The original product was thus evidently the mercapto acid.

A number of the simpler pseudo-thiohydantoins have been oxidized to the corresponding sulfonic acids, usually with potassium chlorate and hydrochloric acid in water solution. This method seemed of doubtful applicability to such insoluble substances as those described in this paper. A number of attempts under rather varied conditions were made to obtain the sulfonic acids in question by oxidation of the mercapto acids, but no products of even approximate purity were isolated except in the case of mercaptocaproic acid.

α-Carboxy-*n*-amylsulfonic Acid.—Barium mercaptocaproate was oxidized in water solution with the calculated amount of barium permanganate. The barium salt of the sulfonic acid was readily soluble in hot water, and melted at 196°.

Anal. Calcd. for $C_6H_{10}O_5SBa$: Ba, 41.43. Found: 41.31.

The free sulfonic acid could not be obtained crystalline.

Summary

1. The pseudo-thiohydantoins corresponding to caproic, lauric, myristic, palmitic and stearic acids have been described, together with the α-mercapto acids obtained from them by hydrolysis.

2. The pseudo-thiohydantoins, while easily obtainable, offer no promise as derivatives for the separation or identification of the higher fatty acids.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

A SUGGESTED MECHANISM OF THE SPLITTING OF THE CYCLOPROPANE RING BY BROMINE

BY BEN H. NICOLET AND LOUIS SATTLER[1]

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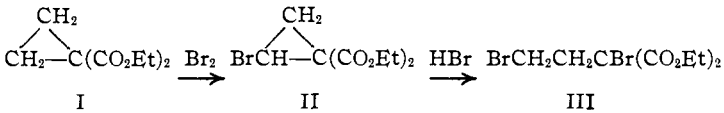
The splitting that occurs when bromine acts on cyclopropane derivatives has usually been considered to take place by the addition of bromine at the bond broken. Cyclopropane carboxylic acid, for example, gives with bromine both the 1-bromo-substitution product and α,γ-dibromobutyric acid. It seems customary to regard these two substances as products of simultaneous and independent reactions.[2] Bruylants[3] remarks that in

[1] The material here presented was used by Louis Sattler in partial satisfaction of the requirements for the degree of Doctor of Philosophy, University of Chicago, 1925.

[2] After this paper had been prepared for publication, a translation of a rather inaccessible article by Kischner [*J. Russ. Phys.-Chem. Soc.*, **41**, 659 (1909)] was obtained. Kischner remarks: "The described results of the bromination of the chloride of trimethylene carboxylic acid, as well as of the acid itself, may be formulated as the addition of one molecule of bromine. It might be more accurate, however, to describe the production of the end product as the result of two successive stages: (a) the formation of the normal substitution product; (b) the addition of hydrogen bromide, which is accompanied by the rupture of the trimethylene ring." He did not test the action of

this case substitution seems to be "an altogether subordinate reaction."

We have studied the action of bromine on diethyl cyclopropane-1,1-dicarboxylate (I) and found that two products can be isolated, the 2-bromo derivative (II) and β-bromoethyl-bromomalonic ester (III).



I II III

When the bromination was carried out at 40–50°, using a powerful quartz-mercury vapor lamp as light source, more II was isolated than when the reaction took place at a higher temperature, with or without illumination. The separation of II and III by fractionation under reduced pressure is tedious, but after four or five distillations moderately pure products were obtained.

The structure of III follows from its reaction with zinc in dil. alcohol; cyclopropane-1,1-dicarboxylic acid was identified. After hydrolysis, III was converted into the phenylhydrazide of α,γ-dihydroxybutyric acid (IV), which was identical with a sample previously obtained in another way.[4]

When II was warmed for nine hours with 80% hydrobromic acid, and the resulting product (presumably α,γ-dibromobutyric acid) hydrolyzed by shaking with silver oxide, the same phenylhydrazide (IV) could be isolated. It was shown to be identical with the other preparations mentioned. It is therefore assumed that hydrogen bromide splits II in such a way as to give III. The formation of IV in this way is evidence for the structure assigned to II, and rules out the alternative possibility that II might be $BrCH_2CH_2CH(CO_2Et)_2$. This conclusion is confirmed by the fact that the bromine of II is very difficult to remove by hydrolysis.

