petroleum ether, yellow granular crystals were obtained, m.p. 107–108° with decomposition. Qualitative analysis showed iodine to be present.

Anal. Calcd. for $C_{12}H_{15}N_2O_3I$: C, 39.79; H, 4.17; N, 7.74. Found: C, 40.05; H, 4.20; N, 7.74.

The compound is insoluble in water but readily soluble in warm benzene. Evidences of decomposition appear after the compound has been allowed to stand for several days at room temperature. The compound dissolves slowly in dilute aqueous hydrochloric acid and in dilute aqueous sodium hydroxide, but in neither case can the original substance be recovered by neutralization of the solution.

(E). Experiments with Other Unsaturated Compounds.—Other compounds mentioned in the discussion above were treated in benzene solution with a mixture of morpholine and morpholine periodide obtained by adding one molecular portion of iodine to four of morpholine. The progress of any reaction which occurred could be followed by observing the rate at which the orange-red iodine complex dissolved and its color then faded from the solution. The results with the individual compounds tested have been described in the course of the discussion presented above.

Preparation of 1-Bromo-1-nitro-2-morpholino-2-phenylethane (X).—To a solution of 20 g. (0.065 mole) of β-nitrostyrene dibromide[17] in 50 ml. of benzene, 22.6 g. (0.259 mole) of morpholine was added slowly, with cooling. A considerable amount of heat was evolved. The morpholine hydrobromide which was precipitated immediately was removed by filtration after the first half of the morpholine had been added. Addition of the remainder of the morpholine had no visible effect. Addition of an equal volume of low-boiling petroleum ether to the solution followed by cooling in a refrigerator caused the crystallization of 15 g. (73%) of light yellow, granular crystals. The compound melted at 119–120° following several recrystallizations from benzene–petroleum ether mixtures. Qualitative analysis showed bromine to be present.

Anal. Calcd. for $C_{12}H_{15}O_3N_2Br$: C, 45.73; H, 4.80; N, 8.89. Found: C, 45.89; H, 4.65; N, 8.82.

Lithium Aluminum Hydride Reduction of 1-Bromo- and 1-Iodo-1-nitro-2-morpholino-2-phenylethanes (VII and X) to β-Morpholino-β-phenylethylamine (XII).—Five grams (0.016 mole) of 1-bromo-1-nitro-2-morpholino-2-phenylethane (X) was dissolved in 50 ml. of tetrahydrofuran and the solution was added gradually to a refluxing solution of 2 g. of lithium aluminum hydride in 50 ml. of tetrahydrofuran. After an hour of heating, water was added cautiously to decompose the excess hydride. The solution was filtered, acidified with dilute hydrochloric acid and evaporated to leave a gummy residue. A solution prepared by adding 100 ml. of water to this residue was made basic with sodium hydroxide, 7 g. (0.05 mole) of benzoyl chloride was added and the mixture was shaken in a separatory funnel. The resulting precipitate was recovered by filtration and purified by crystallization from ethanol–water to yield approximately 1 g. of white crystals melting at 143–144°. The analysis of this substance corresponds to that expected of the benzoyl derivative (XIII) of β-morpholino-β-phenylethylamine.

Anal. Calcd. for $C_{19}H_{22}N_2O_2$: C, 73.52; H, 7.15; N, 9.03. Found: C, 73.39; H, 7.28; N, 8.76.

The benzoyl derivative is soluble in dilute hydrochloric acid and is reprecipitated upon neutralization. The free diamine is water-soluble and has not been obtained in the pure condition.

Reduction of 1-iodo-1-nitro-2-morpholino-2-phenylethane (VII) with lithium aluminum hydride by the same procedure, followed by benzoylation of the crude reduction product also yielded a sample of XIII which was shown by the mixed melting point test to be identical with the sample obtained from the bromo compound (X).

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(17) J. Thiele and S. Haeckel, *Ann.*, **325**, 1 (1902).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Mechanisms of Elimination Reactions. VIII. The Spontaneous Decomposition of Salts of β-Halo Acids. I. *trans-m*-Nitrocinnamic Acid Dibromide[1]

BY STANLEY J. CRISTOL AND WILLIAM P. NORRIS

RECEIVED SEPTEMBER 11, 1952

When *trans-m*-nitrocinnamic acid dibromide was treated with sodium acetate in absolute ethanol, the neutral products found were *cis-m*-nitro-β-bromostyrene and ethyl *cis*-β-(*m*-nitrophenyl)-glycidate. The intermediate formation of *cis*-α-bromo-β-(*m*-nitrophenyl)-β-propiolactone, followed by lactone ethanolysis and subsequent loss of hydrogen bromide to form an epoxide ring, is suggested to explain the presence of this glycidic ester. A structure proof for ethyl *cis*-β-(*m*-nitrophenyl)-glycidate is reported involving an independent synthesis of the corresponding acid and of the *trans* compounds. The stereochemistry of the various transformations involved in these syntheses is discussed. The mechanism of the decomposition of salts of β-haloacids to give olefins, carbon dioxide and halide ion is discussed. The loss of carbon dioxide and bromide ion from *trans-m*-nitrocinnamic acid dibromide was shown to occur in a stereospecific *trans* fashion giving pure *cis-m*-nitro-β-bromostyrene. A concerted elimination mechanism is suggested for the process.

