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Mechanisms of Elimination Reactions. IX. The Spontaneous Decomposition of Salts of β-Halo Acids. II. *trans*-Cinnamic Acid Dibromide[1]

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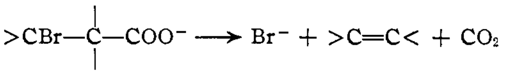
trans-Cinnamic acid dibromide was found to give a mixture of *cis*- and *trans*-β-bromostyrene upon treatment with sodium acetate in ethanol. As this mixture was richer in *cis*-β-bromostyrene than was that reported in an aqueous system, acetone was then tried as solvent, and the substantially pure *cis* isomer was formed. The results are considered in terms of two mechanisms for these decompositions of salts of β-halo acids, one involving a stereospecific concerted process and the other involving an ionization of the carbon–halogen bond and a dipolar ion intermediate.

The decomposition of the salt of *trans*-cinnamic acid dibromide (*erythro*-α,β-dibromo-β-phenylpropionic acid) to give β-bromostyrene has been described by Barisch[2] and has been repeated by a number of other workers.[3] β-Bromostyrene may exist in either the *cis* or *trans* modification, but many of the previous workers did not report data from which it would be possible to determine the isomeric content of their products. From the combined data of v. Auwers,[3d] Dufraisse[3e] and Dann, Howard and Davies,[3f] it appears that decomposition of *trans*-cinnamic acid dibromide in aqueous sodium carbonate led to a mixture, melting at about +2°, containing 80 to 90% of *trans*-β-bromostyrene and 10 to 20% of the *cis* isomer. Other modes of alkaline decomposition led to mixtures of undisclosed composition.[3d]

As we had previously shown that the decomposition of the sodium salt of *trans*-*p*-nitrocinnamic acid dibromide in either absolute ethanol or in a water–acetone mixture led to the pure *cis* isomer of *p*-nitro-β-bromostyrene[1] and, as we were interested in pure *cis*-β-bromostyrene for another research problem, we undertook a study of the stereochemistry of the decomposition of the sodium salt of *trans*-cinnamic acid dibromide. We were concerned with the question as to whether the decomposition reaction was or was not stereospecific—that is, whether the reported mixtures resulted from non-stereospecificity in the reaction or from rearrangements during the subsequent isolation of the product, as it is known that these olefins are subject to isomerization.[3e,f]

Accordingly *trans*-cinnamic acid dibromide was treated with sodium acetate in anhydrous ethanol, conditions wherein the corresponding *m*-nitro[1] and *p*-nitro[4] compounds gave pure *cis* olefins. When the product was worked up, a mixture of β-bromostyrene isomers (58% yield) melting at −17 to −10° was obtained. As *trans*-β-bromostyrene melts at +7° and *cis* at −7°,[3e] it is clear that the product resulting from the reaction in ethanol contained more of the *cis* isomer than did that, m.p. +2°, reported for the aqueous decompositions. The pure *cis* isomer was then exposed to the conditions of this experiment and was found to be stable toward isomerization. Thus it appears that the pure *trans* elimination of carbon dioxide and halide ion which would result in pure *cis* olefin[1] did not obtain under either set of conditions described above and that the non-stereospecific elimination process was more important in the system with better solvating power. This suggested the use of acetone as solvent to obtain pure *trans* elimination and pure *cis* olefin. When *trans*-cinnamic acid dibromide was treated with acetone and sodium bicarbonate, the resulting bromostyrene (84% yield) melted at −11 to −8° without any purification and at −8 to −7° after simple distillation. As our best sample of *cis*-β-bromostyrene melted at −7 to −6° after recrystallization, it appears that the acetone reaction resulted in substantially pure stereospecific *trans* elimination. The use of sodium bicarbonate in acetone may develop into a useful technique for the preparation of other pure *cis*-β-bromostyrenes and analogous compounds.

