[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Reactions of Iodine–Amine Complexes with Unsaturated Compounds. II. An Investigation of the Scope of the Reaction with the Iodine–Morpholine Complex

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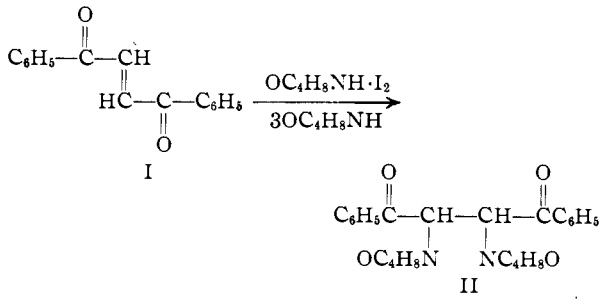
Results are presented of experiments in which the reactivity of the iodine–morpholine complex in the presence of morpholine toward nine unsaturated compounds was tested. Compounds which reacted rapidly at room temperature were *trans*-1,2-dibenzoylethylene, *trans*-β-benzoylacrylic acid, cinnamaldehyde and β-nitrostyrene. Except in the case of cinnamaldehyde, the reaction products were isolated and characterized. Compounds which reacted very slowly or not at all at room temperature were α-phenylbenzalacetophenone, ethyl cinnamate, cinnamonitrile, cyclohexene, and *trans,trans*-1,4-diphenyl-1,3-butadiene. Ethyl cinnamate did, however, react to yield a dimorpholino derivative during a period of about seven weeks at room temperature or several hours at temperatures above 80°. Reaction products which were characterized all appeared to be α,β-dimorpholino derivatives except that obtained from β-nitrostyrene, which was shown to be 1-iodo-1-nitro-2-morpholino-2-phenylethane. Reduction of the latter compound with lithium aluminum hydride yielded β-morpholino-β-phenylethylamine, which was isolated in the form of its benzoyl derivative.

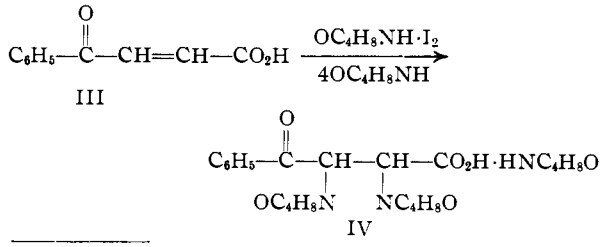
In the first paper of this series[2a,b] were described reactions of benzalacetophenone and benzalacetone with iodine complexes of morpholine, piperidine, cyclohexylamine, benzylamine and ammonia in the presence of an excess of the amine. The iodine complexes of the secondary amines reacted with both ketones to produce α,β-diamino ketones; the complexes formed from the primary amines or from ammonia reacted in a similar way with benzalacetophenone (but not with benzalacetone) to form ethylene imine ketones. In order to investigate the scope of this reaction a study has been made of the effect of morpholine plus the morpholine–iodine complex, "morpholine periodide," $C_4H_9ONI_2$,[3] upon three additional α,β-unsaturated ketones, an α,β-unsaturated aldehyde, an α,β-unsaturated ester, an α,β-unsaturated nitrile, an α,β-unsaturated nitro compound and two unsaturated hydrocarbons, one of which contained a conjugated diene system. The results of this investigation may indicate that the reaction is typical of and confined to unsaturation which is in conjugation with certain electron-withdrawing functional groups.

The reaction is not confined to the class of β-phenyl-α,β-unsaturated ketones typified by benzalacetone and benzalacetophenone. *trans*-1,2-Dibenzoylethylene (I), for example, reacted rapidly with morpholine periodide and excess morpholine to give a 64% yield of 1,2-dibenzoyl-1,2-dimorpholinoethane (II). Purification of the crude



product yielded only one of the two possible diastereoisomeric forms of II, and except for morpholine hydriodide, no other pure compound was obtained. The same substance was also obtained as one product of the reaction between *meso*-dibenzoylethylene dibromide and morpholine. Lutz and Smithey[4] have recently secured a compound probably identical with ours from reactions of morpholine with the dibenzoylethylene dibromides or some derived compounds. Whether this substance is the *meso* or the racemic form of II is not yet known. In the experiments with the unsaturated compounds described below, as in those previously reported with benzalacetophenone and benzalacetone,[2] only one of two possible racemic forms could be isolated following the reaction with the iodine–amine complex.

trans-β-Benzoylacrylic acid (III) also reacted rapidly with morpholine periodide and morpholine, evidently to give the morpholine salt of α,β-dimorpholino-β-benzoylpropionic acid (IV). The



(1) Institute Fellow in Organic Chemistry, 1950–1951.