Spontaneous decomposition of salts of β-halo acids generally leads to the formation of β-lactones as well as olefins formed by loss of halogen and carbon dioxide.[2] When the salt of an α,β-dihalo acid decomposes spontaneously one might therefore expect the formation of some α-halo-β-lactone along with the haloölefin which is usually isolated.[3] This was found to be the case when *trans-m*-nitrocinnamic acid dibromide (II, Ar = *m*-nitrophenyl) was treated with sodium acetate in refluxing ethanol. In addition to *cis-m*-nitro-β-bromostyrene (VII)[4] in the reaction product there was found a neutral compound which was shown to be ethyl *cis*-β-(*m*-nitrophenyl)-glycidate (VI). The formation of this compound can be explained by assuming the intermediate formation of *cis*-β-(*m*-nitrophenyl)-α-bromo-β-propiolactone (IV) which in turn undergoes ethanolysis and dehydrobromination to give (VI).[5]

The glycidic ester (VI) was identified on the

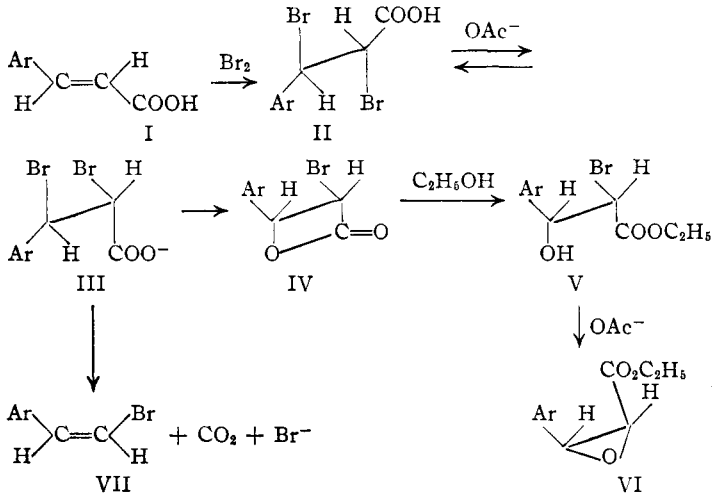
(1) This work was reported at the joint meeting of the Colorado-Wyoming Academy of Science and the Southwestern Division of the American Association for the Advancement of Science in Boulder, Colorado, May 1, 1952. Previous paper in series: S. J. Cristol and A. Begoon, THIS JOURNAL, **74**, 5025 (1952).

(2) (a) A. Einhorn, *Ber.*, **16**, 2208 (1883); (b) A. Basler, *ibid.*, **16**, 3001 (1883); **17**, 1494 (1884); (c) G. Prausnitz, *ibid.*, **17**, 595 (1884); (d) H. Johansson and S. M. Hagman, *ibid.*, **55**, 647 (1922); (e) G. S. Simpson, THIS JOURNAL, **40**, 674 (1918).

(3) (a) E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2078 (1951); (b) J. K. Farrell and G. B. Bachman, THIS JOURNAL, **57**, 1281 (1935); (c) G. B. Bachman, *ibid.*, **55**, 4279 (1933); (d) S. Reich and N. Y. Chang, *Helv. Chim. Acta*, **3**, 235 (1920); (e) F. Straus, *Ber.*, **42**, 2866 (1909).

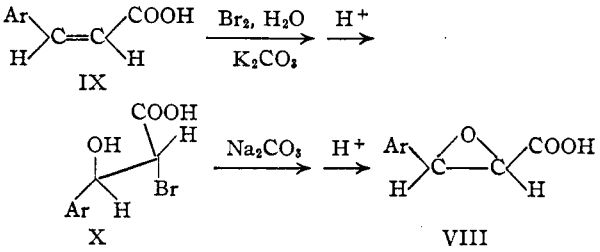
(4) A. Dann, A. Howard and W. Davies, *J. Chem. Soc.*, 605 (1928).

(5) S. Reich, *Arch. Sci. Phys. Nat.*, **45**, 191, 259 (1918); *C. A.*, **12**, 1876 (1918), isolated an acid, m.p. 150° (dec.), from the decomposition of the sodium salt of *trans-m*-nitrocinnamic acid dibromide which he assumed to be *m*-nitrobenzoylacetic acid but which should probably be assigned the structure *cis*-β-(*m*-nitrophenyl)-glycidic acid (VIII).



basis of its carbon and hydrogen analysis and by an alternative synthesis of the glycidic acid (VIII) which showed no depression of melting point when mixed with the acid obtained by the hydrolysis of (VI). Likewise the melting points of the benzylammonium salts of the two samples of the acids were not depressed upon mixing.