The facts at hand appear to compel at least two mechanisms for the debrominative decarboxylation. For the stereospecific *trans* elimination with *trans*-*m*-nitrocinnamic acid dibromide, we have proposed[1] a concerted elimination process involving simultaneous loss, from the anion, of carbon dioxide and bromide ion and formation of the olefinic bond, *viz.*,



$$>\mathrm{CBr}-\underset{|}{\overset{|}{\mathrm{C}}}-\mathrm{COO}^- \longrightarrow \mathrm{Br}^- + >\mathrm{C}=\mathrm{C}< + \mathrm{CO}_2$$

and it is presumed that a similar mechanism obtains in this case. For the non-stereospecific elimination, at least two possibilities may be suggested. The first involves a rate-determining ionization of the β-carbon–halogen bond to give the dipolar ion I, which might then lose carbon dioxide to give a mixture of *cis*- and *trans*-β-bromostyrene.

$$\mathrm{PhCHBrCHBrCOO}^- \longrightarrow \mathrm{Ph\overset{+}{C}HCHBrCOO}^- \ (\mathrm{I}) + \mathrm{Br}^-$$
$$\mathrm{I} \longrightarrow \mathrm{PhCH{=}CHBr} + \mathrm{CO}_2$$

A second possible mechanism for the non-stereospecific elimination involves a rearrangement of the *erythro* dibromo acid to the *threo* acid, possibly through the dipolar ion I–bromide ion pair and presumably by an "internal return" process,[5] followed by elimination from the *threo* acid.

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[1] Previous paper in series: S. J. Cristol and W. P. Norris, THIS JOURNAL, **75**, 632 (1953). This work was reported in part at the Conference on Organic Reaction Mechanisms at Bryn Mawr, Pa., Sept. 10, 1952.

[2] F. Barisch, *J. prakt. Chem.*, [2] **20**, 173 (1879).

[3] (a) J. U. Nef, *Ann.*, **308**, 267 (1899); (b) J. J. Sudborough and K. J. Thompson, *J. Chem. Soc.*, **83**, 666 (1903); (c) F. Straus, *Ber.*, **42**, 2866 (1909); (d) K. v. Auwers, *ibid.*, **45**, 2795 (1912); (e) C. Dufraisse, *Compt. rend.*, **171**, 960 (1920); *Ann. chim.*, [9] **17**, 198 (1922); (f) A. T. Dann, A. Howard and W. Davies, *J. Chem. Soc.*, 605 (1928).

[4] S. Reich and N. Y. Chang, *Helv. Chim. Acta*, **3**, 235 (1920).

[5] W. G. Young, S. Winstein and H. L. Goering, THIS JOURNAL, **73**, 1958 (1951).

Support for either of these ionization processes for the non-stereospecific elimination lies in the effect of solvent variation and in the effect of ring substitution in the cinnamic acid dibromide. The non-stereospecific elimination is favored with respect to the stereospecific elimination when the solvent is changed from acetone to ethanol to water, in agreement with a presumed formation of a dipolar ion and bromide ion in either of the non-stereospecific processes (creation of charge), as compared with the distribution of negative charge in the presumed concerted stereospecific process.[6] The fact that meta- or para-nitro substitution in the phenyl ring of the cinnamic acid dibromide led to pure stereospecific *trans* elimination in aqueous acetone and in ethanol can also be readily reconciled with the two mechanisms, in view of the fact that electron-withdrawing groups (such as nitro) impede the solvolysis of benzyl chloride but favor the direct-displacement process with iodide ion.[7]

When *trans*-cinnamic acid dibromide was treated with sodium acetate in refluxing ethanol, there was obtained, in addition to the β-bromostyrene mixture, a small amount of material, m.p. 18–19°, which analyzed for ethyl β-phenylglycidate. The *cis* structure is tentatively assigned to this substance, by analogy to the corresponding meta-nitro system.[1,8]

