gage pressure of 7–18 atmospheres. There was obtained 39.6 g. of vinyl ester distilling at 106.2–107.5° (0.3 mm.), $n^{25}D$ 1.5187 (57%). *Anal.* Calcd. for $C_9H_{10}O_3S$: C, 54.6; H, 5.1; S, 16.1. Found: C, 55.3, 55.0; H, 5.4, 5.3; S, 16.0, 16.1.

Polymerization of Vinyl Methanesulfonate (VMS).—A round-bottomed flask equipped with stirrer, thermometer and reflux condenser, was flushed with nitrogen and charged with 150 ml. of deoxygenated water, 10.0 g. of vinyl methanesulfonate, 0.2 g. of potassium persulfate and 0.4 g. of sodium bisulfite. The mixture was stirred without external heating. It became milky after 20 minutes with no rise in temperature. Stirring was stopped after 8 hours. Coagulation by addition of 15 ml. of alum solution[5] and steaming yielded a white polymer, which was washed with methanol. It was then dissolved in acetone and reprecipitated in methanol twice. After drying over P_2O_5 for 30 minutes, the polymer had discolored slightly in several spots and was stored in Dry Ice. At this time it was a white solid, weighing 2.2 g. (yield 22%). Relative viscosity of a 0.46% cyclohexanone solution at 25° was 1.121; inherent viscosity, 0.25. *Anal.* Calcd. for $(C_3H_6O_3S)_x$: S, 26.3. Found: S, 25.2, 25.4.

Transparent films, which softened just above room temperature, were pressed at 25°. When dry, the polymer darkened rapidly, but it could be stored under water indefinitely without discoloration, regardless of the acidity of the water.

Mechanism of Decomposition of Polyvinyl Methanesulfonate.—The infrared spectrum of a polyvinyl methanesulfonate film was recorded at successive time intervals in an effort to determine the chemical changes taking place during decomposition. Absorption bands characteristic of ethylenic double bonds were found at 6.0 μ, and this absorption increased in succeeding spectra. This has been interpreted as being caused by increasing carbon–carbon unsaturation. An absorption band developed at 9.5 μ where ionic sulfonates absorb. This band was not visible in the first spectrum but became quite definite in later spectra. A band at 2.9 μ appeared to be developing in the later spectra. This is in a region where hydroxyl absorbs and may corroborate the formation of sulfonic acid groups. Strong absorption bands at about 7.5 and 8.5 μ, which are characteristic of $-SO_3-$, did not change noticeably. These results are interpreted as indicating that during the decomposition of polyvinyl methanesulfonate, methanesulfonic acid is eliminated with the introduction of ethylenic linkages into the polymer.

Copolymers of Vinyl Methanesulfonate.—Copolymers of vinyl methanesulfonate with vinyl acetate, acrylonitrile, styrene, methyl methacrylate, methyl acrylate and allylidene diacetate were prepared by similar procedures. Acrylonitrile copolymers containing 7–74% by weight of vinyl methanesulfonate and vinyl acetate copolymers containing 11–78% by weight of vinyl methanesulfonate were examined for the effect of VMS content on physical properties. As indicated in the tables below, the yields, inherent viscosities and stick temperatures decrease with increasing vinyl methanesulfonate content.

ACRYLONITRILE/VINYL METHANESULFONATE COPOLYMERS

VMS content wt., %	Conversion, %	Inherent viscosity	Stick temp., °C.
7	85	0.90	200
22	10	.41	145
35	57	.28	115
60	36	.20	110
74	32	.13	110

VINYL ACETATE/VINYL METHANESULFONATE COPOLYMERS

11	71	0.33	68
17	73	.11	..
50	28	.08	49
78	34	.04	36

Polymerization of Vinyl Benzenesulfonate.—A solution of 5 g. of vinyl benzenesulfonate and 0.1 g. of 1,1-azodicyclohexanecarbonitrile was heated at 100° for 4 hours in an atmosphere of deoxygenated nitrogen. During this time the monomer polymerized to a soft, sticky, extremely viscous homopolymer.

Vinyl benzenesulfonate polymerized vigorously with evolution of heat when 0.1 g. of a boron trifluoride–methanol addition compound was added to 2 g. of the monomer. The resulting homopolymer was very viscous at room temperature.