The *cis* configuration of the glycidic acid (VIII) has been assigned on the basis of the known *trans* addition of hypohalous acid to an ethylenic system[6] followed by a Walden inversion of the carbon losing the halogen in the oxide formation,[7] as illustrated in the conversion IX → X → VIII.

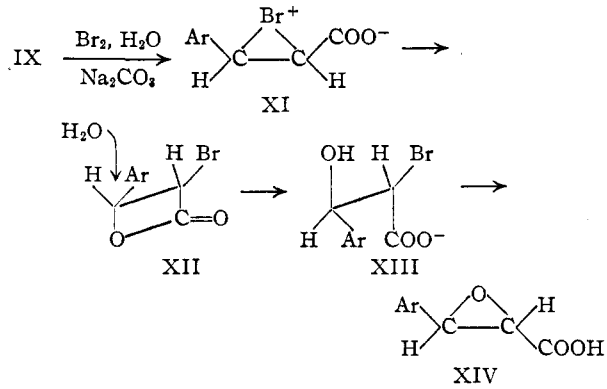


Kuhn and Ebel[7b] reported that the addition of hypochlorous acid to sodium maleate gave only *erythro*-halohydrin which represents a *cis* addition of hypochlorous acid to the double bond. In view of the work by Tarbell and Bartlett[8] in which they obtained bromo-β-lactones by treatment of the salts of dimethylmaleic and dimethylfumaric acids with bromine and water, it seems probable that a similar lactone was involved in the hypochlorination of sodium maleate and that the intermediate chloro-β-lactone underwent an alkyl–oxygen cleavage[9] to give what appears to be *cis* addition of hypochlorous acid. The possibility that *cis* addition of hypobromous acid to the salt of *cis*-*m*-nitrocinnamic acid (IX) occurred leading ultimately to a *trans*-glycidic acid rather than to the *cis*-oxide is considered in detail below and shown to be incorrect.

In the first series of formulas are outlined the reactions which lead to the formation of the *cis*-β-(*m*-nitrophenyl)-glycidic ester (VI). The addition of bromine to *trans*-*m*-nitrocinnamic acid gives the *erythro*-*m*-nitrocinnamic acid dibromide (II).[6a,b,c] The anion (III) of this acid may undergo the transformation indicated to give *cis*-β-(*m*-nitrophenyl)-α-bromo-β-propiolactone (IV) by displacement of bromine by the carboxylate group which inverts the carbon atom on which the displacement has occurred.[9a,10]

The presumed lactone intermediate is not stable under the conditions of the experiment and the ethanol solvent attacks the carbonyl carbon of the lactone to give the *threo*-α-bromo-β-(*m*-nitrophenyl)-β-hydroxypropionic ester (V). The epoxide formation which follows occurs with inversion of the α-carbon[7] to give the *cis*-glycidic ester (VI).

The *cis* configuration of (VI) is based on the assumption that only two inversions occur in the preparation of the *cis*-glycidic acid (VIII) from *cis*-*m*-nitrocinnamic acid (IX). Because, as mentioned above, there is a possibility that three inversions could occur due to participation of the carboxyl group (IX → XI → XII → XIII → XIV) in this synthesis it seemed desirable to carry out a similar series of reactions in which the carboxyl group was esterified. This would of course prevent any β-lactone formation in the hypobromination step. As *trans*-*m*-nitrocinnamic acid is more readily available than the *cis* isomer the *trans*-acid was selected as the starting material.



trans-Addition of hypobromous acid to methyl *trans*-*m*-nitrocinnamate (XV) gives the *erythro*-α-bromo-β-(*m*-nitrophenyl)-β-hydroxypropionic ester (XVII) which is the same substance as is obtained by the esterification of the product (XVI) obtained by hypobromination of sodium *trans*-*m*-nitrocinnamate in aqueous solution. This is demonstrated since the esters obtained by the different routes have the same melting points and show no melting point depression upon mixing. This shows that there is no

(6) (a) A. McKenzie, *J. Chem. Soc.*, **101**, 1196 (1912); (b) P. F. Frankland, *ibid.*, **101**, 654 (1912); (c) B. Holmberg, *Svensk. Kem. Tids.*, **24**, 105 (1912), *C. A.*, **6**, 2072 (1912); (d) E. M. Terry and L. Eichelberger, THIS JOURNAL, **47**, 1067 (1925); (e) I. Roberts and G. E. Kimball, *ibid.*, **59**, 947 (1937).