It is believed that the formation of the dibromide III from the bromo-derivative II has been definitely demonstrated. This result is somewhat surprising, as there was perhaps more reason for expecting the formation of $Br_2CHCH_2CH(CO_2Et)_2$ in such a reaction. This is, so far as we know, the first case in which the product obtained by the splitting of a bromocyclopropane derivative with hydrogen bromide has been determined. The chief interest in the result, however, lies in the identity of the product formed from II and hydrogen bromide with the one to be expected if bromine had added directly to I. The suggestion is obvious that much or all of the III obtained by the action of bromine on I, was formed through II

hydrogen bromide on 1-bromocyclopropane-1-carboxylic acid, and assumed such an action as possible only because it involved addition of the bromine (of hydrogen bromide) to the carbon *not* attached to carboxyl.

[3] Bruylants, *Bull. soc. chim. Belg.*, **32**, 358 (1923).

[4] Glattfeld and Sander, THIS JOURNAL, **43**, 2675 (1921). A sample for comparison was kindly supplied by Dr. Glattfeld.

as an intermediate. While it remains possible that III may also be formed directly from I by bromine addition, the evidence for this latter reaction is distinctly less definite. The suggestion is made that the normal action of bromine on the cyclopropane ring may well be not the addition of bromine, but substitution, followed by addition of hydrogen bromide.

There is, of course, no compelling reason why the subsequent addition of hydrogen bromide should always result in the breaking of one of the two bonds adjacent to the carbon carrying the bromine. In fact, Gustavson[5] found that bromine gave with 1,1-dimethyl cyclopropane, $Me_2CBrCHBrCH_0$, a product not derivable by direct bromine addition. He assumed that traces of hydrogen bromide first caused ring splitting to yield Me_2CBrEt, which then underwent bromination to give the observed product, at the same time supplying the hydrogen bromide necessary for the first stage of the reaction. The mechanism he has suggested could not apply to the case discussed in this paper. To settle the question, other monobromo-derivatives of cyclopropane isolated in brominations will have to be heated with hydrogen bromide to see whether the dibromo-compounds obtained are the same as those resulting from "direct" bromination.

The action of bromine on cyclopropylcyanide, 1-cyanocyclopropane-1-carboxylic acid, cyclopropane-1,1-dicarboxylic acid, and ethyl 1-cyanocyclopropane-1-carboxylate is described in the experimental part.

In a further attempt to find reactions in which addition might take place with splitting of the cyclopropane ring, the action of HOCl and HOBr in water solution and that of ICl in glacial acetic acid, were tried on 1-cyanocyclopropane-1-carboxylic acid and on cyclopropane-1,1-dicarboxylic acid. There was no evidence of reaction in any case.

Experimental Part

Preparation of Required Cyclopropane Derivatives.—Ethyl cyclopropane-1,1-dicarboxylate was prepared by the method of Dox and Yoder[6] with slight modifications. The yield obtained was consistently about 75% of that given by the authors mentioned. The corresponding acid was isolated as described by Stohmann and Kleber.[7] The yields were decidedly poor. For ethyl 1-cyanocyclopropane-1-carboxylate, the method of Jones and Scott[8] was used. For 1-cyanocyclopropane, the method of Haller and Benoist[9] was modified. A 15% excess of potassium hydroxide[10] was pulverized and

[5] Gustavson, *J. prakt. Chem.*, [2] **62**, 270 (1900).

[6] Dox and Yoder, THIS JOURNAL, **43**, 2097 (1921).