WILMINGTON, DELAWARE

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[5] The alum solution was prepared by dissolving 200 g. of aluminum potassium sulfate in 200 cc. of concentrated HCl and diluting with 2 l. of H_2O.

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

Decarboxylation. II. The Stereochemistry of the Transformation of *cis*-Cinnamic Acid Dibromide to β-Bromostyrene[1,2]

BY ERLING GROVENSTEIN, JR., AND SPYROS P. THEOPHILOU

RECEIVED FEBRUARY 7, 1955

The stereochemistry of the conversion of sodium or potassium salts of *cis*-cinnamic acid dibromide to β-bromostyrene has been studied in solvents acetone, ethanol and water. In the first two solvents the β-bromostyrene formed is found to be essentially 100% *trans*-isomer while in water about 97% *trans* and 3% *cis*. These results are compared with those obtained with *trans*-cinnamic acid dibromide and are discussed in light of probable mechanisms for the decarboxylation. Improved procedures are given for the preparation of *cis*-cinnamic acid and *cis*-cinnamic acid dibromide.

The stereochemistry and mechanism of the conversion of *trans*-cinnamic acid dibromide to β-bromostyrene has been reported earlier from this Laboratory[1] and simultaneously by Cristol and Norris.[3] These studies and recent interest in related decarboxylative eliminations[4] have prompted us to extend our studies to include *cis*-cinnamic acid dibromide.

cis-Cinnamic acid dibromide was prepared by addition of bromine to *cis*-cinnamic acid. A somewhat improved procedure for preparation of the latter from *trans*-cinnamic acid by irradiation with ultraviolet light is described in the Experimental portion. The addition of bromine to *cis*-cinnamic acid was effected in acetic acid as sol-

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[1] Paper I, E. Grovenstein, Jr., and D. E. Lee, THIS JOURNAL, **75**, 2639 (1953).

[2] Abstracted in part from the M.S. thesis of Spyros P. Theophilou, Georgia Institute of Technology, June, 1954.

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

[4] In addition to the references given in Paper I and in ref. 3 see the following: (a) W. R. Vaughan and K. M. Milton, *ibid.*, **74**, 5623 (1952); W. R. Vaughan, M. V. Anderson, Jr., and R. Q. Little, Jr., *ibid.*, **76**, 1748 (1954); W. R. Vaughan and R. Q. Little, Jr., *ibid.*, **76**, 2952 (1954); (b) W. v. E. Doering and L. H. Knox, *ibid.*, **73**, 828 (1951); (c) G. Stork and R. Breslow, *ibid.*, **75**, 3292 (1953); (d) L. J. Hals, T. S. Reid and G. H. Smith, Jr., *ibid.*, **73**, 4054 (1951); *ibid.*, **75**, 4525 (1953); (e) T. J. Brice and J. H. Simons, *ibid.*, **73**, 4017 (1951); (f) R. N. Haszeldine, *J. Chem. Soc.*, 4259 (1952).

vent in presence of hydrogen bromide to give about 50% yield of *cis*-cinnamic acid dibromide. Hydrogen bromide almost doubled the yield of *cis*-cinnamic acid dibromide over that obtained in its absence. The influence of hydrogen bromide is perhaps to be attributed to bromide or tribromide ion participating in a termolecular[5] or "nucleophilic"[6] mechanism. The procedure of Liebermann[7a] for bromine addition in carbon disulfide as solvent is reported to give about 30% yield of *cis*-cinnamic acid dibromide; however, in our hands this method was rather less satisfactory than reported.

In Table I are recorded the data for decarboxylative elimination upon *cis*-cinnamic acid dibromide as well as a summary of data obtained previously upon *trans*-cinnamic acid dibromide. In addition the bromostyrene from the *trans*-acid dibromide in acetone has been analyzed by the infrared technique and the recorded results are seen to be in good agreement with the conclusions of Cristol and Norris[3] based upon the melting point of the product.