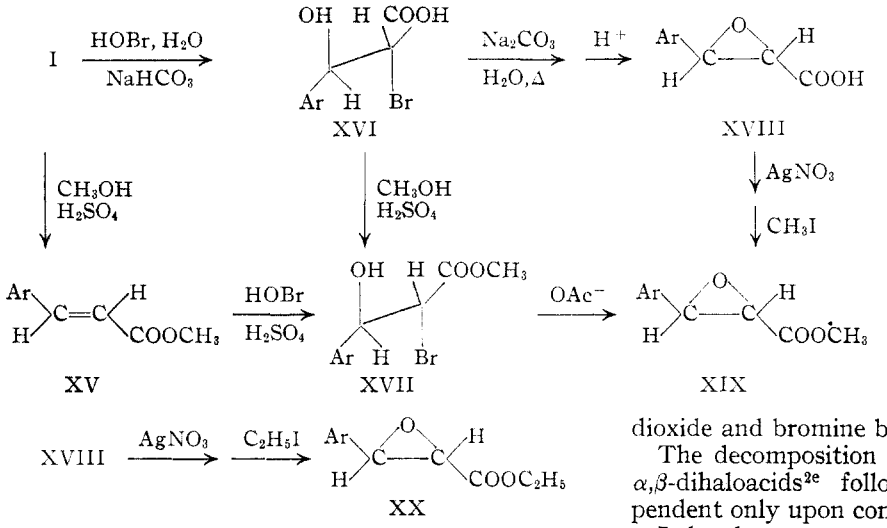
(7) (a) P. D. Bartlett, *ibid.*, **57**, 224 (1935); (b) R. Kuhn and F. Ebel, *Ber.*, **58**, 919 (1925); (c) R. Kuhn and T. Wagner-Jauregg, *ibid.*, **61**, 483 (1928); (d) S. Winstein and H. J. Lucas, THIS JOURNAL, **61**, 1576 (1939); (e) S. Winstein and H. J. Lucas, *ibid.*, **61**, 2845 (1939).

(8) D. S. Tarbell and P. D. Bartlett, *ibid.*, **59**, 407 (1937).

(9) A. R. Olson and R. J. Miller, *ibid.*, **60**, 2687 (1938); A. R. Olson and J. L. Hyde, *ibid.*, **63**, 2459 (1941); B. Holmberg, *J. prakt. Chem.*, **88**, 553 (1913); H. N. K. Rørdam, *J. Chem. Soc.*, 2931 (1932).

(10) B. Holmberg, *Ber.*, **45**, 1713 (1922).

β-lactone formation followed by alkyl-oxygen cleavage in the hypobromination of sodium *trans-m*-nitrocinnamate. Hence the product from *cis-m*-nitrocinnamic acid (IX) is the isomeric *threo*-α-bromo-β-(*m*-nitrophenyl)-β-hydroxypropionic acid (X) as indicated above.



Methyl *trans*-β-(*m*-nitrophenyl)-glycidate (XIX) was prepared by direct dehydrobromination of the bromohydrin ester (XVII) and also by dehydrobromination of the bromohydrin acid (XVI) followed by esterification of the glycidic acid (XVIII). The identity of the *trans*-glycidic esters obtained by the two routes was demonstrated by a mixed melting point determination. This result shows that there are no unexpected inversions occurring due to possible participation of the carboxylate group in the epoxide ring formation.

It was found that methanolic sodium acetate is a sufficiently strong base to cause epoxide formation by the dehydrobromination of the *erythro*-bromohydrin ester (XVII). This is the condition postulated above for dehydrobromination of the *threo*-bromohydrin ester (V) intermediate in the formation of ethyl *cis*-β-(*m*-nitrophenyl)-glycidate (VI).

Thus the ethyl β-(*m*-nitrophenyl)-glycidate (VI), m.p. 94–94.5°, is assigned the *cis* configuration and the *trans* configuration is assigned to its isomer (XX), m.p. 58–59°.

An interesting feature of the decomposition of salts of β-halo acids is the often reported stereospecificity of the reaction with respect to the formation of the olefinic component of the reaction product. For example, Braude and Coles[3a] found that the decomposition of the salt of *trans*-crotonic acid dibromide in water gave pure *cis*-1-bromopropene as the olefinic component. However, Reich and Chang[3d] report that treatment of *trans-p*-nitrocinnamic acid dibromide gives *trans-p*-nitro-β-bromostyrene upon treatment with aqueous sodium acetate or sodium carbonate and the *cis* isomer with ethanolic sodium acetate and report analogous results with the ortho isomer and Reich[5] reports the formation of both *cis*- and *trans-m*-nitro-β-bromostyrenes from the corresponding meta acid dibromide with aqueous sodium carbonate. Dann, Howard and Davies[4] also observed that ethanolic sodium acetate gave pure *cis*-bromoölefins from the nitrocinnamic acid dibromides but found substantial quantities of *cis* as well as *trans* in the aqueous decompositions. It seems likely to us that in each case the reaction is stereospecific, yielding only the *cis* isomer, but that the *cis*-olefin was isomerized to the *trans* in the course of the refluxing of the solution and the working up of the product. In accord with this conclusion, we have decomposed *trans-p*-nitrocinnamic acid dibromide with sodium bicarbonate in aqueous acetone (containing 25 volume % acetone) at 69°, avoiding higher temperatures and steam distillations, and we have found only the *cis* isomer. It thus appears that the reaction is truly stereospecific, carbon dioxide and bromine being lost in a *trans* fashion.[11]

