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Ring-Chain Tautomerism of the β -(*p*-Bromobenzoyl)-crotonic Esters

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The tautomeric esters of *cis* β -(*p*-bromobenzoyl)-crotonic acid (I) have been studied because in this series the stereochemistry is established and the *trans* isomers are available for comparison and reference.¹

The Open Chain Esters.—The methyl and ethyl esters of *cis* β -bromobenzoylcrotonic acid (IV) have been prepared from the silver salt of the *cis* acid (I) and the corresponding alkyl iodides. They are hydrolyzed to the original *cis* acid. In contrast with the cyclic esters, they undergo reduction normally with zinc and glacial acetic acid to give the expected β -bromobenzoylbutyric esters (VII) which are prepared also by esterification of the reduced acid or by reduction of the *trans* esters (III).

The open chain structure of these *cis* esters might be presumed from the mode of preparation through the silver salt, since the cyclic isomers (VI) are known and are different. Evidence is available in support of this. The *cis* methyl ester is obtained by the action of sunlight on a methanol solution of the *trans* isomer and is rearranged back into the *trans* isomer by the action of sunlight on a chloroform solution containing iodine. The *trans* ester, which has been described in an earlier paper,¹ must have the open chain structure (III) on steric grounds and the *cis* ester in question (IV) must correspond since, of the two tautomers, the other (VI) is stable and not rearranged into or prepared directly from the *trans* ester under the conditions described. The various reactions concerned are illustrated in the accompanying diagram.

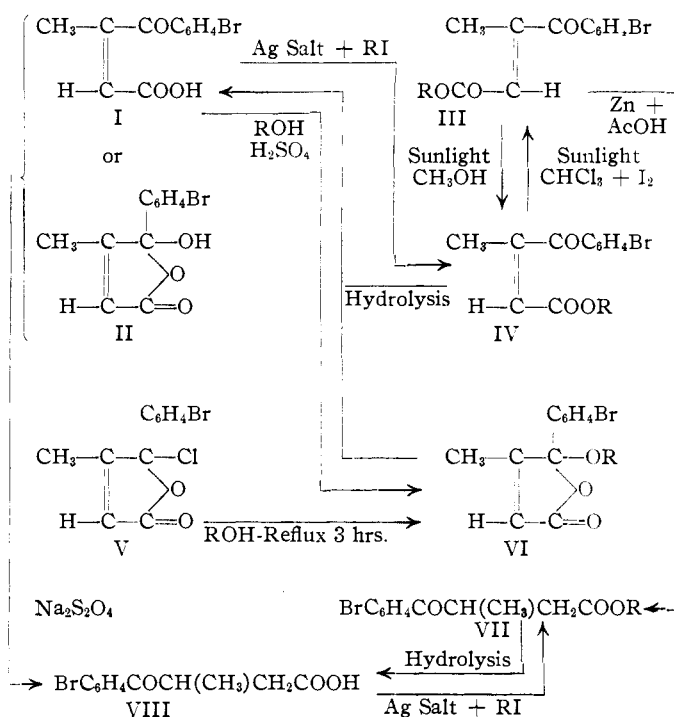
The Cyclic Esters.—The cyclic methyl and ethyl esters (VI) are obtained (a) by direct esterification of the *cis* acid with alcohol and either sulfuric acid or hydrogen chloride,² (b) by the rearrangement of the *cis* ester through the action of alcohol and sulfuric acid, and (c) by alcoholysis of the acid chloride of the *cis* acid (V). Hydrolysis of these esters yields the original *cis* acid.

(1) Lutz and Taylor, THIS JOURNAL, 55, 1168 (1933).
 (2) The oily *cis* methyl ester reported by Lutz and Taylor (Ref. 1) was found to consist largely of the cyclic tautomer.

From the direction of rearrangement, the *cis* ester seems to be the labile tautomer of the two, at least in acid solution, but it is not rearranged noticeably under ordinary conditions, and is not altered in the presence of small amounts of acid under conditions such as exist during the alcoholysis of the acid chloride.

