intractable mixtures, no attempt was made to prepare its symmetrical anhydride. We found that mandelic acid undergoes carbethoxylation when treated with equimolar amounts of ethyl chloroformate and triethylamine in the usual mixed anhydride method. Similar results were reported earlier by Fischer and Fischer[9] when they treated mandelic acid with excess methyl chloroformate. This procedure also appears inapplicable to phenols as exemplified by the results with *p*-hydroxycinnamic acid. Attempts to prepare the amide of this acid using the mixed anhydride method led to carbethoxylation of the phenolic hydroxyl rather than to mixed anhydride formation, so again symmetrical anhydride formation was not attempted. Examination of the applications and limitations of this symmetrical anhydride-forming system with other hydroxy acids is now in progress.

Experimental[10]

All melting points were obtained in capillary tubes in an electrically heated block and are uncorrected. Infrared spectra were obtained as Nujol mulls; a Perkin-Elmer Model 137 Infracord with sodium chloride optics was used. Mixed carboxylic–carbonic anhydrides were prepared at 0° in tetrahydrofuran, as previously described,[2b] and used without isolation.

Symmetrical Anhydrides.—Table I. Equimolar quantities (typical 0.01-mole scale) of hydroxy acid and freshly distilled triethylamine were dissolved in about 50 ml. of tetrahydrofuran (THF) for each 0.01 mole of acid. This solution was added from a dropping funnel to a well stirred solution of the corresponding mixed anhydride in tetrahydrofuran kept at or near 0° with an ice–salt bath. One molar equivalent of acid salt was used for each equivalent of mixed anhydride. After this addition, the system was allowed to come to room temperature, with stirring, and to stand overnight. The solution was then filtered from the triethylamine hydrochloride, which had precipitated during preparation of the mixed anhydride, and the precipitate was washed with tetrahydrofuran. The filtrate and washings were combined and the solvent removed *in vacuo* at room temperature on a rotary evaporator. The product was taken up in ether or chloroform, depending on its solubility, and washed with dilute hydrochloric acid and 1 *M* sodium carbonate solution followed with water until the washes tested neutral to pH paper. The organic solutions were dried over magnesium sulfate, filtered, and returned to the rotary evaporator for removal of solvent at room temperature. Yields were determined at this point. After this work-up, all of the compounds were essentially pure (Table I) and free of starting acid (Fig. 1); the only further treatment prior to analysis in the case of the saturated hydroxy anhydrides and 12-hydroxy-*trans*-9-octadecenoic anhydride was drying in a vacuum oven at room temperature and 0.01 mm. The 12-hydroxy-*cis*-9-octadecenoic anhydride was recrystallized from petroleum ether at −10°, then dried at room temperature and 0.01 mm.

Anhydride Derivatives.—Table II. Anhydrous ammonia gas was passed through a solution of hydroxy acid anhydride in tetrahydrofuran at room temperature. The tetrahydrofuran was removed on the rotary evaporator to leave an equimolar mixture of hydroxy acid ammonium salt and the corresponding amide. Weights obtained corresponded to theory. These product mixtures were dissolved in absolute methanol and separated on a column of macrorecticular quaternary ammonium ion-exchange resin.[11] After recovery of the amide, a methanol solution of acetic acid was used to remove the hydroxy acid from the column. Each of the derivatives was recrystallized from 95% ethanol, the amides at room temperature and the slightly more soluble acids at 0°, and dried *in vacuo* at 40°.

Acknowledgment.—We thank Miss Geraldine E. Secor for performing the elemental analyses.