(2a) P. L. Southwick and D. R. Christman, THIS JOURNAL, **74**, 1886 (1952).

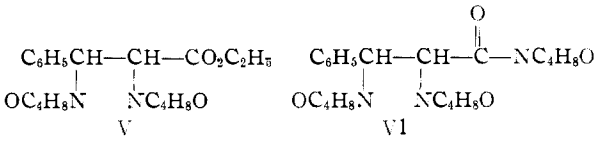
(2b) In a footnote added in proof to our previous paper (Ref. 2a), the opinion was expressed that the form of α,β-dimorpholinobenzylacetophenone produced by the reaction of benzalacetophenone with morpholine and the iodine-morpholine complex was identical with the "isomer B" of R. H. Jordan, R. E. Lutz and D. F. Hinkley, Jr., *J. Org. Chem.*, **16**, 1442 (1951). Mixed melting point tests, made possible by the use of samples generously supplied by Professor Robert E. Lutz, have since confirmed this conclusion. However, although from the reaction of benzalacetophenone dibromide with morpholine at room temperature (see N. H. Cromwell, THIS JOURNAL, **62**, 2897 (1940)), isomer B was, as we reported, the only form of the compound which we obtained in the pure condition, Professor Lutz has informed us that in his experience the benzalacetophenone dibromide–morpholine reaction, when conducted at room temperature without cooling, has always produced the other racemic form, isomer A, in a sufficient proportion to make it the first compound to be separated from the mixed crude product by crystallization. He therefore feels that of his two isomers, isomer B is probably the one which had not previously been described. Since he has found (see reference cited above) that a preponderance of isomer B is formed near 0° and a preponderance of isomer A at 50°, he suggests that the difference between his results and ours may be attributed to a somewhat higher reaction temperature in his experiments, possibly due to a higher room temperature initially, and/or to a larger temperature rise during the reaction as a consequence of conducting the reaction on a larger scale.

(3) R. V. Rice and G. D. Beal, U. S. Patent, 2,290,710 (July 21, 1943); *C. A.*, **37**, 502 (1943).

(4) R. E. Lutz and W. R. Smithey, Jr., *J. Org. Chem.*, **16**, 51 (1951).

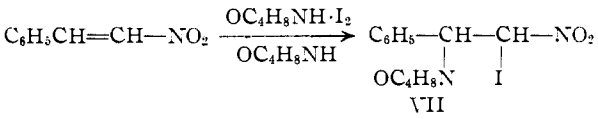
results with still another α,β-unsaturated ketone, however, demonstrated that a high degree of substitution may prevent the reaction of a compound of this type; α-phenylbenzalacetophenone ("benzaldesoxybenzoin") failed to give any evidence of reaction under similar conditions during a period of several days.

Cinnamaldehyde reacted rapidly, as indicated by the fading of the orange-red color of the iodine complex, but efforts to isolate the reaction product or products derived from the aldehyde were unsuccessful. On the other hand, ethyl cinnamate did not appear at first to react at all. However, when a reaction mixture was allowed to stand for 48 days at room temperature, the color of the iodine complex faded and there was obtained a 29% yield of a compound having the composition expected of ethyl α,β-dimorpholino-β-phenylpropionate (V). A 5% yield of the same product was

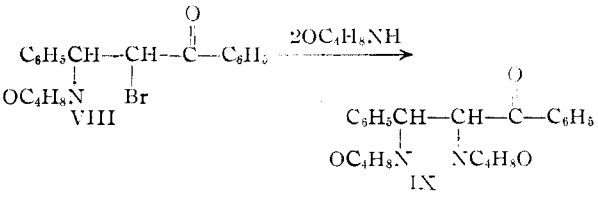


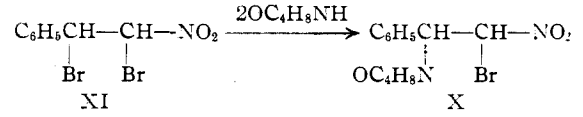
produced during a 13-hour reaction period in refluxing benzene. The morpholide (VI), corresponding to the ethyl ester (V), has been prepared by Cromwell and Caughlan by the action of morpholine on the dibromide of N-cinnamoylmorpholine.[5] An experiment with cinnamonitrile indicated that, as in the case of ethyl cinnamate, no noticeable reaction occurs at room temperature within a period of several days.