The cyclic structure of these esters seems clearly established from the relation to the open chain tautomers and from the stereochemical considerations discussed above.

It is possible that the *cis* β -bromobenzoylcrotonic acid (one form only is known) in the



solid state has the γ -hydroxylactone structure (II) because it dissolves extremely slowly in sodium bicarbonate solution, in contrast with the *trans* acid and β -bromobenzoylbutyric acid which dissolve immediately under similar conditions. The *cis* acid does not react with acetyl chloride, however.

The cyclic structure for the acid chloride (V) which has been discussed in an earlier paper,¹ would appear to be confirmed by the fact that alcoholysis yields the cyclic ester (VI), rearrange-

ment of the open chain ester during the reaction being excluded since the latter is stable under these conditions.

Reduction of the Cyclic Esters.—Zinc and glacial acetic acid reacted with both the methyl and the ethyl esters in several experiments³ under the conditions described for the reduction of the open chain esters, and gave yields of 30–40% and 40–43% of *p*-bromobenzoic acid and its esters, respectively. Attempts to repeat these experiments several months later gave small amounts of bromobenzoic acid only in the reduction of the cyclic ethyl ester. In searching for the reason for the failure it was found that different samples of zinc dust behaved quite differently. Two new substances were obtained under apparently the same conditions, one (the primary product) an acid, and the other an ester, both isomeric with β -bromobenzoylbutyric ester, and both easily hydrolyzed to β -bromobenzoylbutyric acid. The primary product we believe to be the result of a 1,6 addition of hydrogen (or its equivalent) to the system $O=C-C=C-O$, and the formation of bromobenzoic acid and esters due to hydrolytic fission of this (or of some similar intermediate product) through a variation in the reaction conditions which we have been as yet unable to determine. In any case, the reduction of the cyclic esters takes a course different from that of the *cis* and *trans* open chain esters. These reduction studies, which have not yet been completed, will be described in detail in a later paper.

Experimental Part

Cis β -(*p*-Bromobenzoyl)-crotonic acid (I) is best prepared from citraconic anhydride according to Lutz and Taylor,¹ using three equivalents of good grade anhydrous aluminum chloride, it having been found that with a poor grade, or with a smaller proportion, there is obtained a difficultly separable mixture of the *cis* acid and *trans* β -bromobenzoyl- α -methylacrylic acid.

Cis β -(*p*-Bromobenzoyl)-crotonic Methyl Ester (IV).—Five grams of the acid was dissolved in the calculated amount of aqueous sodium carbonate and treated with one equivalent of silver nitrate, the silver salt precipitating. This, after decantation, was washed with methanol, and shaken for two hours with a methanolic solution of 3 g. of methyl iodide. The silver iodide was filtered off, and the solution poured into ice water containing sodium carbonate. The ester was extracted with ether and recrystallized from methanol; yield 4.95 g. (94%); m. p. 69° (corr.).

Anal. Calcd. for $C_{12}H_{11}O_3Br$: C, 50.88; H, 3.92. Found: C, 50.77; H, 3.95.

(3) One run on the methyl ester and three on the ethyl.

The ester was hydrolyzed completely on standing for ten minutes in a solution of an excess of sodium in 95% ethanol, the sodium salt of the acid crystallizing out.

Reduction of the ester with zinc and glacial acetic acid (stirring for two hours at 30–40°) gave β -bromobenzoylbutyric methyl ester in a yield of 69%; identified by boiling point and by hydrolysis to the corresponding acid which was identified by a mixed melting point.

A sample of the ester (0.5 g.) in 50 cc. of chloroform containing a crystal of iodine was exposed to sunlight for six hours. The product, 0.48 g. (96% yield), was identified by a mixed melting point as *trans* β -bromobenzoyl-crotonic methyl ester.

