furic acid gave in the usual way a black crude phenol. Two treatments of this material in benzene solution with charcoal gave, in turn, a gray, waxy solid, which was sublimed to give 2,3-dimethyl-5-phenylphenol as colorless needles of m.p. 51–52°.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.11. Found: C, 84.74; H, 6.94.

α-Naphthylurethan of 2,3-Dimethyl-5-phenylphenol.—Heating a mixture of 2,3-dimethyl-5-phenylphenol with α-naphthyl isocyanate and a catalytic amount of pyridine gave crude α-naphthylurethan of 2,3-dimethyl-5-phenylphenol. One crystallization from heptane gave pale yellow crystals, m.p. 135–136°.

Anal. Calcd. for $C_{25}H_{21}NO_2$: C, 81.72; H, 5.76; N, 3.81. Found: C, 81.55; H, 5.81; N, 3.53.

3,4-Dimethyl-5-phenylacetanilide.—A sample of the crude hydrochloride of 3,4-dimethyl-5-phenylaniline was converted with hot acetic anhydride to 3,4-dimethyl-5-phenylacetanilide, m.p. 167–168.3°, after crystallization from dilute acetic acid.

Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.86. Found: C, 80.28; H, 7.19; N, 5.82.

3,4-Dimethyl-5-phenylaniline (XIV).—Acid hydrolysis of 3,4-dimethyl-5-phenylacetanilide and liberation of the free amine from the separated amine hydrochloride gave a waxy solid. This was crystallized from dilute methanol to give 3,4-dimethyl-5-phenylaniline as colorless needles, m.p. 71–72°.

Anal. Calcd. for $C_{14}H_{15}N$: C, 85.23; H, 7.66; N, 7.10. Found: C, 85.28; H, 7.73; N, 7.11.

3,4-Dimethyl-5-phenylphenol (XV).—A solution of diazotized 3,4-dimethyl-5-phenylaniline in dilute sulfuric acid was slowly added to boiling 40% sulfuric acid, and the reaction mixture was boiled for ten minutes. Extraction of the cooled reaction mixture with ether gave, after removal of the solvent, crude 3,4-dimethyl-5-phenylphenol. Sublimation gave colorless needles of 3,4-dimethyl-5-phenylphenol, m.p. 106.5–107.5°, with no depression of m.p. on admixture with an authentic sample (Beringer and Kuntz, ref. 17). The ultraviolet absorption spectra of the two samples of the phenol were superimposable.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.11. Found: C, 84.88; H, 6.93.

α-Naphthylurethan of 3,4-Dimethyl-5-phenylphenol.—Heating a mixture of 3,4-dimethyl-5-phenylphenol with α-naphthyl isocyanate and a catalytic amount of pyridine gave crude α-naphthylurethan of 3,4-dimethyl-5-phenylphenol. This was crystallized twice from heptane to give colorless needles, m.p. 171–172°; reported[18] 171–172°. Admixture with an authentic sample[18] of this urethan showed no depression of the m p.

Anal. Calcd. for $C_{25}H_{21}NO_2$: C, 81.72; H, 5.76; N, 3.81. Found: C, 81.63; H, 5.60; N, 3.60.

BROOKLYN 2, N. Y.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, GEORGIA INSTITUTE OF TECHNOLOGY]

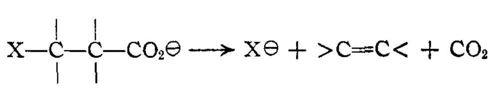
The Stereochemistry and Mechanism of the Transformation of Cinnamic Acid Dibromide to β-Bromostyrene[1]

BY ERLING GROVENSTEIN, JR., AND DONALD E. LEE

RECEIVED DECEMBER 17, 1952

The sodium salt of *trans*-cinnamic acid dibromide in absolute ethanol has been found to give β-bromostyrene which consists predominantly of the *cis* isomer, while in water predominantly the *trans* isomer results. Possible mechanisms for these reactions are considered and it is concluded that in absolute ethanol *trans* elimination of the elements of carbon dioxide and bromide ion occurs in a concerted process somewhat analogous to the bimolecular elimination reaction (E2) of alkyl halides. In water there appears to be a preliminary ionization followed by decarboxylation, a process which recalls the unimolecular elimination reaction (E1) of alkyl halides. The effect of substituents upon the stereochemistry, rate and product composition of analogous decarboxylative eliminations is discussed and found to be in general agreement with these mechanistic considerations. Dufraisse's synthesis of *cis*-β-bromostyrene is discussed.

The preparation of olefins from the salts of β-halo acids may be expressed by the equation



$$X{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}{-}CO_2^{\ominus} \longrightarrow X^{\ominus} + {>}C{=}C{<} + CO_2$$

One of the oldest known examples of this reaction is the transformation of cinnamic acid dibromide[2] to β-bromostyrene in boiling water or, frequently at lower temperature, in aqueous sodium carbonate. It seemed to us that such elimination reactions[3] might resemble elimination reactions of alkyl halides. One method of comparison would be by study of stereochemical interrelationships between products and reactants.