Since it was not practicable according to present techniques to prepare large amounts of the necessary *cis*-cinnamic acid dibromide entirely free of its diastereoisomer, the results must be interpreted in light of the known amount of this isomer present. The composition of the *cis*-cinnamic acid dibromide was estimated from its melting point and is given in Table I (footnotes *a* and *b*). In the fourth column of this table, the amount of *cis*-β-bromostyrene in the product due to the *trans*-cinnamic acid dibromide present is calculated on the assumption that the two diastereoisomeric cinnamic acid dibromides are converted to β-bromostyrene in the same yield and that the proportion of isomers of β-bromostyrene from *trans*-cinnamic acid dibromide is as shown in the fifth column.[7b] If the maximum experimentally determined yields of β-bromostyrene in each solvent as shown in the table, are used in the previous calculation, re-estimated values do not differ by more than 0.5% from those recorded for these cases.[7c]

The amount of *cis*-β-bromostyrene found (column 5) minus that calculated to come from *trans*-cinnamic acid dibromide (column 4) gives the *cis*-β-bromostyrene which is estimated to come solely from the *cis*-cinnamic acid dibromide under the reaction conditions. In the solvents acetone and absolute ethyl alcohol, *cis*-cinnamic acid dibromide gives β-bromostyrene which is within the experimental error of being entirely *trans*-β-bromostyrene; that is, decarboxylative elimination occurs by *trans* elimination of the elements of carbon dioxide and bromide ion. The near equality here of the values shown in columns four and five supports the melting point method used for the estimation of the composition of the cinnamic acid dibromide.

TABLE I

OLEFINS FROM THE ALKALI METAL SALTS OF CINNAMIC ACID DIBROMIDES

Solvent	Base	Yield of PhCH=CHBr, %	Compn. of PhCH=CHBr Calcd. due to *trans*-dibromide % *cis*	Found % *cis*
		cis-Cinnamic acid dibromide		
Acetone	NaHCO$_3$	85	4.5 ± 1.0[a]	4.7
Acetone	NaHCO$_3$	73	4.5 ± 1.0[a]	4.7
Ethanol	KOAc	64.5	3.9 ± 0.9[a]	2.8
Ethanol	KOAc	54.5	3.9 ± 0.9[a]	3.7
Water	NaOH	35	1.0 ± 0.2[a]	0.1
Water	NaHCO$_3$	82.5	2.0 ± 0.2[b]	4.9
		trans-Cinnamic acid dibromide		
Acetone	NaHCO$_3$	93.5		99.5
Ethanol[c]	NaOEt	58[d]		86.5
Water[c]	NaOH	60.5		22

[a] The *cis*-cinnamic acid dibromide used here is estimated from its melting point to contain 4.5 ± 1.0% of *trans*-cinnamic acid dibromide. [b] The *cis*-cinnamic acid dibromide is estimated to contain 9.0 ± 1.0% *trans*-cinnamic acid dibromide. [c] From data of ref. 1. [d] From data for use of NaOAc as base (ref. 3).

The run in water with sodium hydroxide also gave essentially only *trans*-β-bromostyrene from *cis*-cinnamic acid dibromide; however, in this reaction twice as much alkali was used as in the previous case[1] with *trans*-cinnamic acid dibromide. This excess alkali, in addition to giving a low yield of product, might be expected to destroy preferentially any *cis*-β-bromostyrene formed. Cristol and Norris[8] report that the *cis*-isomer undergoes elimination of hydrogen bromide with sodium hydroxide in isopropyl alcohol 2.1×10^5 times faster than the *trans*-isomer. Accordingly another run was made in water using sodium bicarbonate as base. A product containing about 5% *cis*-β-bromostyrene resulted; from this it is calculated that pure *cis*-cinnamic acid dibromide gives β-bromostyrene containing about 3% of *cis*-β-bromostyrene. This composition of product is probably close to that obtained by previous workers,[7,9] who, however, had no satisfactory method of product analysis.

Comparison of the present work upon *cis*-cinnamic acid dibromide with previous work upon *trans*-cinnamic acid dibromide, as summarized in Table I, shows that while both diastereoisomers undergo decarboxylative elimination in a stereospecific *trans* manner in dry acetone, the *cis*-acid dibromide reacts more stereospecifically in absolute ethanol and in water than the *trans*-acid dibromide. The apparent explanation is that for the stereospecific concerted *trans* mechanism of elimination,[1,3,4a] *cis*-cinnamic acid dibromide (I) has a more favorable transition state for elimination than its diastereoisomer (II) because of less steric hindrance. This is illustrated by the following formulas in which it is seen that the α-bromine and β-phenyl groups are further apart in both the transition

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(5) K. Nozaki and R. A. Ogg, Jr., THIS JOURNAL, **64**, 704 (1942).