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Experimental

Treatment of *trans*-Cinnamic Acid Dibromide with Ethanol and Sodium Acetate.—To 1200 ml. of 99.5% ethanol was added 155 g. (0.50 mole) of *trans*-cinnamic acid dibromide and 155 g. (1.9 moles) of anhydrous sodium acetate. The reaction mixture was heated at reflux for 6 hours; the alcohol was then removed under reduced pressure. The residue was treated with water to dissolve the salts, and the organic material was extracted with ether. The ether layer was washed with saturated sodium bicarbonate solution until the wash solution remained basic and was then washed once with cold water. The ether was evaporated and 81 g. of a pale yellow oil was obtained. Thirty grams of this oil was dissolved in 100 ml. of petroleum ether, b.p. 60–70°, and poured onto an alumina column containing 200 g. of activated alumina (80–200 mesh). Twenty grams (58%) of β-bromostyrene, m.p. −17 to −10°, came off with 200 ml. of petroleum ether, b.p. 60–70°. Elution with benzene removed 1.4 g. of material and elution with methanol removed 1.5 g. of material.

The material which was eluted with benzene was distilled and 0.7 g. of material, b.p. 104–105° (1 mm.), m.p. 17–18°, was obtained. After recrystallization from methanol the substance had a melting point of 18–19°. This material had the correct analysis for ethyl β-phenylglycidate.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.30. Found: C, 68.63; H, 6.39.

The material which was eluted with methanol was distilled and 1.0 g. was obtained, b.p. 137–140° (1 mm.). This substance gave a positive test for halogen. The compound was not investigated further.

Treatment of *trans*-Cinnamic Acid Dibromide with Sodium Bicarbonate in Dry Acetone.—To one liter of dry acetone (dried over anhydrous magnesium sulfate) was added 48 g. (0.16 mole) of *trans*-cinnamic acid dibromide and 40 g. (0.48 mole) of sodium bicarbonate. The mixture was stirred and heated at reflux for 8 hours. The acetone was then removed under reduced pressure. Water was added to the residue, and the organic material was extracted with ether. The ether extract was washed once with cold water, after which the ether was evaporated to give 24 g. (84%) of crude *cis*-β-bromostyrene, m.p. −11 to −8°. This material was divided into three 8-g. fractions and each fraction was distilled *in vacuo* to give a combined total of 18 g. (64%) of *cis*-β-bromostyrene, b.p. 55–56° (2 mm.), m.p. −8 to −7°. The distilling flask was heated in a water-bath held at 65°. Recrystallization of the distillate from methanol raised the melting point to −7 to −6°.

During all steps of the reaction and isolation of the product the solutions containing *cis*-β-bromostyrene were kept in darkness.

Attempt to Isomerize *cis*-β-Bromostyrene.—A solution of 1.04 g. of *cis*-β-bromostyrene (m.p. −8 to −7°), 0.5 ml. of acetic acid and 1 g. of sodium acetate in 25 ml. of 99.5% ethanol was heated at reflux for five hours in the dark. The ethanol was then removed under reduced pressure, after which the residue was dissolved in ether. The ethereal solution was washed twice with dilute aqueous sodium bicarbonate and once with water. After the solvent was removed under reduced pressure, the residual oil melted at −9 to −7°. A mixed m.p. with the original *cis* isomer was −9 to −7°; thus no isomerization of β-bromostyrene occurred under conditions approximating those of the preparation.

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(6) For a discussion of pertinent solvation theory, *cf.* E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

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

(8) Although the *cis* configuration may be tentatively assigned by analogy to the previous case, there is a possibility that this compound may arise from the *threo* dibromide, should it be true that this is the substance which is involved in the formation of *trans*-β-bromostyrene. This might result in the *trans* glycidic ester. We hope to investigate this further.

(9) E. Grovenstein, Jr., and D. E. Lee, THIS JOURNAL, **75**, 2639 (1953).