An extremely rapid reaction was observed with β-nitrostyrene. The product obtained, however, was not an α,β-dimorpholino derivative, but 1-iodo-1-nitro-2-morpholino-2-phenylethane (VII). Compound VII, which was subject to gradual



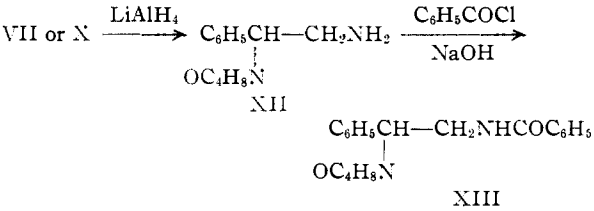
decomposition upon standing, did not appear to react with morpholine at room temperature. This behavior is in sharp contrast to that of α-bromo-β-morpholino ketones such as VIII, which react readily with morpholine to yield dimorpholino ketones (IX).[6] A bromo derivative (X) corresponding to the iodo compound VII was readily obtained by treating the dibromide of β-nitrostyrene (XI) with an excess of morpholine; compound X, like compound VII, appears to be inert toward morpholine at room temperature. There are reports in the literature of the preparation of three





other compounds analogous to compound X by the addition of toluidine,[7] piperidine[8] and ammonia[8] to β-bromo-β-nitrostyrene.

Compounds VII and X are both reduced by use of lithium aluminum hydride to β-morpholino-β-phenylethylamine (XII), isolated in the form of its benzoyl derivative (XIII). The structures VII and X for the iodo and bromo compounds, respectively, and XII for their reduction product appear to be well established on the basis of the stability of the latter compound; no reasonable structure isomeric with XII can be written for the stable diamine and no plausible structure other than VII and X for the halogen compounds could yield the diamine XII by reduction.



The hydrocarbons investigated, cyclohexene and *trans,trans*-1,4-diphenyl-1,3-butadiene, failed to react to a detectable extent either at room temperature or at the reflux temperature of benzene solutions and were recovered unchanged. At the reflux temperature the iodine complex was consumed and some morpholine hydroiodide separated, but the same result was observed in refluxing benzene solutions containing no olefinic compound. Evidently at moderately elevated temperature the complex can undergo decomposition, or perhaps reaction with benzene, with the formation of morpholine hydroiodide.

The fact that functional groups thus far found to promote reaction are those recognized to be capable of withdrawing electrons from an attached double bond might suggest that the reactions are initiated by a conjugate addition of the amine which is present, but in the case of the benzalacetophenone–morpholine–iodine reaction the product of such a conjugate addition is apparently not an intermediate.[2] Therefore, it is considered more likely that benzalacetophenone and other reacting compounds undergo an initial direct addition of the elements of N-iodomorpholine[9] to the olefinic double bond, the iodine atom becoming attached to the α-carbon, the amino nitrogen to the β-carbon. Such a result might be the consequence of the operation of any of a number of different reaction mechanisms. The range of possibilities includes the following: (1) an essentially one-stage bimolecular addition reaction of one molecule of the unsaturated ketone with one molecule of N-iodomorpholine or of the iodine–morpholine complex (2) a concerted attack in which the nucleophilic

(5) N. H. Cromwell and J. A. Caughlan, THIS JOURNAL, **67**, 903 (1945).

(6) N. H. Cromwell, *ibid.*, **62**, 2897 (1940).

(7) D. B. Worrall, *ibid.*, **43**, 920 (1921).

(8) J. Loevenich and H. Gerber, *Ber.*, **63B**, 1707 (1930).