(6) I. D. Morton and P. W. Robertson, *J. Chem. Soc.*, 129 (1945); D. A. Evans, T. R. Watson and P. W. Robertson, *ibid.*, 1624 (1950); P. W. Robertson, N. T. Clare, K. J. McNaught and G. W. Paul, *ibid.*, 335 (1937).

(7a) C. Liebermann, *Ber.*, **27**, 2037 (1894).

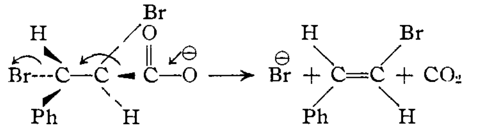
(7b) The percentage *cis*-β-bromostyrene recorded in columns four and five of Table I is calculated such that it represents the percentage of the β-bromostyrene formed which is the *cis*-isomer from the source indicated. A typical calculation of the per cent. *cis*-β-bromostyrene recorded in column four of Table I is as follows for the run in water with sodium bicarbonate: $(9.0 \pm 1.0)(0.22) = 2.0 \pm 0.2\%$.

(7c) From the maximum yields of β-bromostyrene in water as solvent, a typical calculation of the amount of *cis*-β-bromostyrene from the 9.0% *trans*-cinnamic acid dibromide in the starting cinnamic acid dibromide is: $9.0 \times 0.605 \times 0.22 \times 100/82.5 = 1.5\%$.

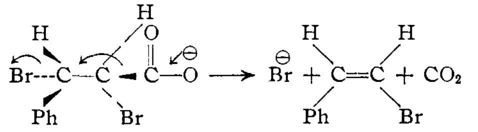
(8) S. J. Cristol and W. P. Norris, THIS JOURNAL, **76**, 3005 (1954).

(9) K. V. Auwers, *Ber.*, **45**, 2795 (1912).

state and product from I than from II (only one enantiomorph shown in each case)



I



II

Consequently *cis*-cinnamic acid dibromide should undergo decarboxylative elimination faster by the concerted *trans* mechanism of elimination than its diastereoisomer. On the other hand, since the dibromides I and II probably have about the same free energy content in solution and since they should give the same dipolar ion $PhCH^+CHBrCO_2^-$ (if the ion is, indeed, free from the departing bromide ion and from covalent interaction with neighboring groups), then these diastereisomers should react at nearly the same rate for the non-stereospecific ionization mechanism.[1,3] The net result then is that *cis*-cinnamic acid dibromide decarboxylates in alcohol and water move exclusively by the stereospecific *trans* mechanism than does its diastereoisomer. A corollary is that *cis*-cinnamic acid dibromide should undergo decarboxylative elimination in acetone, ethanol and water faster[10] than does its diastereoisomer. The stereochemical control of related elimination reactions has been discussed recently especially by Vaughan[4a] and co-workers, Cristol and Norris,[8] and by Curtin.[11]

Experimental Details

Preparation of *cis*-Cinnamic Acid.—*trans*-Cinnamic acid, Eastman Kodak Co., was recrystallized from benzene and converted into *cis*-cinnamic acid by the photochemical method of Stoermer[12] but in methyl alcohol as solvent.[13] The apparatus for irradiation was made by Hanovia Chemical and Mfg. Co. of Newark, N. J., and contained a high pressure quartz mercury lamp (type LL) of 30 cm. arc length. The lamp operated on about 1000 watts at a current of 3.8 to 4.2 amperes and was surrounded by a cylindrical, water-cooled quartz cell which held the solution of cinnamic acid. This apparatus greatly reduced the time (120 to 240 hours) required for irradiation as reported by previous workers.[12–14] Thus in a typical procedure, 325 ml. of a methanol solution containing 66 g. of *trans*-cinnamic acid gave after 6 hours of irradiation a light yellow solution containing 49% *cis*- and 47% *trans*-cinnamic acid with about 4% by-product formation. Longer periods of irradiation did not increase the yield of *cis*-cinnamic acid by more than 2 or 3% and in 20 hours the solution had acquired a brown color, by-product formation being increased to about 10%. These yields were determined by infrared analysis and are close to those reported by Olson and Hudson[15] for the photostationary concentrations of *cis*- and *trans*-cinnamic acid in aqueous solution with light of wave length chiefly 2536 Å.[16] (as opposed to our unfiltered light source). Partial separation of the *cis*- and *trans*-acids was effected by fractional extraction and crystallization of the more soluble *cis*-isomer from *n*-hexane (or carbon tetrachloride). Final purification through the aniline salt[17] gave 25 to 30% yield of 99% pure *cis*-cinnamic acid, a yield which agrees with that of Stoermer[12] for the pure product.