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Reaction of Cinnamic Acid Dibromide with Iodide Ion

Elmer R. Trumbull[1] and Khairat M. Ibne-Rasa

Department of Chemistry, Brown University,
Providence, Rhode Island

Received February 4, 1963

The conversion of vicinal dibromides to olefins by reaction with iodide ion has been investigated by several groups.[2-10] The reaction is usually reported to be first order in iodide ion and first order in dibromide. It has been shown that the elimination may follow a direct mechanism involving nucleophilic attack of iodide ion on bromine in a typical E2 process resulting in *trans* elimination[7] or may involve S_N2 replacement of bromine by iodine on carbon followed by rapid collapse of the iodobromide.[8] This process gives the appearance of *cis* elimination of the bromine atoms.[9] The E2 mechanism apparently is preferred except for 1,2-dibromo compounds where displacement of the primary bromide is facile.

In connection with other work[11] we had occasion to use the reaction of iodide ion with cinnamic acid dibromides as an analytical method. In view of the fact that third-order kinetics had been reported for this process and because the stereochemistry had not been studied, we investigated the reaction of *erythro*-2,3-dibromo-3-phenylpropionic acid, hereafter referred to as *trans*-cinnamic acid dibromide, in the solvents 80% aqueous acetic acid and 80% aqueous methanol. The reaction was followed by titrating the iodine liberated.

Results

***trans*-Cinnamic Acid Dibromide.**—The conditions and specific rate constants obtained for the second-order reaction of *trans*-cinnamic acid dibromide with iodide ion are listed in Table I. The order of the reaction with respect to iodide ion and with respect to dibromo acid was determined by the method of initial slopes.[12] The values for the order with respect to iodide ion as determined for three different sets of reaction conditions were 0.96, 0.98, and 0.97. Similarly the order with respect to dibromo acid was found to be 1.0. The effect of ionic strength and the specific effect of bromide ion were tested by the addition of sodium perchlorate or of potassium bromide. The specific rate constants were calculated from the rate expression for a second-order reaction in the integrated form. The

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TABLE I

RATE CONSTANTS FOR ELIMINATION OF CINNAMIC ACID DIBROMIDE

a	b	Added anion	μ^c	T, °C. ± 0.1	10^4k_2 l. mole^{-1} sec.$^{-1}$	% Reaction
Solvent, 80% acetic acid						
0.030	0.240	0.30 Br$^-$	0.54	29.9	4.60	68
.030	.240	...	.24	29.9	4.30	76
.030	.180	.18 ClO_4^-	.36	29.9	4.33	61
.030	.090	...	.09	29.9	4.08	44
.015	.240	...	.24	29.9	4.28	71
.030	.180	...	.18	38.4	9.18	64
.030	.180	.18 Br$^-$	.36	38.4	9.42	65
.030	.180	.18 Br$^-$	.36	38.4	9.47	64
.030	.180	.27 ClO_4^-	.45	38.4	10.03	62
.015	.120	...	.12	46.0	17.56	
Solvent, 80% methanol						
0.030	0.24	...	0.24	25.0	1.37	56
.0134	.117	0.12 Br$^-$	.24	45.5	9.63	63
.0134	.117	...	.12	45.5	9.43	63

[a] Initial molarity of *trans*-cinnamic acid dibromide. [b] Initial molarity of iodide ion. [c] μ = ionic strength.

values of k remained constant during each run, the mean deviations being on the order of 3–4%.

The product of reaction was shown to be *trans*-cinnamic acid, isolated in 88% yield from a run in 80% acetic acid. *cis*-Cinnamic acid was shown to be stable under the reaction conditions.

***cis*-Cinnamic Acid Dibromide.**—The reaction of *threo*-2,3-dibromo-3-phenyl propionic acid (*cis*-cinnamic acid dibromide) with iodide ion in 80% acetic acid or in 80% methanol was not simple. Only 40–50% of the theoretical amount of iodine was liberated and an attempt to identify the products of reaction was not successful. It was clear, however, that liberation of iodine from the *cis*-dibromide was considerably slower than is the case for the *trans* isomer. The reaction in 80% acetic acid was followed and specific rate constants calculated from the initial slope of the rate of formation of iodine. Assuming that this is a measure of the elimination reaction and that the elimination is a second-order process, values for the specific rate constant were calculated. At 90.6° runs under identical conditions gave the values 5.5×10^{-4} and 6.0×10^{-4} l. mole^{-1} sec.$^{-1}$. At 72.6° the specific rate constant was 1.9×10^{-4} l. mole^{-1} sec.$^{-1}$.