In 1904 Pfeiffer,[4] in his interesting repudiation of the van't Hoff–Wislicenus theory of *cis* elimination and *cis* addition, proposed that carbon dioxide and halide ion are eliminated from β-halo acids in the *trans* sense. Pfeiffer's theory does not seem to have received appreciable attention. In part, at least, this is due to the fact that diastereoisomeric β-halo acids have been reported in a number of cases to give the same olefin. Thus Liebermann[5] reported that the β-bromostyrene obtained from *cis*-cinnamic acid dibromide, m.p. 91–93°, in aqueous solution was about the same as that from *trans*-cinnamic acid dibromide, m.p. 200° (dec.). K. v. Auwers[6] has confirmed the observations of Liebermann and in addition reports that *trans*-cinnamic acid dibromide yields the same product when treated with alcoholic potassium acetate solution. Since these results are in opposition to Pfeiffer's theory and since Dufraisse[7] reports that *cis*- and *trans*-β-bromostyrene are readily isomerized by light, we have undertaken a repetition of the work of Liebermann and v. Auwers with respect to *trans*-cinnamic acid dibromide.

---

[1] Presented in part before the Division of Organic Chemistry, American Chemical Society, Atlantic City, N. J., Sept. 16, 1952.

[2] (a) A. Schmitt, *Ann.*, **127**, 319 (1863); (b) E. Erlenmeyer, *Z. Chem. Pharm.*, 546 (1864); *Ber.*, **13**, 306 (1880); (c) C. Glaser, *Ann.*, **147**, 84 (1868); *ibid.*, **154**, 168 (1870); (d) R. Fittig and F. Binder, *ibid.*, **195**, 141 (1879); R. Fittig and H. Kast, *ibid.*, **206**, 33 (1881); (e) J. U. Nef, *ibid.*, **308**, 267 (1899); (f) J. J. Sudborough and K. J. Thompson, *J. Chem. Soc.*, **83**, 666 (1903).

[3] It will be convenient to designate eliminations in which carbon dioxide and halide ion are lost as "decarboxylative eliminations." This term seems to have been used first in connection with an apparently similar reaction by E. J. Corey and G. Fraenkel, paper before the Division of Organic Chemistry, American Chemical Society, Sept. 16, 1952.

[4] P. Pfeiffer, *Z. physik. Chem.*, **48**, 40 (1904).

[5] C. Liebermann, *Ber.*, **27**, 2039 (1894).

[6] K. v. Auwers, *ibid.*, **45**, 2795 (1912).

[7] C. Dufraisse, *Ann. chim. (Paris)*, [9] **17**, 199 (1922).

Results

First it is necessary to assign configurations to the two stereoisomeric β-bromostyrenes.[7] As an aid in this assignment, ultraviolet absorption spectra have been determined and are shown in Fig. 1. We give the designation "*trans*" to the β-bromostyrene which has the higher refractive index and the higher melting point and which absorbs light at longer wave length and somewhat higher intensity. This assignment is based upon reasoning analogous to that of Cram[8] for the 2-phenyl-2-butenes.

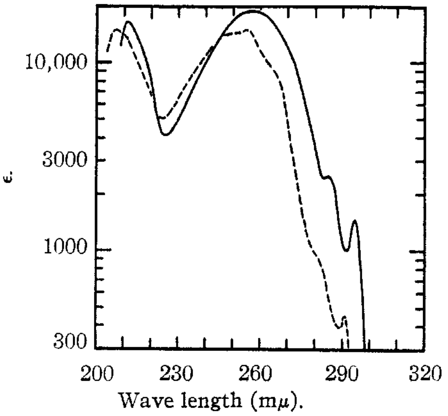


Fig. 1.—(- - -) *cis*- and (—) *trans*-β-bromostyrene in 95% ethanol.

The infrared spectra of *cis*- and *trans*-β-bromostyrene were found to be strikingly different in the region of 10 to 14 μ as is shown in Fig. 2. The four major absorption bands shown here provided a convenient method for quantitative estimation of the two geometrical isomers and lend support to the assignment of configurations (ref. 17).

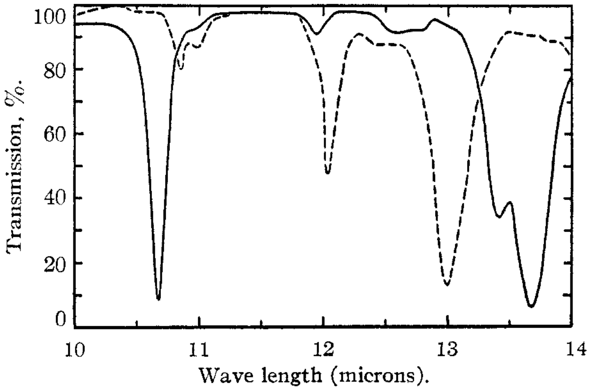


Fig. 2.—Infrared spectra of (- - -) *cis*- and (—) *trans*-β-bromostyrene, 200 mg./ml. isoöctane, in 0.1 mm. cell.

The sodium salt of *trans*-cinnamic acid dibromide at temperatures not exceeding 80° gives β-bromostyrenes of composition and yield as shown in Table I. Test experiments have shown that the β-bromostyrenes are readily isomerized by both heat and light; failure to recognize this probably explains the variant results in alcohol of v. Auwers. Our results in water are in agreement with the qualitative observations of previous investigators, that predominantly the higher melting (*trans*) isomer is formed. We are inclined to accept the value of 86% *cis* as the most reasonable estimate of the composition of the bromostyrenes formed in ethanol since most chance factors—presence of water in the ethanol or possible isomerization by heat, light or catalysts—would tend to give an enrichment with respect to the *trans*-isomer.