Preparation of *cis*-Cinnamic Acid Dibromide.—A preliminary run upon bromine addition to *cis*-cinnamic acid in carbon disulfide as solvent according to the procedure of Liebermann[7] gave 66% yield of crude *trans*-cinnamic acid dibromide (m.p. 185–191°) and only 24% of an impure product (m.p. 55–80°) which doubtless contained much *cis*-cinnamic acid dibromide.

The following procedure proved more successful. *cis*-Cinnamic acid, 100 g. (0.675 mole), m.p. 66–68°, was dissolved in 250 ml. of acetic acid (commercial glacial acetic acid, refluxed over and distilled from chromium trioxide,[18] b.p. 117–118°). In another 300-ml. portion of acetic acid 45 g. (0.55 mole) of anhydrous hydrogen bromide and 190 g. (1.19 moles) of bromine were dissolved. The second solution was added to the first within a period of ten minutes. The temperature of the mixture rose to 75° and the reactants were allowed to stand in a red flask made of low-actinic glassware for 8 hours. The solution was poured into three liters of ice-water and the mixture extracted with three 400-ml. portions of diethyl ether. The combined ether extracts were washed with sulfurous acid (80 g. of sodium sulfite plus 56 ml. of concd. sulfuric acid in 600 ml. of water) to remove excess bromine and twice with water. After drying over anhydrous magnesium sulfate, the ether was evaporated and the residue extracted with three 250-ml. portions of carbon disulfide. The insoluble portion of the residue was slightly impure *trans*-cinnamic acid dibromide formed in yield of 20% of product, m.p. 193–195°. The material soluble in the carbon disulfide is mostly *cis*-cinnamic acid dibromide and a dark-colored oily impurity. The carbon disulfide was removed and the residue extracted with two 600-ml. portions of boiling *n*-hexane; each time the hexane solution was separated from the undissolved oily impurity by decantation. The hexane solutions upon slow evaporation at room temperature deposited crystals of *cis*-cinnamic acid dibromide. Where necessary the product was recrystallized from *n*-hexane with use of decolorizing charcoal. A yield of 125 g. (60 ± 2%) of crude *cis*-cinnamic acid dibromide, m.p. 75–94.5°, was obtained or 50% of product, m.p. 87–94.5° (when well mixed, m.p. 88.0–92.5°). This 50% of product is estimated (see below) to contain 95.5 ± 1% of *cis*-cinnamic acid dibromide with the remainder *trans*-cinnamic acid dibromide. The dark-colored oils produced during the bromination could not be obtained in a crystalline state under any of the conditions tried.

The most highly purified sample of *cis*-cinnamic acid dibromide obtained had m.p. 93.5–95.0°; the recorded value[7] is 91–93°. It proved impracticable, however, to obtain *cis*-cinnamic acid dibromide in amounts required for the present work in such a high state of purity. Consequently it was necessary to ascertain the purity of the *cis*-cinnamic acid dibromide samples used. The most likely impurity seems to be *trans*-cinnamic acid dibromide. The infrared spectra of *cis*- and *trans*-cinnamic acid dibromide in carbon disulfide proved to be too similar for accurate analysis of mixtures containing largely the *cis*-dibromide. The melting points of these diastereoisomers differ by about 105° and so an analysis based upon a mixed-melting point diagram was devised. Synthetic mixtures of highly purified *cis*- and *trans*-cinnamic acid dibromides were prepared and were

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(10) Qualitative indication that this is true in water is supplied by the work of Liebermann (ref. 7). Dr. E. R. Trumbull has kindly informed us that he is studying the kinetics of decarboxylative elimination of *cis*- and *trans*-cinnamic acid dibromides in various solvents.