The decomposition of the salts of β-halo-[2d] and α,β-dihaloacids[2e] follow first-order kinetics dependent only upon concentration of the salt.

It has been suggested[12] that the olefin formation goes by way of a β-lactone intermediate, *i.e.*, loss of carbon dioxide by the β-lactone. Although this is a reaction common to β-lactones[2c] it usually requires more vigorous reaction conditions than those used to obtain olefin in the decomposition of the salts of β-haloacids. Ordinarily the β-lactone is hydrolyzed to a β-hydroxyacid under alkaline conditions.

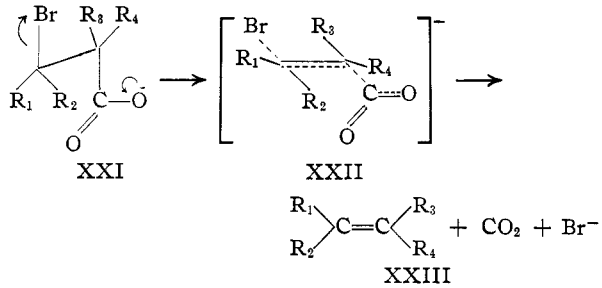
In experiments designed to test whether or not the lactone was an intermediate in olefin formation or whether the two reaction products were obtained as distinct fates for salts of β-bromo acids, Johansson and Hagman[2d] showed that the decomposition of α-methyl-β-bromobutyrate ion in aqueous sodium carbonate at room temperature led to the formation of a 66% yield of butene and carbon dioxide, and they were able to isolate 29% of α-methyl-β-butyrolactone by extraction with chloroform. Similar work with α-ethyl-β-bromobutyrate ion gave 63% of amylene and 32% of α-ethyl-β-butyrolactone. In each case the lactone was shown to be stable to heating well above the temperature of the alkaline decomposition of the bromoacid.

An acceptable alternative mechanism for the formation of olefin by the decomposition of the salt of a β-haloacid must then account for the stereospecificity (*trans* elimination) of the reaction, the first-order kinetics, and the probable inoperation of a β-lactone as an intermediate. Reactions (XXI → XXIII) illustrate a mechanism which meets these requirements. The pair of electrons on the carboxylate group in (XXI) attack the carbonyl carbon displacing the carbon–carbon bond electrons which in turn attack the β-carbon by a

(11) There is the possibility that an alternative mechanism for the decomposition intercedes under certain conditions leading to *cis* elimination and giving *trans* olefin from *erythro* dibromide, but in the work herein described, elimination occurs entirely in a *trans* fashion.

(12) (a) E. Erlenmeyer, *Ber.*, **13**, 305 (1880); (b) R. B. Woodward and R. B. Loftfield, THIS JOURNAL, **63**, 3167 (1941).

direct inversion process, forming the carbon–carbon double bond and displacing bromide ion. The reaction may proceed through the transition state (XXII) and the whole process may be a concerted one in which the various bonds are made or broken simultaneously. This mechanism is similar to that proposed for base-promoted *trans* elimination of the elements of hydrogen halides from alkyl halides.[13] The *trans* requirement of carboxylate and bromine may be reconciled with the energy gain in the formation of the double bond with loss of halide ion when the β-carbon atom may be inverted. This concept is borne out by the facile decarboxylation of salts of acids when a β-halogen is present so that olefin and halide ion may form, as opposed to the more difficult decarboxylation of salts of ordinary acids[14] where a carbanion intermediate is most likely formed.[15]



XXI XXII

XXIII

Acknowledgments.—The authors wish to acknowledge support of this work by a contract with the Office of Naval Research, and by the American Cyanamid Company for a research fellowship for one of us (W. P. N.). The analyses were carried out by the Galbraith Laboratories.