TABLE I

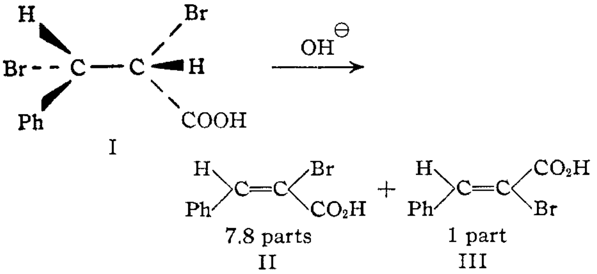
OLEFINS FROM THE SODIUM SALT OF *trans*-CINNAMIC ACID DIBROMIDE

Solvent	Yield[a] of β-bromostyrene, %	Composition of β-bromostyrene, % *cis*	*trans*
Abs. ethanol	47	78	22
Abs. ethanol	27[b]	86.5	13.5
Water	60.5	22	78
Water	55.5	21.5	78.5

[a] The yields are obtained by actual isolation of pure olefin.
[b] This yield is thought to be low due to adding inadvertently excess NaOEt during the early stages of the reaction.

Discussion

The Configuration of *trans*-Cinnamic Acid Dibromide.—*trans*-Cinnamic acid adds bromine under a wide variety of conditions to give a dibromide of melting point *ca.* 200° (dec.); only trace amounts[2f,9] of the diastereoisomeric lower melting dibromide are ordinarily formed. *cis*-Cinnamic acid adds bromine in carbon disulfide in the dark to give about 70% of the high melting and 30% of the low melting dibromide.[5] If we assume, as is generally recognized, that halogens tend to add preferentially in the *trans* sense to olefinic double bonds, then the above data indicate that the higher melting cinnamic acid dibromide has the configuration I (only one enantiomorph shown). This assignment is confirmed by the observation that treatment of *trans*-cinnamic acid dibromide with two equivalents of aqueous alkali in the cold results in the formation predominantly of α-bromocinnamic acid, (II), m.p. 120° with smaller amounts of the thermodynamically more stable isomer III, m.p. 131°.[2f,10] The configurations of II and III are well established on the basis that treatment with



cold concentrated sulfuric acid followed by dilution with water regenerates III but converts II into a polymer of bromoindenone,[11] that II has a higher acid dissociation constant than III,[12] that reduction of II with zinc dust in ethanol gives a predominance

---

(8) D. J. Cram, THIS JOURNAL, **71**, 3884 (1949).

(9) A. Michael, *Ber.*, **34**, 3664 (1901).

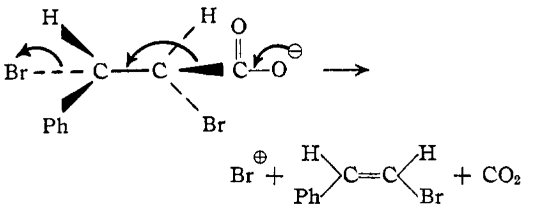
(10) T. C. James and J. J. Sudborough, *J. Chem. Soc.*, **95**, 1538 (1909).

(11) R. Leuckart, *Ber.*, **15**, 16 (1882); W. Manthey, *ibid.*, **32**, 2475 (1899).

(12) W. Ostwald, *Z. physik. Chem.*, **3**, 278 (1889); R. Schaller, *ibid.*, **25**, 520 (1898).

of *cis*-cinnamic acid from II and *trans*-cinnamic acid from III,[13,14] and that III undergoes elimination much more readily with alcoholic potassium hydroxide to give phenylpropiolic acid than does II.[15] The configuration of *trans*-cinnamic acid dibromide is further confirmed by its reaction with aqueous alcoholic potassium iodide to regenerate *trans*-cinnamic acid.[16] The validity of the use of such data as these in the assignment of configuration to olefins has been reviewed recently.[17]

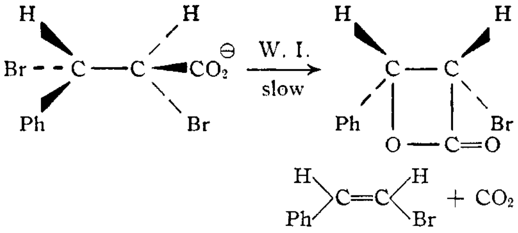
Mechanism of Decarboxylative Elimination.—With the configuration of *trans*-cinnamic acid dibromide established, it may be seen that *cis*-β-bromostyrene results from this acid in ethanol by *trans* elimination of the elements of carbon dioxide and halide ion. Sudborough and Thompson[2f] have presented evidence that β-bromostyrene is not formed from cinnamic acid dibromide by preliminary loss of hydrogen bromide to give either of the α-bromocinnamic acids (since these acids do not yield β-bromostyrene under the reaction conditions) nor by initial loss of carbon dioxide to give styrene dibromide (since styrene dibromide in presence of alkali gives both α- and β-bromostyrene). These authors concluded, "It is highly probable that the elimination of hydrogen bromide and the withdrawal of carbon dioxide, required for the production of bromocinnamene [β-bromostyrene] from cinnamic acid dibromide, occur simultaneously." We propose the following mechanism for this reaction



(1)

The anion of cinnamic acid dibromide is considered to decompose by a concerted mechanism which is rather analogous to the bimolecular elimination reaction (E2) of alkyl halides.[18]

An alternative mechanism was proposed at an early date by Erlenmeyer,[19] namely, that a β-lactone of transitory existence is formed and then decomposes immediately into olefin and carbon dioxide. This mechanism is capable of accounting for the stereochemical results in ethanol if a Walden inversion occurs in the formation of the β-lactone (this is known to be generally true[20]) and if the lactone loses carbon dioxide by *cis* elimination as shown below.