(11) D. Y. Curtin and D. B. Kellom, THIS JOURNAL, **75**, 6011 (1953); D. Y. Curtin, Fifth Conference on Reaction Mechanisms, Durham, New Hampshire, Sept. 8, 1954.

(12) R. Stoermer, *Ber.*, **42**, 4865 (1909); *ibid.*, **44**, 666 (1911).

(13) B. K. Vaidya, *Proc. Roy. Soc.* (*London*), **A129**, 299 (1930).

(14) H. Stobbe and A. Lehfeldt, *Ber.*, **58**, 2415 (1925).

(15) A. R. Olson and F. L. Hudson, THIS JOURNAL, **55**, 1410 (1933).

(16) Olson and Hudson (ref. 15) report that light of wave length chiefly 3130 Å. gives a photostationary concentration of 77% *cis*-cinnamic acid (see also Vaidya, ref. 13). The report by Stobbe and Lehfeldt (ref. 14) that irradiation of aqueous suspensions of cinnamic acid with unfiltered ultraviolet light gives 70% of the *cis* isomer is probably erroneous since these authors assumed that all of the material soluble in petroleum ether corresponded to the *cis*-isomer; we find that the material soluble in *n*-hexane at room temperature contains only about 76% of the *cis*-acid.

(17) C. Lieberman, *Ber.*, **23**, 2510 (1890); *ibid.*, **24**, 1101 (1891); J. Guy, *Bull. soc. chim. France*, 731 (1949).

(18) K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, **125**, 960 (1924).

intimately mixed, first mechanically and then by heating ten minutes in an oven at 100° (samples containing 90% or more of *cis*-cinnamic acid dibromide are completely molten at this temperature). Melting points were determined in capillary tubes. Since samples melt with some decomposition, the calibration curve is empirical and subject to variations in melting point technique and is, therefore, not given here. The two dibromides form a minimum melting mixture, perhaps a eutectic, of m.p. near 90°, containing about 92% *cis*-cinnamic acid dibromide. Unknown samples were analyzed by determining their melting points and then the melting point of a mixture with a small but measured quantity of pure *cis*-cinnamic acid dibromide in order to ascertain on which side of the minimum melting mixture the sample lay. The thermal analyses were probably accurate within one per cent. and were confirmed by the infrared analyses upon the β-bromostyrenes obtained from the cinnamic acid dibromides.

β-Bromostyrenes from Cinnamic Acid Dibromides.—All the samples of *cis*-cinnamic acid dibromide, unless otherwise indicated, were from a large well-mixed batch of *cis*-cinnamic acid dibromide of m.p. 88–92.5°, which was estimated by the melting point technique to contain 95.5% of *cis*-cinnamic acid dibromide. The decarboxylative eliminations were run in solvents ethanol and water as previously described[1] with the following exceptions. For the runs in absolute ethanol, 90 g. (0.292 mole) of *cis*-cinnamic acid dibromide and 140 g. (1.42 moles) of anhydrous potassium acetate oven dried one hour *in vacuo* (at 70°) were refluxed with stirring in 1000 ml. of absolute ethanol for three hours. For one run in water, 90 g. of *cis*-cinnamic acid dibromide suspended in one liter of water reacted with 1020 ml. (1.25 equiv.) of 1.23 *N* sodium hydroxide. The addition of sodium hydroxide was made slowly during heating of the solution; 1.5 hours were required to bring the solution up to 78 ± 2° and the solution was maintained at this temperature for 30 minutes. Phenolphthalein seems to be an unreliable indicator in this reaction mixture and excessive amounts of alkali were added relative to that used with *trans*-cinnamic acid dibromide.[1] Accordingly in a second run, 95 g. (0.308 mole) of *cis*-cinnamic acid dibromide (m.p. 86–96°, 91% *cis*-dibromide) was suspended in 400 ml. of water and 84 g. (1.0 mole) of sodium bicarbonate dissolved in 600 ml. of water was added in a period of 30 minutes to the slowly heated and stirred suspension of the dibromide. The reaction mixture attained a temperature of 75 ± 2° in 1.15 hours and was kept at this temperature for 20 minutes.