Discussion

The reaction of *trans*-cinnamic acid dibromide in 80% acetic acid and in 80% methanol is first order in iodide ion and first order in dibromo acid. The reaction shows a slight positive salt effect and no retardation by bromide ion. The difference between 80% acetic acid and 80% methanol as solvent for this reaction is not great, roughly a factor of two at 45°, and is in the direction of greater rate in the solvent of greater Y value.[13] Much larger salt effects are reported for debromination reactions in absolute methanol,[14] a solvent whose Y value is much more negative than is that of 80% methanol. The positive salt effect and tendency for rate to be greater in a solvent of higher ion-solvating power indicate a greater role for solvation in the transition state than in the ground state. This is possible if release of the bromide ion has occurred to a considerable extent in the transition state since the solvation energy of bromide ion is expected to be greater than that of iodide ion.

The production of *trans*-cinnamic acid from the *erythro*-dibromide indicates *trans* elimination and taken together with the kinetic order indicates that the direct mechanism is operative in this case. The entropies of activation, −19.3 e.u. and −18.0 e.u. in aqueous acetic acid and methanol. respectively, are also consistent with this mechanism. Although the molecule contains a bromine atom in the benzylic position, apparently displacement on carbon does not compete successfully with the E2 mechanism. The absolute rate of reaction of cinnamic acid dibromide with iodide ion in 80% methanol is greater than the rate of 2,3-dibromobutane in 99% methanol by a factor of the order of 10^3 at 60°. To some degree this may be a solvent effect but it seems probable that the stabilization of the incipient double bond by conjugation with the phenyl and carboxyl groups is an important factor in this difference in rate.

A ratio for the reactivity of the *erythro* dibromide to the *threo* dibromide was determined by calculating the rate expected of the *erythro* compound at the temperature where the *threo* compound was measured. The ratio for $k_{erythro}/k_{threo}$ was 85. This number is reasonable[15] but of questionable significance because of the uncertainty in the meaning of the rate constant determined for the *threo* dibromide.

Experimental

cis-Cinnamic acid dibromide and *trans*-cinnamic acid dibromide were prepared as described previously.[11] Kinetic runs in 80% acetic acid at temperatures below 50° were carried out by removing samples at intervals, quenching the reaction by running the sample onto crushed ice, and titrating the iodine quickly against thiosulfate. Runs in 80% methanol at 45° and the runs with *cis*-cinnamic acid dibromide at 73° and 91° were conducted in sealed tubes. Blanks were run to correct for the formation of iodine from iodide ion by oxidative processes other than the one under investigation.

Isolation of *trans*-Cinnamic Acid.—A solution of 39.8 g. (0.249 mole) of potassium iodide and 9.24 g. (0.030 mole) of *trans*-cinnamic acid dibromide in 300 ml. of 80% acetic acid was heated at 46° for 6 hr. The solvent was distilled at 40–50° at the aspirator. The residue was treated with 300 ml. of water containing 10 g. of potassium iodide. Insoluble material was collected on a Büchner funnel and washed with water. The solid was taken up in ether and washed with 0.1 N thiosulfate solution. The ether was removed by distillation and the residue dried in a desiccator. The material weighed 3.91 g. (88%) and had m.p. 133–134°, m.m.p. with *trans*-cinnamic acid, 133–134°.

A solution of 4.0 g. (0.013 mole) of *cis*-cinnamic acid, m.p. 57–58°, in 200 ml. of 80% acetic acid containing 20.0 g. of potassium iodide was heated at 46° for 6 hr. The reaction mixture was treated as described earlier to yield 3.52 g. of crude product. This material was recrystallized from low-boiling petroleum ether and 3.37 g. (84%) of *cis*-cinnamic acid, m.p. 57–58°, was recovered.

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