(2)

The decomposition of the β-lactone as shown is somewhat similar to the *cis* elimination of xanthates and acetates upon pyrolysis.[21]

The isolation[22] of β-lactones from decomposition of the salts of β-halo acids disproves Erlenmeyer's hypothesis insofar as he considered the lactone to be but a transitory intermediate, incapable of existence; however, this does not eliminate the possibility that β-lactones are stable but reactive intermediates in the formation of olefin. This latter interpretation was accepted by early workers since β-lactones were in fact generally found to yield olefin and carbon dioxide when heated.[22a–e] Johansson[23] has pointed out, however, that while the sodium salt of β-bromobutyric acid decomposes in water at 32° to the extent of 15% into propylene and carbon dioxide, the β-butyrolactone, isolable from this reaction in a yield of 60 to 70%, shows no tendency toward a similar decomposition under such conditions (or at higher temperature) but instead undergoes irreversible hydrolysis to β-hydroxybutyric acid. Indeed Basler[22b] noted that while β-*p*-nitrophenyl-β-propiolactone gave *p*-nitrostyrene when heated alone above its melting point (92°) or in anhydrous acetic acid, yet when refluxed in water the corresponding β-hydroxy acid was produced. Indeed most of the successful decompositions of β-lactones into olefin and carbon dioxide seem to have been conducted in absence of solvent,[24] in an inert solvent,[24] or in the gaseous phase[25]; the formation of polyesters may be a competing reaction.[26a] The reported decomposition of β-*o*-nitrophenyl-β-propiolactone[20a] into olefin and carbon dioxide upon boiling with water is probably to be attributed to the insolubility of this lactone (m.p. 124°) in water.[26c] We favor, therefore, mechanism (1) to explain our results in ethanol and we do not believe that mechanism (2) is of much general importance for olefin formation from other

---

(13) E. Erlenmeyer, *Ann.*, **287**, 5 (1895).

(14) C. Liebermann, *Ber.*, **28**, 134 (1895).

(15) J. J. Sudborough and T. C. James, *J. Chem. Soc.*, **89**, 110 (1906).

(16) C. F. van Duin, *Rec. trav. chim.*, **45**, 345 (1926).

(17) L. Crombie, *Quart. Rev.* (*London*), **VI**, 101 (1952).

(18) Thus see the following and references therein: (a) E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941); (b) M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw and L. I. Woolf, *J. Chem. Soc.*, 2093 (1948); (c) S. J. Cristol, N. L. Hause and J. S. Meek, THIS JOURNAL, **73**, 674 (1951).

(19) E. Erlenmeyer, *Ber.*, **13**, 303 (1880).

(20) (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 175; (b) P. D. Bartlett and P. N. Rylander, THIS JOURNAL, **73**, 4275 (1951).

(21) E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 120.

(22) The following examples are illustrative: (a) A. Einhorn, *Ber.*, **16**, 2208 (1883); (b) A. Basler, *ibid.*, **16**, 3001 (1883); (c) A. Einhorn and W. Hess, *ibid.*, **17**, 2015 (1884); (d) G. Prausnitz, *ibid.*, **17**, 595 (1884); (e) A. Eichengrun and A. Einhorn, *ibid.*, **23**, 2876 (1890); (f) A. Einhorn and P. Lehnkering, *Ann.*, **246**, 160 (1888); (g) A. Baeyer and V. Villiger, *Ber.*, **30**, 1954 (1897).

(23) H. Johansson and S. M. Hagman, *ibid.*, **55**, 647 (1922).

(24) H. Staudinger, *ibid.*, **41**, 1355 (1908).

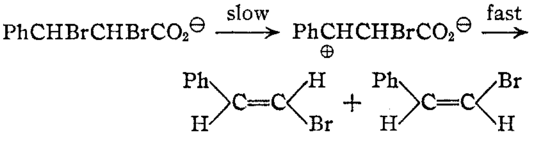
(25) H. Salkowski, Jr., *J. prakt. Chem.*, **106**, 253 (1923).

(26) (a) T. L. Gresham, J. E. Jansen and F. W. Shaver, THIS JOURNAL, **70**, 998 (1948); (b) T. L. Gresham, J. E. Jansen, F. W. Shaver and J. T. Gregory, *ibid.*, **70**, 999 (1948).

(26c) In certain cases, however, a non-stereospecific conversion of β-lactones into olefins probably can occur in ionizing solvents *via* an initial ionization to give a dipolar ion (see mechanism (3)). A possibe example is the recently reported decomposition in water of β-isovalerolactone into isobutylene and carbon dioxide (see T. L. Gresham, J. E. Jansen, F. W. Shaver and W. L. Beears, *Am. Chem. Soc. Abst.*, Los Angeles, March, 1954, p. 25M).