Experimental

Treatment of *trans-m*-Nitrocinnamic Acid Dibromide (II) with Sodium Acetate in Ethanol.—A solution of 69.5 g. (0.186 mole) of *trans-m*-nitrocinnamic acid dibromide[16] and 70 g. (0.85 mole) of sodium acetate in 1500 ml. of 99.5% ethanol was maintained at reflux for 5 hours. The ethanol was then removed under reduced pressure. The residue was dissolved in ether and the ether solution was extracted with 5% sodium bicarbonate solution to remove any unreacted acid and was then washed with water. Evaporation of the ether left 40 g. of an orange oil. A 10-g. portion of the oil was dissolved in carbon tetrachloride and the solution was poured onto an alumina column containing approximately 100 g. of Fisher activated alumina (80–200 mesh). One liter of carbon tetrachloride removed 6.7 g. (64%) of *cis-m*-nitro-β-bromostyrene (VII), m.p. 5–8°. Elution with 500 ml. of chloroform gave 1.1 g. (15%) of ethyl *cis*-β-(*m*-nitrophenyl)-glycidate (VI), m.p. 90–92°.

When the 6.7 g. of *cis-m*-nitro-β-bromostyrene (VII) was recrystallized from ether at −70°, 4.5 g. of material was obtained, m.p. 7.5–8.5°.[4]

Anal. Calcd. for $C_8H_6BrNO_2$: C, 42.12; H, 2.65. Found: C, 42.23; H, 2.50.

Recrystallization of the ethyl *cis*-β-(*m*-nitrophenyl)-glycidate (VI) from carbon tetrachloride gave a product melting 94–94.5°.

Anal. Calcd. for $C_{11}H_{11}NO_5$: C, 55.69; H, 4.68. Found: C, 55.7; H, 4.7.

Hydrolysis of Ethyl *cis*-β-(*m*-Nitrophenyl)-glycidate (VI).—To a solution of 200 mg. (0.85 mmole) of the ester (VI) in 10 ml. of 95% ethanol was added 10 ml. of 95% ethanol containing 0.34 g. (8.5 mmoles) of sodium hydroxide. The reaction mixture was allowed to stand at room temperature for 2 hours. Water (75 ml.) was added and the solution was extracted with 25 ml. of ether. The aqueous layer was acidified with dilute hydrochloric acid. The aqueous solution was extracted 3 times with 25-ml. portions of ether. Evaporation of the ether gave 180 mg. of acid, m.p. 151–152° (dec.). Recrystallization from benzene gave 80 mg. (45%), m.p. 155–157° (dec.).[5] A mixed melting point with (VIII) showed no depression.

The benzylammonium derivative of the above acid was prepared by dissolving 40 mg. of the acid in 5 ml. of dry ether and adding two drops of benzylamine. A white gummy precipitate formed which when recrystallized from ethyl acetate gave 37 mg. of salt, m.p. 126–127°.

Anal. Calcd. for $C_{16}H_{16}N_2O_5$: C, 60.75; H, 5.10. Found: C, 60.69; H, 5.10.

Preparation of *threo*-α-Bromo-β-(*m*-nitrophenyl)-β-hydroxypropionic Acid (X).—One gram (0.0052 mole) of *cis-m*-nitrocinnamic acid (IX), m.p. 155–156°, was added to 50 ml. of water containing 1.5 g. of potassium carbonate. The solution was cooled to 0° in an ice–salt-bath and bromine vapor in an air stream was bubbled through the solution until a faint brown color persisted. The solution was allowed to sit in an ice-bath for two hours and then allowed to warm to room temperature. A slight excess of dilute hydrochloric acid was added and the solution was extracted 3 times with 25-ml. portions of ether. The ether was evaporated and the resultant oil was dissolved in hot chloroform–carbon tetrachloride solvent. Cooling the solution gave 0.95 g. (63%) of acid (X), m.p. 126–128°; after recrystallization from chloroform, the material melted at 127–128°.

Anal. Calcd. for $C_9H_8BrNO_5$: C, 37.26; H, 2.79. Found: C, 37.34; H, 2.86.

Preparation of *cis*-β-(*m*-Nitrophenyl)-glycidic Acid (VIII) from *threo*-α-Bromo-β-(*m*-Nitrophenyl)-β-hydroxypropionic Acid (X).—A solution of 270 mg. (1 mmole) of the *threo*-bromohydrin acid (X) and 1.0 g. (9.5 mmoles) of sodium carbonate in 25 ml. water was heated to boiling and then allowed to cool to room temperature. The solution was acidified with dilute hydrochloric acid and then extracted twice with 25-ml. portions of ether. The ether was evaporated and 200 mg. (95%) of the glycidic acid (VIII), m.p. 153–154° (dec.), was obtained. After two recrystallizations from chloroform the compound melted at 154–156° (dec.).

Anal. Calcd. for $C_9H_7NO_5$: C, 51.68; H, 3.38. Found: C, 51.68; H, 3.46.

The benzylammonium salt of (VIII) was prepared by adding benzylamine to an ethyl acetate solution of the glycidic acid. The resulting salt was recrystallized once from ethyl acetate to give m.p. 125–126° and showed no depression when mixed with the benzylammonium salt prepared from the glycidic acid obtained by hydrolysis of ethyl *cis*-β-(*m*-nitrophenyl)-glycidate (VI).