A sample (0.5 g.) of *trans* β -bromobenzoyl crotonic methyl ester in 50 cc. of absolute ethanol was exposed to sunlight for six hours and gave 0.45 g. (90%) of the *cis* ester which was identified by a mixed melting point.

β -Methyl- γ -(*p*-bromophenyl)- γ -chloro- γ -crotonolactone (*cis* β -bromobenzoylcrotonyl chloride) (V) is best prepared by refluxing the acid with thionyl chloride, evaporating, and crystallizing from ligroin; yields averaged over 80%. Hydrolysis with moist silver oxide gave the acid almost quantitatively.

β -Methyl- γ -(*p*-bromophenyl)- γ -methoxy- γ -crotonolactone (Cyclic β -Bromobenzoylcrotonic Methyl Ester) (VI).—A methanol solution of 5 g. of the above acid chloride was refluxed for three hours. On diluting with ice and sodium carbonate solution and extracting with ether, 2.8 g. of the cyclic ester (60%) was isolated; crystallized from methanol, m. p. 64°.

Anal. Calcd. for $C_{12}H_{11}O_3Br$: C, 50.88; H, 3.92. Found: C, 50.68; H, 3.97.

Esterification of the *cis* acid with methanol saturated with dry hydrogen chloride gave an oil¹ which partly crystallized and gave yields of about 70% of the cyclic ester.

On refluxing a solution of 0.5 g. of the open chain methyl ester in 20 cc. of methanol and 1 cc. of sulfuric acid, 0.4 g. (80%) of the cyclic ester was isolated and identified.

Hydrolysis with alcoholic sodium hydroxide gave a nearly quantitative yield of *cis* acid.

Cis β -(*p*-Bromobenzoyl)-crotonic Ethyl Ester (IV).—Prepared by the silver salt method with ethyl iodide (*cf.* methyl ester); yield from 5 g. of acid was 4.9 g. (92%); colorless crystals from ethanol; m. p. 42°.

Anal. Calcd. for $C_{13}H_{13}O_3Br$: C, 52.52; H, 4.41. Found: C, 52.52; H, 4.52.

Hydrolysis of 0.5 g. with alcoholic sodium hydroxide gave 0.48 g. (94%) of *cis* acid.

Reduction with zinc and glacial acetic acid (stirring for two hours at 30–40°) gave a 70% yield of β -bromobenzoylbutyric ethyl ester, identified by mixed melting point and hydrolysis to the acid.

β -Methyl- γ -(*p*-bromophenyl)- γ -ethoxy- γ -crotonolactone (Cyclic β -Bromobenzoylcrotonic Ethyl Ester) (VI).—Prepared from the *cis* acid chloride with ethanol (see cyclic methyl ester); colorless oil of b. p. 165–168° at 5 mm. (yield 61%).

Anal. Calcd. for $C_{13}H_{13}O_3Br$: C, 52.52; H, 4.41. Found: C, 52.52; H, 4.51.

Hydrolysis of 0.5 g. with alcoholic sodium hydroxide gave 0.42 g. (93%) of the *cis* acid which was identified by a mixed melting point.

β -(*p*-Bromobenzoyl)-butyric Acid (VIII).—*Cis* β -bromobenzoylcrotonic acid was dissolved in a warm solution of sodium carbonate and heated for a short time with a solution of a large excess of sodium hydrosulfite. On acidifying, the reduced acid was precipitated pure in practically quantitative yield.

β -(*p*-Bromobenzoyl)-butyric Methyl Ester (VII).—A solution of 5 g. of the acid in 50 cc. of methanol containing 1 cc. of sulfuric acid was refluxed for two hours. The ester was isolated as a colorless oil of b. p. 193–194° at 20 mm., yield 3.9 g. (74%).

Anal. Calcd. for $C_{12}H_{13}O_2Br$: C, 50.50; H, 4.60. Found: C, 50.40; H, 4.33.

The silver salt preparation gave similar results but was less convenient because of the gelatinous nature of the silver salt.

Hydrolysis of the ester with alcoholic sodium hydroxide gave an almost quantitative yield of the acid.