β-halo acids in nucleophilic solvents such as ethanol and water.[27]

In water, instead of alcohol, the sodium salt of *trans*-cinnamic acid dibromide decomposes to give predominantly *trans*-β-bromostyrene in an amount approaching the equilibrium composition (approximately 90% *trans*[7]). Since this non-stereospecific reaction is promoted by a good solvent for ion formation, a reasonable assumption is that ionization occurs to give an intermediate carbonium ion with loss of stereospecific configuration about the center of ionization. While the detailed structure and reaction path of this carbonium ion cannot be fully judged from the evidence now available, a simple explanation of olefin formation is that the carbonium ion loses carbon dioxide as shown below.



$$\mathrm{PhCHBrCHBrCO_2^{\ominus}} \xrightarrow{\text{slow}} \underset{\oplus}{\mathrm{PhCHCHBrCO_2^{\ominus}}} \xrightarrow{\text{fast}}$$

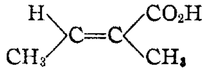
(3)

(predominant)

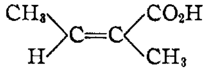
This mechanism resembles in principle the unimolecular elimination reaction (E1) of alkyl halides.[18] The intermediate carbonium ion is similar to that postulated by Johnson and Heinz[28] for the acid-catalyzed decarboxylation of certain cinnamic acids in aqueous acetic acid. It is possible that the *trans*-β-bromostyrene which seems to be formed to some extent even in absolute alcohol results from some participation of the above ionization mechanism or else a mechanism intermediate between (1) and (3) occurs.[29]

Stereochemistry of Related Decarboxylative Eliminations.—In addition to the early examples cited by Pfeiffer,[4] the following cases are instructive. *trans-p*-Nitrocinnamic acid dibromide when heated with alcoholic sodium acetate gives the pure low-melting form of *p*-nitro-β-bromostyrene (doubtlessly the *cis* isomer), and even in aqueous solution gives a mixture consisting mostly of the low-melting isomer.[30a] *trans-o*-Cyanocinnamic acid dibromide when boiled with aqueous sodium acetate gives *cis-o*-cyano-β-bromostyrene and *cis-o*-cyanocinnamic acid dibromide when merely boiled with water gives *trans-o*-cyano-β-bromostyrene.[30b,17] What is doubtless *trans-p*-cyanocinnamic acid dibromide gives *cis-p*-cyano-β-bromostyrene when heated with aqueous sodium acetate.[30b] These examples show that introduction of electron withdrawing nitro or cyano groups into cinnamic acid dibromide reduces the tendency for the ionization mechanism to occur relative to the mechanism for *trans* elimination. An alkyl group should be less effective in stabilizing a carbonium ion than a phenyl group hence it is not surprising that crotonic acid dibromide when treated with aqueous sodium carbonate gives an olefin which consists mainly of *cis*-propenyl bromide.[31]

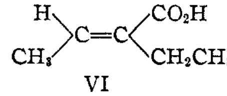
The hydroiodide of tiglic acid (IV) gives *trans*-2-butene, while the hydriodide of angelic acid (V) gives *cis*-2-butene upon treatment with aqueous sodium carbonate.[32] The two hydroiodides of 2-pentenoic acid likewise give the corresponding *cis*- or *trans*-2-pentene.[33] The hydrobromide[34] and hydroiodide[35] of 2-ethyl-2-butenoic acid, m.p. 41.4°, of the probable configuration VI shown, give *trans*-2-pentene upon treatment with aqueous sodium carbonate. The interpretation of the stereochemistry of these reactions is complicated by the unknown stereochemistry of hydrogen halide addition products.[36] A reasonable assumption[17] is that for these acids the addition of hydrogen halide proceeded in the *trans* sense; on this basis it is evident that decarboxylative elimination also proceeded in the *trans* sense.



IV



V



VI

Influence of Substituents upon Rate and Product Composition.—Mechanisms (1), (2) and (3) demand that the rate of decarboxylative elimination be first order in the concentration of the anion of the β-halo acid (neglecting salt effects[27]). This was true of the cases studied by Johansson[37] and Hagman,[23] Olson and Miller[38] and Lane and Heine.[39] In a preliminary investigation, we have found that the sodium salt of *trans*-cinnamic acid dibromide in refluxing ethanol loses carbon dioxide in accordance with the first-order law; the specific rate constant for carbon dioxide evolution is 2.5×10^{-2} min.$^{-1}$ and is constant within an average deviation of 6% over seven half-lives, decarboxylation constituting 58% of the total reaction. Ogata[40] and co-workers have published kinetic data for a considerable number of additional β-halo acids; their first-order rate constants fall appreciably with time, in part, at least, since they failed to keep their solutions at constant *p*H.

---

(27) β-Lactones have been found to react with sodium halides to regenerate the corresponding β-halo acid (see ref. 26b and 44). To be sure, β-lactones may in this sense occasionally serve as intermediates, but not direct intermediates, in the formation of olefin. Since the reaction with halide ion should occur with a Walden inversion, the regenerated β-halo acid would have the same configuration as the starting acid, such that this reaction would be of kinetic but not of stereochemical importance.