Preparation of Methyl *erythro*-α-Bromo-β-(*m*-Nitrophenyl)-β-hydroxypropionate (XVII) from Methyl *trans-m*-Nitrocinnamate (XV).—A solution of hypobromous acid was prepared by treating 3.2 g. (0.020 mole) of bromine in 25 ml. of 9% sulfuric acid with sufficient aqueous silver nitrate (30%) to just decolorize the solution. The solution was kept at 0° during the addition of the silver nitrate; 2.07 g. (0.0101 mole) of methyl *trans-m*-nitrocinnamate in 50 ml. of dioxane was then added to the acid solution. The reaction mixture was then allowed to warm to room temperature and was then heated rapidly to 50° and held there for 10 minutes. The reaction mixture was filtered and the filtrate was poured into 200 ml. of cold water. This mixture was then extracted with 50 ml. of ether. The ether layer was washed with 50 ml. of 5% sodium bicarbonate solution and then with 50 ml. of cold water. The ether layer was then separated and evaporated to give 3.12 g. of an oily residue. The oily residue was dissolved in hot methyl alcohol and upon cooling 0.23 g. of a solid, m.p. 128–132°, was filtered off. Recrystallization from cyclohexane gave m.p. 133–134°. This compound has the correct analysis for the nitric acid ester of methyl *erythro*-α-bromo-β-(*m*-nitrophenyl)-β-hydroxypropionate.

(13) See, for example, S. J. Cristol, N. L. Hause and J. S. Meek, THIS JOURNAL, **73**, 674 (1951).

(14) T. S. Oakwood and M. R. Miller, *ibid.*, **72**, 1849 (1950).

(15) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 361–364; H. Schenkel and M. Schenkel-Rudin, *Helv. Chim. Acta*, **31**, 514 (1948).

(16) R. E. Buckles, E. A. Hausman and N. G. Wheeler, THIS JOURNAL, **72**, 2494 (1950).

Anal. Calcd. for $C_{10}H_9BrN_2O_7$: C, 34.41; H, 2.60; Br, 22.90. Found: C, 34.30; H, 2.65; Br, 22.71.

Oxidation of this compound with potassium permanganate solution gave *m*-nitrobenzoic acid. This rules out the possibility of a dinitro compound which would have the same analysis.

When the filtrate was concentrated and cooled, 0.73 g. of material, m.p. 95–100°, was obtained. By removing methyl alcohol from the residue and adding carbon tetrachloride an additional 0.93 g. of material, m.p. 95–100°, was obtained for a total yield of 1.66 g. (55%) of crude methyl *erythro*-α-bromo-β-(*m*-nitrophenyl)-β-hydroxypropionate. Recrystallization of 730 mg. of crude ester from cyclohexane gave 610 mg. of bromohydrin ester (XVII), m.p. 101–102°.

Anal. Calcd. for $C_{10}H_{10}BrNO_5$: C, 39.49; H, 3.31. Found: C, 39.60; H, 3.32.

Preparation of *erythro*-β-(*m*-Nitrophenyl)-β-hydroxy-α-bromopropionic Acid (XVI).—A solution of 1.93 g. (0.0100 mole) of *trans*-*m*-nitrocinnamic acid and 2.7 g. of sodium bicarbonate in 100 ml. of water was added to a solution of hypobromous acid prepared by bubbling bromine vapor into 50 ml. of water containing 3.4 g. (0.020 mole) of silver nitrate. The reaction mixture was allowed to stand at room temperature for an hour, then was filtered, acidified with dilute sulfuric acid and extracted with ether. The ether was evaporated and the residue was recrystallized from a carbon tetrachloride–chloroform mixture. The yield of crude material, m.p. 120–123°, was 1.44 g. (50%). An analytical sample crystallized from chloroform twice had m.p. 124–125°.

Anal. Calcd. for $C_9H_8BrNO_5$: C, 37.26; H, 2.79. Found: C, 37.22; H, 2.84.

Preparation of Methyl *erythro*-α-Bromo-β-(*m*-nitrophenyl)-β-hydroxypropionate (XVII) from *erythro*-α-Bromo-β-(*m*-nitrophenyl)-β-hydroxypropionic Acid (XVI).—A solution of 400 mg. of (XVI) in 75 ml. of absolute methanol containing 10 drops of 95% sulfuric acid was refluxed for 3 hours. After 25 ml. of dry benzene was added, solvent was slowly distilled until the reaction solution volume was approximately 25 ml. The solution was poured into 200 ml. of cold water and extracted with two 50-ml. portions of ether. The ether fractions were combined and extracted with 100 ml. of 5% sodium bicarbonate solution. The ether layer was evaporated to give 370 mg. (88%) of ester (XVII), m.p. 99–101°. Recrystallization from carbon tetrachloride gave 270 mg. of material, m.p. 101–102°. A mixed melting point determination with the methyl ester obtained by adding hypobromous acid to methyl *trans*-*m*-nitrocinnamate showed no depression.