(9) It was previously suggested (ref. 2a) that morpholine periodide might be regarded as equivalent to a hydroiodide of N-iodomorpholine.

nitrogen atom of a molecule of morpholine attacks the β-carbon and an electrophilic iodine atom of an iodine molecule attacks the α-carbon (3) a concerted attack similar to (2) but involving electrophilic iodine atoms of N-iodomorpholine or the iodine–morpholine complex rather than those of free iodine molecules. Cromwell and Graff[10] have pointed out that an initial *trans* addition of the elements of an N-iodoamine to *trans*-benzalacetophenone would account for the observed formation (as final products) of ethylene imine ketones of the *trans* configuration in reactions with iodine–benzylamine and iodine–cyclohexylamine complexes.[2a] The mechanisms (2) and (3) involving concerted attack would readily explain the required *trans* addition of the elements of an N-iodoamine.

Further studies on iodine–amine complexes are in progress and complexes of amines with other halogens may also prove to be worthy of investigation.

Experimental[11,12]

Reactions of Unsaturated Compounds with Morpholine Periodide and Morpholine. (A). ***trans*-1,2-Dibenzoylethylene—Preparation of 1,2-Dibenzoyl-1,2-dimorpholinoethane (II).**—To a solution of 10 g. (0.042 mole) of *trans*-1,2-dibenzoylethylene[13] in 100 ml. of benzene was added 14.8 g. (0.17 mole) of morpholine. To the resulting solution 10.6 g. (0.042 mole) of iodine dissolved in 100 ml. of benzene was added rapidly, with stirring. The orange-red color of the solution faded to light yellow in a short time and a white precipitate of morpholine hydroiodide separated. After removal of the morpholine hydroiodide by filtration, the solvent was removed from the filtrate by evaporation, and the residue was washed with methanol. The yield of crude product obtained in this way was 11 g., corresponding to a 64% yield of 1,2-dimorpholino-1,2-dibenzoylethane. Following purification by several recrystallizations from benzene–petroleum ether mixtures, white needles were obtained. The compound separates from methanol in the form of light yellow prisms. It melts with darkening and decomposition, with most of the melting occurring over the range 179–181° when the melting point is taken in a capillary tube in the usual way. However, the upper limit of the melting range may be raised to 185° (cor.) if samples are placed in a bath preheated to about 180°.

Anal. Calcd. for $C_{24}H_{28}O_4N_2$: C, 70.56; H, 6.91; N, 6.86. Found: C, 70.27; H, 6.62; N, 6.87.

This substance was also isolated as one product of the reaction of morpholine with the *meso* form of dibenzoylethylene dibromide, m.p. 179–180°, conducted as described by Lutz, Bailey and Shearer.[14] From the mixture of the products obtained it was possible to separate by means of extraction with dilute hydrochloric acid (in which the dimorpholino ketone is the most soluble component), followed by fractional crystallization from methanol and from benzene–petroleum ether, the 1,2-dibenzoyl-1,2-dimorpholinoethane (II), m.p. 179–181°, and 1-morpholino-1,2-dibenzoylethylene (XIV), m.p. 177–178°. The former product was identical in its properties with the product of the morpholine–morpholine periodide reaction described above and produced no melting point depression when mixed with that substance. The monomorpholino unsaturated ketone (XIV) crystallized from benzene and petroleum ether in the form of yellow prisms which were analyzed.

Anal. Calcd. for $C_{20}H_{19}NO_3$: C, 74.74; H, 5.96; N, 4.36. Found: C, 74.71; H, 5.78; N, 4.33.

Both of these products were recently described by Lutz and Smithey.[4]