β -(*p*-Bromobenzoyl)-butyric Ethyl Ester (VII).—Prepared by esterification of the acid with absolute ethanol and sulfuric acid as above; yield 3.6 g. (71%); crystallized from ethanol; m. p. 34.5°.

Anal. Calcd. for $C_{13}H_{15}O_2Br$: C, 52.17; H, 5.06. Found: C, 52.10; H, 5.35.

Hydrolysis of 0.5 g. with alcoholic sodium hydroxide gave 0.41 g. (90%) of the acid which was identified by a mixed melting point.

Summary

A study of the open chain and cyclic esters of *cis* β -bromobenzoylcrotonic acid is described and evidence for the structures is presented.

The reduction of the open chain esters gives β -bromobenzoylbutyric ester.

Cyclic structures for *cis* β -bromobenzoylcrotonic acid and its acid chloride are considered.

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The Allyltoluenes¹

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Recently the pyrolysis of four unsaturated hydrocarbons, $R-\beta-CH_2-\alpha-CH=CH_2$, was reported.⁴ The R was of low electron attraction (R = allyl, isopropyl, cyclohexyl, benzyl). The formation of much more propylene than ethylene indicated that the bond which was alpha to the unsaturation was stronger than the beta. The present paper deals with *o*- and *p*-allyltoluenes, compounds isomeric with the 4-phenyl-1-butene previously studied. The allyltoluenes are new compounds. They differ from 4-phenyl-1-butene in possessing a strongly electronegative R (tolyl).

p-Allyltoluene, $CH_3-\text{C}_6\text{H}_4-\text{CH}_2-\text{CH}=\text{CH}_2$, contains no beta bonds but only alpha bonds. These should be comparatively resistant to heat. The findings are in agreement with this viewpoint. Methane predominated in the gaseous products and more ethylene was formed than propylene. These facts suggest rupture at all three C-C positions in both side chains. Of course, some of the methane and ethylene are secondary products because of the high tempera-

tures involved. As would be expected, the allyltoluenes were somewhat more stable than 4-phenyl-1-butene.

The hydrocarbons were pyrolyzed as previously described.⁴ An empty quartz tube was used, the heated volume of which was 17 cc. Data are summarized in Table I.

Liquid Products.—The liquid products from *o*-allyltoluene gave toluene, *o*-xylene and unchanged *o*-allyltoluene between 110–190°. The fraction boiling above 190°, which made up one-third of the recovered material, yielded a solid which was distilled at reduced pressure. Naphthalene was the major product in this solid. Bromination of the 110–190° fraction in carbon tetrachloride removed the allyltoluene, allylbenzene and other unsaturates from the toluene and xylene. The last two, separated by fractional distillation, were confirmed by formation of dinitrotoluene (m. p. 68°) and the sulfonamide derivative of *o*-xylene (m. p. 141°).

Similarly, *p*-allyltoluene yielded toluene and *p*-xylene in the condensed liquids; derivative, trinitro-*p*-xylene, m. p. 135°. The liquid products from the 575° experiment gave these fractions: (°C., g., n_D^{20}) 110–140, 2.8, 1.501; 140–176, 2.3, 1.517; 176–181, 8.0, 1.521; 181–189, 11.7, 1.527; 116–120 at 70 mm., 1.9, 1.538; and 10.0 g. of residue. The quantity of benzene from *o*- or *p*-allyltoluene was always negligible.

Non-Rearrangement of 4-Phenyl-1-butene into *o*-Allyltoluene.—To ascertain whether or not 4-phenyl-1-butene (allylphenylmethane) would rearrange into *o*-allyltoluene,

(1) A part of this investigation was financed from funds donated to the American Petroleum Institute by the Universal Oil Products Company. The investigation was listed as Project No. 18.

(2) Director, Project No. 18.

(3) American Petroleum Institute Research Fellow.

(4) Hurd and Bollman, THIS JOURNAL, **55**, 699 (1933).