(28) W. S. Johnson and W. E. Heinz, THIS JOURNAL, **71**, 2913 (1949).

(29) *Cf.* S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951); C. G. Swain and W. P. Langsdorf, Jr., *ibid.*, **73**, 2813 (1951).

(30) (a) A. T. Dann, A. Howard and W. Davies, *J. Chem. Soc.*, 605 (1928); *cf.* S. Reich and N. Y. Chang, *Helv. Chim. Acta*, **8**, 240 (1920). (b) W. Davies, B. M. Holmes and J. F. Kefford, *J. Chem. Soc.*, 357 (1939).

(31) E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2078 (1951).

(32) W. G. Young, R. T. Dillon and H. J. Lucas, THIS JOURNAL, **51**, 2528 (1929).

(33) H. J. Lucas and A. N. Prater, *ibid.*, **59**, 1682 (1937).

(34) W. M. Lauer and F. H. Stodola, *ibid.*, **56**, 1216 (1934).

(35) M. L. Sherill and E. S. Matlack, *ibid.*, **59**, 2134 (1937).

(36) G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 302.

(37) H. Johansson, *Ber.*, **48**, 1262 (1915).

(38) A. R. Olson and R. J. Miller, THIS JOURNAL, **60**, 2687 (1938).

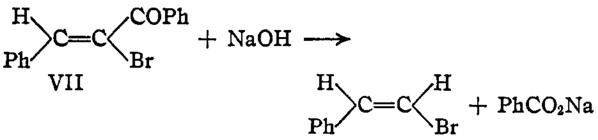
(39) J. F. Lane and W. H. Heine, *ibid.*, **73**, 1348 (1951). These authors failed to note that some 15% of the reaction of β-bromocaproate anion must have been decarboxylative elimination.

(40) Y. Ogata, R. Kometani, K. Tsunemitsu and R. Oda, *Bull. Inst. Phys. Chem. Research* (*Tokyo*), *Chem. Ed.*, **23**, 22 (1944). We are greatly indebted to Mr. Takashi Sakaye for aid in translation of this article.

Since the formation of olefin from the salts of β-halo acids proceeds simultaneously with formation of β-hydroxy acid or β-lactone,[23,41] it is of interest to consider the effect of substituents upon both reaction rate and product composition. From the above cited kinetic work, the following conclusions may be drawn. Alkyl substituents in alpha or beta positions increase both the rate and extent of olefin formation; a β-phenyl group is about as effective in this regard as two β-methyl substituents. An α-bromo substituent also increases the yield of olefin. These conclusions with respect to the yield of olefin are supported by much additional work, especially that of Bachman[42] and co-workers. The effect of substituents upon the rate of decarboxylative elimination and the yield of olefin formed in competition with β-lactone or β-hydroxy acid qualitatively parallels the effect of substituents upon the rate of unimolecular and bimolecular elimination reactions of alkyl halides[18b] and the yield of olefin formed in competition with products of substitution. The data of Ogata[40] and co-workers also show that increase in temperature favors decarboxylative elimination relative to formation of β-lactone[43] or β-hydroxy acid just as is also true of elimination *versus* substitution reactions of alkyl halides.[18a]

Zaugg[44] has found that for compounds of type $XCH_2C(C_6H_5)_2CO_2Na$ the per cent. olefin in the product (olefin plus β-lactone) was approximately 0, 27 and 67 as X was, respectively, Cl, Br and I. A similar but not generally so striking an effect is observed in the bimolecular reactions of alkyl halides with bases. The fact then that cinnamic acid hydrobromide and hydroiodide[40] give about the same percentage olefin suggests[18a] that these acids yield a common carbonium ion intermediate and hence react by mechanism (3) above.

Dufraisse's Synthesis of *cis*-β-Bromostyrene.—Until the present work the only suitable synthesis of *cis*-β-bromostyrene was by Dufraisse[45] who treated α-bromobenzalacetophenone, m.p. 42–43°, with powdered sodium hydroxide at 70°. Recently the configuration of this starting compound has been shown[46] to be VII and hence this reaction represents still another type of replacement at a trigonal carbon atom with retention of configuration.[17,47] As in some of the related cases, a vinyl anion is probably a reactive intermediate; the anion maintains its configuration just as do isoelectronic Schiff bases or related oximes. If one accepts the idea that such replacements at a trigonal carbon atom do occur with retention of configuration, then Dufraisse's synthesis of the low-melting β-bromostyrene confirms our designation of this olefin as being of *cis* configuration.



Experimental Details

Reagents.—*trans*-Cinnamic acid, Eastman Kodak Co., and bromine, Baker's reagent grade, were used without further purification. Absolute ethanol was purified by the method of Manske as cited by Fieser.[48] Cinnamic acid dibromide was prepared by addition of bromine to *trans*-cinnamic acid in chloroform in presence of a 300-watt unfrosted tungsten lamp. The crude dibromide (94% yield) was recrystallized from chloroform to give a product of m.p. *ca.* 200° (dec.).