(B). ***trans*-β-Benzoylacrylic Acid—Preparation of the Morpholine Salt of α,β-Dimorpholino-β-benzoylpropionic Acid (IV).**—Five grams (0.028 mole) of β-benzoylacrylic acid[15] was dissolved in a mixture prepared from 75 ml. of benzene and 15 ml. of methanol. To a solution of 7.2 g. of iodine in an equal quantity of the same solvent mixture 13 g. (0.15 mole) of morpholine was added, and the resulting mixture was added rapidly to the solution of β-benzoylacrylic acid with stirring. The orange-red color of the mixture faded to light yellow within 10 minutes. The white solid which had precipitated (10.5 g., probably consisting mainly of morpholine hydroiodide) was removed by filtration and the solvent was allowed to evaporate from the filtrate at room temperature. There remained 13.2 g. of a solid residue. Assuming that the yield of morpholine hydriodide equaled the theoretical maximum, the total yield of solid products, 23.7 g., would require the presence of 11.2 g., or 90% of the other product, the morpholine salt of α,β-dimorpholino-β-benzoylpropionic acid (IV). Because both products were of similar solubility, however, purification of the morpholine salt of the organic acid was difficult, and a yield of only 25% of fully purified IV, in the form of white needles melting with decomposition at about 190°, was obtained after repeated fractional crystallization from methanol.

Anal. Calcd. for $C_{22}H_{33}O_6N_3$: C, 60.67; H, 7.64; N, 9.65. Found: C, 60.90; H, 7.45; N, 9.30.

(C) **Ethyl Cinnamate—Preparation of Ethyl α,β-Dimorpholino-β-phenylpropionate (V).**—To a solution prepared from 10 g. (0.057 mole) of ethyl cinnamate, 19.9 g. (0.23 mole) of morpholine and 50 ml. of benzene, was added a solution of 14.4 g. (0.057 mole) of iodine in 100 ml. of benzene. The bright orange-red color of morpholine periodide faded to light orange after a period of about seven hours at the reflux temperature and did not fade any more during an additional six-hour heating period. The solution was cooled, the morpholine hydriodide was removed by filtration and the filtrate was concentrated by evaporation until a red-colored oil remained. The oil was taken up in methanol. The methanol solution, when cooled in a Dry Ice chest, deposited some crystals which melted to an oil when allowed to warm to room temperature. Dilution of the methanol filtrate from these crystals with water yielded additional oily material. However, a second treatment of both portions of the oil with methanol gave a solid product which yielded 1 g. (5% yield) of white needles melting at 145–146° after repeated crystallization from methanol.

Anal. Calcd. for $C_{19}H_{28}O_4N_2$: C, 65.49; H, 8.10; N, 8.04. Found: C, 65.47; H, 8.06; N, 8.12.

An identical reaction mixture underwent decolorization in a period of about 48 days when allowed to stand at room temperature. In this case, however, evaporation of the filtrate from the reaction mixture left a solid residue rather than an oil (7 g., m.p. 136–140° after washing with water), and a single recrystallization from ethanol gave 5.7 g. (28.8%) of material melting at about 138–141°. This melting point was not depressed by admixture with a purified sample of V (mixed m.p. 140–143°). It is possible that the crude product contains small amounts of a second racemic form of this compound.

(D). **β-Nitrostyrene—Preparation of 1-Iodo-1-nitro-2-morpholino-2-phenylethane (VII).**—A solution of 17 g. (0.067 mole) of iodine in 100 ml. of methanol was added rapidly, with stirring, to a solution prepared from 10 g. (0.067 mole) of β-nitrostyrene,[16] 23.4 g. (0.269 mole) of morpholine and 100 ml. of methanol. The mixture faded to a light red color in a very short time at room temperature and a precipitate separated. Filtration of the mixture yielded 7.6 g. of bright yellow crystals and an additional 9.2 g. was precipitated by dilution of the filtrate with water, bringing the total yield to 16.8 g. or 69.1%. The crude product melted with decomposition at about 103–107°, with the first evidence of decomposition at about 90°. Following recrystallization by dissolving the product in benzene with a minimum of heating and diluting the solution with

(10) N. H. Cromwell and M. A. Graff, *J. Org. Chem.*, **17**, 414 (1952).

(11) Melting points are corrected.

(12) Microanalyses by Clark Microanalytical Laboratory, Urbana, Illinois, and by Drs. G. Weiler and F. B. Strauss, Oxford, England.

(13) R. E. Lutz, *Org. Syntheses*, **20**, 29 (1940).

(14) R. E. Lutz, P. S. Bailey and N. H. Shearer, THIS JOURNAL, **68**, 2224 (1946).

(15) O. Grummitt, E. I. Becker and C. Meisse, *Org. Syntheses*, **29**, 11 (1949).

(16) D. E. Worrall, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 413.

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

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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).