.p. 45–46°. Recrystallization from pentane yielded product with m.p. 48–49° (lit.[14] m.p. 48–49°).

b. In Water.—A solution of 6.39 g. (0.0180 mole) of *p*-nitrocinnamic acid dibromide in 200 ml. of water containing 1.68 g. of sodium bicarbonate was heated at 82–85° for 6 hr. The solution was extracted with three 200-ml. portions of ether and the combined ether extracts washed with two 200-ml. portions of 5% sodium carbonate and with three 300-ml. portions of water. The ether solution was dried over sodium sulfate and the ether was distilled, leaving 1.74 g. (43%) of yellow solid, m.p. 42–110°. This solid was treated with two 30-ml. portions of hot pentane and the pentane extracts combined. The residue, 0.56 g., m.p. 146–147° was shown to contain 68 ± 2% of *trans*-*p*-nitro-β-bromostyrene and 32 ± 2% of an unidentified substance by measurement of the absorbance in the infrared region at 939 cm.$^{-1}$, 820 cm.$^{-1}$, and 740 cm.$^{-1}$. Recrystallization of this solid from ethanol gave pure *trans* olefin, m.p. 160° (lit.[8] m.p. 160°).

The pentane extract was distilled to dryness leaving 1.18 g. of solid, m.p. 44–46°, containing 89 ± 3% *cis*-*p*-nitro-β-bromostyrene and 11 ± 3% of the *trans* isomer as determined by comparison with spectra of mixtures of known composition at the wave lengths given above. The yield of *cis* isomer was accordingly 1.05 g. and the total yield of the *trans* isomer, 0.51 g.; 67% and 33%, respectively, in the mixture. The total yield of pure *cis* plus *trans* olefin was 39%.

It was shown that *cis*-*p*-nitro-β-bromostyrene does not isomerize to *trans* under the reaction conditions by heating 0.519 g. of the *cis* olefin, m.p. 47–48°, with 0.840 g. of sodium bicarbonate at 85° for 6 hr. The olefin was recovered in 83% yield, m.p. 46–48°. The infrared spectrum of the recovered olefin was identical with that of pure *cis*-*p*-nitro-β-bromostyrene.

***trans*-*p*-Methoxycinnamic Acid Dibromide. a. In Water.**—A solution of 3.38 g. (0.0100 mole) of the dibromide in 30 ml. of diethylene glycol was added to 400 ml. of phosphate buffer at pH 8.0 and the solution allowed to stand at room temperature for 30 min. The solution was washed with four 200-ml. portions of ether and the combined ether extracts washed with 400 ml. of water. Ether was removed by distillation and the solid residue washed onto a Buchner funnel with water. The product was washed well with water and dried to constant weight. The crude product weighed 1.85 g. (86%) and had an infrared absorption spectrum identical with that of pure *trans*-*p*-methoxy-β-bromostyrene. The sample was recrystallized from ethanol giving pure olefin, m.p. 55.0–55.5° (lit.[18] m.p. 55°).

b. In Methyl Ethyl Ketone.—To a solution of 3.38 g. (0.0100 mole) of *p*-methoxycinnamic acid dibromide in 190 ml. of methyl ethyl ketone and 10 ml. of diethylene glycol was added 2.52 g. of sodium bicarbonate and the mixture heated at 36° with constant stirring for 7 hr. Methyl ethyl ketone was removed from the solution by distillation at reduced pressure. The residue was poured into 300 ml. of water and the product isolated in the manner described above. The crude *trans*-*p*-methoxy-β-bromostyrene weighed 1.65 g. (78%) and was identical in its infrared spectrum with pure *trans* olefin.

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