β-Bromostyrene from *trans*-Cinnamic Acid Dibromide in Ethanol.—In a 5-liter 3-necked flask equipped with stirrer, dropping funnel and reflux condenser was placed 200 g. (0.649 mole) of cinnamic acid dibromide dissolved in 2000 ml. of absolute ethanol. Enough sodium ethoxide in absolute ethanol was added to make the solution just neutral toward phenolphthalein. The solution was refluxed for 1.6 hours with addition of enough sodium ethoxide to keep neutral. In all 925 ml. (1.09 moles) of 1.176 *N* sodium ethoxide was required. The solution was concentrated to 1000 ml. and added to 2300 ml. of water in a separatory funnel. The resulting oil was separated and the aqueous layer extracted with three 250-ml. portions of carbon tetrachloride. The combined oil and carbon tetrachloride extracts were washed three times each with 200-ml. portions of saturated sodium bicarbonate solution, 200-ml. portions of 0.5 *M* sodium thiosulfate, and finally 400-ml. portions of water. The carbon tetrachloride after drying overnight over anhydrous calcium chloride was stripped of solvent and finally distilled *in vacuo* through a Claisen flask with indented side-arm. Care was taken not to heat the flask above 80° while the β-bromostyrene remained undistilled. There was obtained 56.3 g. (47% yield) of β-bromostyrene, b.p. 38–46° (0.2 mm.), $n^{25}D$ 1.5975–1.6000, whose infrared analysis gave 78% *cis*- and 22% *trans*-β-bromostyrene. In addition there was obtained 20.3 g. of a fraction of b.p. 74–80° (0.2 mm.), $n^{25}D$ 1.5120–1.5150. This fraction was saponified by refluxing for a half hour with 22% aqueous sodium hydroxide; ethanol was isolated and identified as its 3,5-dinitrobenzoate, m.p. and mixed m.p. of 92–93°. The unknown ethyl ester gave the following analysis[49]: C, 68.20; H, 6.5; Br, 2.96. These values are close to those—C, 67.8; H, 6.15; Br, 2.62—calculated for the ethyl ester of β-phenylglycidic acid contaminated with 6% by weight of β-bromostyrene. β-Phenylglycidic acid has been identified from the analogous reaction run in water.[2b] In other runs the yield of β-bromostyrene was sometimes lower although the ratio by weight of high boiling ester to β-bromostyrene remained essentially the same (0.39 ± 0.04). The lower yields are probably to be attributed to addition of excess alkali, the excess converting cinnamic acid dibromide to α-bromocinnamic acid.[2f,10] The older use of potassium[6] or sodium acetate[30a] in place of sodium ethoxide is probably to be preferred in synthetic work.

β-Bromostyrene from *trans*-Cinnamic Acid Dibromide in Water.—Cinnamic acid dibromide (200 g.) was treated as described above except that water and sodium hydroxide were used in place of ethanol and sodium ethoxide. The solution was heated at 78 ± 3° for 45 minutes (much of the reaction seems to have occurred before this temperature was attained). In all 1377 ml. (1.32 equiv.) of 0.959 *N* NaOH was added to keep the solution neutral toward phenolphthalein. Upon cooling the solution was extracted directly with carbon tetrachloride and worked up as previously described for the reaction in ethanol. There was

---

(41) In some cases there may be a little α,β-unsaturated acid formed; thus in a favorable case, the sodium salt of cinnamic acid hydrobromide in water is reported to give about 5% cinnamic acid (see R. Fittig and F. Binder, *Ann.*, **195**, 131 (1879)).

(42) G. B. Bachman, THIS JOURNAL, **55**, 4279 (1933); J. K. Farell and G. B. Bachman, *ibid.*, **57**, 1281 (1935); A. A. Alberts and G. B. Bachman, *ibid.*, **57**, 1284 (1935).

(43) For a case where increase in temperature is reported to have little effect upon the yield of olefin see ref. (23).

(44) H. E. Zaugg, THIS JOURNAL, **72**, 2998 (1950). Because of the reversible formation of the β-lactone, the per cent. olefin cited may be a little high for comparison in the case of the iodide but this can hardly be true for the bromide and chloride.

(45) C. Dufraisse, *Ann. chim.* (*Paris*), [9] **17**, 161 (1922).

(46) R. E. Lutz, D. F. Hinkley and R. H. Jordan, THIS JOURNAL, **73**, 4647 (1951).

(47) D. Y. Curtin and E. E. Harris, *ibid.*, **73**, 2716, 4519 (1951); M. C. Hoff, K. W. Greenlee and C. E. Boord, *ibid.*, **73**, 3329 (1951); E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2078 (1951).

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

(49) Analyses by Clark Microanalytical Laboratory.

obtained 71.9 g. (60.5% yield) of β-bromostyrene, b.p. 44–54° (0.2–0.8 mm.), $n^{25}D$ 1.6037, whose infrared analysis gave 22% *cis*- and 78% *trans*-β-bromostyrene. A duplicate run (but with *n*-pentane in place of carbon tetrachloride for the extractions) gave similar results.

Effect of Heat and Light upon β-Bromostyrene.—Small portions of β-bromostyrene, $n^{20.5}D$ 1.6024, were sealed in glass ampules which were heated directly in the refluxing liquid for the specified time and the refractive indices of the heated samples were then determined as recorded below.

Refluxing liquid	Time (hr.)	Final $n^{20.5}D$
Toluene	4.0	1.6065
Toluene	3.75	1.6051
Ethanol	3.75	1.6024

Samples of β-bromostyrene were subjected directly to irradiation under the conditions shown below.