The decarboxylative eliminations in acetone were run according to the general procedure of Cristol and Norris.[3] Ninety grams (0.292 mole) of *cis*-cinnamic acid dibromide, 80 g. (0.955 mole) of sodium bicarbonate, and 1000 ml. of acetone (dried over anhydrous magnesium sulfate) were refluxed with stirring for eight hours. Most of the acetone was removed under reduced pressure and the β-bromostyrene separated as previously described,[1] *n*-pentane being used as the extraction liquid. *trans*-Cinnamic acid dibromide (100 g.) was similarly treated with sodium bicarbonate (90 g.) in two liters of acetone.

The yield and composition of the β-bromostyrenes obtained from these reactions are given in Table I.

Infrared Analyses.—A Perkin-Elmer, Model 21, double beam recording infrared spectrophotometer was used in the present work. The β-bromostyrene mixtures were analyzed as previously reported[1] except that the concentration of β-bromostyrene was one third that previously used. The lower concentration permits a more accurate analysis of samples composed largely of the *trans*-isomer. The average deviation of the individual values from the average of the four values (determined at the four wave lengths) was 0.8% or less; the maximum deviation of any of the individual values was 1.5%.

For analysis of mixtures of *cis*- and *trans*-cinnamic acids, 3 mm. rock salt cells were used and samples were dissolved in carbon disulfide. The extinction coefficients of such solutions were satisfactorily constant over a concentration range of 0.7 to 3 g. of sample per liter and analyses were made at the following wave lengths in microns, 10.13 (*trans*), 12.08 (*cis*), 14.13 (*trans*) and 14.44 (*cis*), which correspond to maxima of the *cis*- and *trans*-acids as labeled. The first two and then the last two wave lengths were used separately to calculate the *cis–trans* composition of irradiated cinnamic acid samples, the values were averaged, and the difference from 100% was assumed to correspond to the amount of by-product present in such samples. The method was probably accurate within 3 or 4% and the values reported are generally the average obtained from several different samples.

ATLANTA, GEORGIA

[CONTRIBUTION FROM THE STERLING-WINTHROP RESEARCH INSTITUTE]

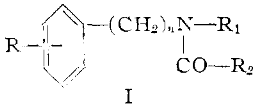
New Amebacides. II. The Preparation of Some N-Alkyl-N-benzylhaloacetamides

BY ALEXANDER R. SURREY AND MARCIA K. RUKWID[1]

RECEIVED FEBRUARY 15, 1955

The preparation of a series of N-alkyl(aralkyl, cycloalkyl)-N-benzyldichloroacetamides is reported. Some monochloroacetamides and trichloroacetamides also are included. The use of methyl dichloroacetate as an acylating agent in the present work is discussed.

In the first paper in this series[2] we have reported the synthesis of some N-(substituted benzyl)-N-hydroxyalkyldihaloacetamides as part of an investigation of potential amebacidal agents derived from the general formula



I

The present communication deals with the preparation of a second series of compounds in which R = H, alkyl, alkoxy, chloro, dichloro and nitro; n = 1; R_1 = alkyl, aralkyl and cycloalkyl; and R_2 = CH_2Cl, $CHCl_2$ and CCl_3.

All of the N-alkyl-N-benzyldichloroacetamides in Table II as well as the monochloroacetamides and trichloroacetamides listed in Table III were prepared by acylation of the appropriate N-alkylbenzylamine with monochloroacetyl, dichloroacetyl and trichloroacetyl chloride in the presence of dilute sodium hydroxide solution. For the most part the yields ranged from 45–80%. About one-half of the dichloroacetamides were obtained as oils which were purified by distillation under reduced pressures.

The use of methyl dichloroacetate or ethyl dibromoacetate as the acylating agent which was successful with the N-(hydroxyalkyl)-benzylamines even under mild experimental conditions, was not satisfactory in most of the present work. Only in the case of the N-methylbenzylamines was it

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(1) Mallinckrodt Chemical Works, St. Louis, Mo.

(2) A. R. Surrey, THIS JOURNAL, **76**, 2214 (1954).