Preparation of *trans*-β-(*m*-Nitrophenyl)-glycidic Acid (XVIII).—A solution of 100 mg. (0.34 mmole) of the *erythro*-bromohydrin acid (XVI) in 10 ml. water containing 0.1 g. of sodium carbonate was heated to boiling, then allowed to cool to room temperature, acidified with dilute sulfuric acid and extracted with ether. The ether was evaporated to give 55 mg. (76%) of glycidic acid, m.p. 138–140°. A sample for analysis was recrystallized from benzene and had m.p. 139–140°.

Anal. Calcd. for $C_9H_7NO_5$: C, 51.68; H, 3.38. Found: C, 51.65; H, 3.43.

Preparation of Methyl *trans*-β-(*m*-Nitrophenyl)-glycidate (XIX) from Methyl *erythro*-α-Bromo-β-(*m*-nitrophenyl)-β-hydroxypropionate (XVII).—A solution of 500 mg. (1.6 mmoles) of the bromohydrin ester (XVII) and 1.0 g. of fused sodium acetate in 25 ml. of absolute methyl alcohol was refluxed for 15 minutes. The solution was poured into 100 ml. of cold water and extracted with ether. Evaporation of the ether left 290 mg. (90%) of the glycidic ester (XIX), m.p. 98–98.5°. This compound was identical (mixed m.p.) with the analyzed product described below prepared from the corresponding acid (XVIII).

Preparation of Ethyl *trans*-β-(*m*-Nitrophenyl)-glycidate (XX).—Sufficient potassium hydroxide solution was added to 1.0 g. (4.8 mmoles) of *trans*-β-(*m*-nitrophenyl)-glycidic acid (XVIII) to bring it in solution. Dilute nitric acid was then added until a faint cloudiness appeared. A solution of 1.0 g. of silver nitrate in 10 ml. of water was then added. The silver salt came down rather slowly. The precipitate was filtered off, washed with acetone and when dried weighed 1.4 g. (93%).

One-half gram of the silver salt was treated with 10 ml. of ethyl iodide at reflux for 30 minutes. The silver iodide was removed by filtration and washed with ether. After evaporation of the ethyl iodide and ether, there remained 380 mg. (100%) of ester (XX), m.p. 57–59°. Recrystallization from cyclohexane–carbon tetrachloride mixture gave a product melting at 58–59°.

Anal. Calcd. for $C_{11}H_{11}NO_5$: C, 55.69; H, 4.68. Found: C, 55.76; H, 4.61.

Preparation of Methyl *trans*-β-(*m*-Nitrophenyl)-glycidate (XIX).—One-half gram of the silver salt of *trans*-β-(*m*-nitrophenyl)-glycidic acid was treated with 10 ml. of methyl iodide at reflux for one hour. The solids were filtered off and washed with ether. The solvent was evaporated from the filtrate and 230 mg. (62%) of ester (XIX), m.p. 98–99°, was obtained. Recrystallization from methyl alcohol gave m.p. 98.5–99°.

Anal. Calcd. for $C_{10}H_9NO_5$: C, 53.81; H, 4.06. Found: C, 54.04; H, 4.16.

Treatment of *trans*-*p*-Nitrocinnamic Acid Dibromide with Sodium Bicarbonate in an Acetone–Water Solvent.—To a solution of 3.6 g. (0.043 mole) of sodium bicarbonate in 200 ml. of acetone–water mixture (25 vol. % acetone) was added 5 g. (0.014 mole) of *trans*-*p*-nitrocinnamic acid dibromide.[3d] The reaction mixture was heated to reflux (69°) for 5 hours. The cooled mixture was extracted with ether and 1.2 g. (37%) of material, m.p. 42–45°, was obtained upon evaporation of the ether. Recrystallization from petroleum ether, b.p. 30–60°, gave 0.60 g. of *cis*-*p*-nitro-β-bromostyrene, m.p. 48–49°.[3d]

Preparation of Methyl *trans*-*m*-Nitrocinnamate (XV).—*trans*-*m*-Nitrocinnamic acid was esterified by using absolute methanol and concentrated sulfuric acid catalyst to give a 93% yield of ester, m.p. 123–124°.[17]

Preparation of *cis*-*m*-Nitrocinnamic Acid (IX).—The method of Wollring[18] was employed whereby ammonium *trans*-*m*-nitrocinnamate was converted to an equilibrium mixture of *cis*- and *trans*-ammonium salts by irradiation with ultraviolet light. The *cis*-acid was separated from the *trans*-acid by fractional precipitation with hydrochloric acid. The melting point of the acid (IX) was 155–156° (Wollring[18] reported a melting point of 158°).

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