Light source	Time of irradn., hr.	$n^{20.5}D$ Initial	Final
300-w. tungsten lamp (frosted bulb)	4.3	1.6024	1.6026
G. E. 100-w. AH-4 ultraviolet lamp	1.7	1.5997	1.6073
Direct sunlight	2.0	1.5997	1.6045

From the above data it is concluded that the isomerization of β-bromostyrene should not occur at temperatures near that of refluxing ethanol (78°) for periods of time approximating those used in the syntheses of β-bromostyrene nor upon moderate exposure to diffuse daylight or artificial illumination. For additional protection the Pyrex reaction vessels were wrapped with cloth towels and samples awaiting infrared analysis were stored in a refrigerator in opaque containers or generally in low-actinic glassware.

Analysis for *cis*–*trans*-Isomers of β-Bromostyrene.—Pure *trans*-β-bromostyrene was prepared by crystallization of a sample of β-bromostyrene, $n^{25}D$ 1.6059, obtained by fractional distillation of the practical grade β-bromostyrene of Eastman Kodak Co. through a 3-foot column packed with glass helices. Two crystallizations from methanol at −30° gave a product of $n^{25}D$ 1.6069. Two additional crystallizations gave a product of $n^{25}D$ 1.6071, $n^{20.5}D$ 1.6093. Dufraisse[45] reports the value of $n^{20.5}D$ 1.6094.

Pure *cis*-β-bromostyrene was prepared by crystallization of the β-bromostyrene obtained above from the salt of *trans*-cinnamic acid dibromide in ethanol. After three recrystallizations from *n*-pentane at −45°, the sample had $n^{25}D$ 1.5980, $n^{22.2}D$ 1.5996. Dufraisse reports the value of $n^{22.2}D$ 1.5990. The best criterion which we have for the purity of our samples of *cis*- and *trans*-β-bromostyrene is provided by their infrared absorption spectra (see Fig. 2). The ultraviolet absorption spectra are also helpful; these were determined by means of a Beckman Quartz Spectrophotometer, Model DU (see Fig. 1).

It was initially hoped that analyses could be made for mixtures of *cis*- and *trans*-β-bromostyrene by means of refractive index measurements. This method was, however, found to be unreliable by our procedure. Thus refractive indices indicated that a particular sample of β-bromostyrene had some 20% less *trans* isomer than was found by infrared measurements. This result can be readily explained if it is assumed that this sample of β-bromostyrene (and probably some of the others) was contaminated with as little as 0.6% of a third component of low refractive index such as ethanol.

Infrared spectra were determined by means of a Beckman Model IR2 infrared spectrophotometer using 0.1-mm. rock salt cells and solutions which contained 0.200 g. of β-bromostyrene per milliliter of pure isoöctane. Empirical calibration curves were prepared based upon synthetic mixtures of the above pure *cis*- and *trans*-β-bromostyrene; plots of optical density *versus* percentage composition were almost linear. The absorption maxima at 10.7 and 13.7 microns for *trans*-β-bromostyrene and at 12.1 and 13.0 microns for the *cis* isomer were used in the analyses and the results reported are based upon the average of the four values thus obtained. The average deviation of the individual values from the average value was less than 1% in the region of 80% *cis* and did not exceed 2% in the vicinity of 80% *trans;* the maximum deviation of any of the individual values was 3%.

Kinetic Data.—Approximate kinetic data for the rate of the decarboxylative elimination reaction in ethanol were obtained by measurement over mercury of the volume of carbon dioxide evolved. Zero time was taken at the point when the solution began vigorous reflux (the volume here checked essentially the contraction volume upon cooling). The initial concentration was 0.25 *M* in the sodium salt of *trans*-cinnamic acid dibromide and the solution was kept neutral by dropwise addition of alcoholic sodium ethoxide containing a little phenolphthalein. For the salt of a β-halo acid undergoing any number of simultaneous first-order reactions, one of which is decarboxylation, the following equation is derivable

$$k_D = \frac{2.303}{t} N_D \log\left(\frac{V_\infty}{V_\infty - V_t}\right)$$

where

k_D = rate constant for carbon dioxide evolution

V_∞ and V_t are the volumes of carbon dioxide evolved at infinite time and time t, respectively

t = time measured from $t = 0$ at $V = 0$

N_D = fraction of reacted β-halo acid which has undergone decarboxylation or $N_D = V_\infty / V_{\text{theoretical}}$ for 100% decarboxylation

Basically this same equation was used in recalculation of the data of Ogata, *et al.*[40] Extrapolation of k_D to $t = 0$ makes k_D independent of the value selected for N_D provided that the corresponding values are used for V_∞.

Acknowledgments.—The authors are indebted to Dr. W. M. Spicer and Dr. W. H. Eberhardt for aid in derivation of the kinetic equations, again to the latter and to Mr. N. H. Horton for assistance with the infrared analyses, and to Dr. Jack Hine for helpful discussions. After the work described in this paper was completed, it became known to us that Cristol and Norris[50] had completed work of a similar nature. We are indebted to Dr. Cristol for interesting discussions of their work and our own.

ATLANTA, GA.

---

(50) S. J. Cristol and W. P. Norris, THIS JOURNAL, **75**, 2645 (1953).