[7] Stohmann and Kleber, *J. prakt. Chem.*, [2] **45**, 477 (1892).

[8] Jones and Scott, THIS JOURNAL, **44**, 413 (1922).

[9] Haller and Benoist, *Ann. chim.*, [9] **17**, 28 (1922); little detail is given, but results are surely much less good than the text implies.

[10] Potassium hydroxide was fused for 10 minutes in a silver crucible at about 300°, and poured into warmed test-tubes which were promptly stoppered and placed in a desiccator. This product could be ground effectively as required.

placed in a 100cc. distilling flask fitted with a rather fine capillary and a dropping funnel. The flask was attached to a pump and heated (without fusing the potassium hydroxide) to remove some of the water which had been absorbed during grinding. When the flask had cooled, it was attached, through a condenser and receiver, to the pump, placed in a water-bath at 85°, and γ-chlorobutyronitrile (32 g.) allowed to run in slowly. The reaction should take place rapidly, and the product be removed by distillation as promptly as possible. To obtain a halogen-free product, the distillate was again treated similarly with potassium hydroxide. The yield was 8–11 g. (40–55%) of cyanocyclopropane, boiling at 134°.

Action of Bromine on Ethyl Cyclopropane-1,1-dicarboxylate (I).—Bromine reacts easily with I, even in diffused light. The nature of the product depends on the conditions of bromination. Apparently, both ethyl 2-bromocyclopropane-1,1-dicarboxylate (II) and ethyl β-bromo-ethyl-bromomalonate (III) are formed in each case, but the proportion of the latter was much larger when bromination was carried out at higher temperatures, and with illumination by a mercury arc.

I, preheated to 50°, was treated slowly with 1 mole of bromine in the presence of the arc. The reaction rate increased as hydrobromic acid accumulated and as the solution became warmer. Unless considerable care was taken, the reaction finally became quite violent. On distillation, a typical product (23 g.) gave, in addition to lower-boiling material, (a) 9 g. b_{13} 150–160° and (b) 6 g. b_{13} 160–165°; both fractions consisted chiefly of III.

Anal. Calcd. for $C_9H_{14}O_4Br_2$: C, 31.22; H, 4.07. Found: (a) C, 31.70; H, 4.35. (b) C, 30.91; H, 4.27.

The best sample of III prepared boiled under 10 mm. pressure at 146–151°.

A larger portion of the monobromo derivative (II) was formed when 155 g. of I was placed in a flask attached to a reflux condenser and cooled in an ice-bath while 1 mole of bromine was added during two hours. No special illumination was used. The reaction appeared to be decidedly autocatalytic. After five careful fractionations at pressures of 10–17 mm., II and III were not completely separated.

Anal. Calcd. for $C_9H_{13}O_4Br$: Br, 30.17. Calcd. for $C_9H_{14}O_4Br_2$: Br, 46.20. Found: (a) b_{15} 135–140°; Br, 31.8. (b) b_{15} 140–145°; Br, 32.6, 32.3. (c) b_{10} 146–151°; Br, 45.0.

Formation of Cyclopropane-1,1-dicarboxylic Acid from III. Four g. of an analyzed sample of III was boiled under reflux for five hours with an excess of zinc dust. The solution was then diluted with water, filtered from undissolved zinc, and boiled for some time with excess potassium hydroxide to saponify the ester. From the acidified solution, cyclopropane-1,1-dicarboxylic acid was extracted with ether and recrystallized from chloroform. Three-tenths g. (20%) of the pure acid was obtained. It had the correct melting point, which was not lowered by mixture with a known sample.

Preparation of the Phenylhydrazide of α,γ-Dihydroxybutyric Acid from β-Bromo-ethyl-bromomalonic Ester.—Ten g. of a fraction of the ester III b_{15} 150–155° was refluxed with constant-boiling hydrobromic acid until solution was complete, and the ester presumably converted to α,γ-dibromobutyric acid. Excess hydrobromic acid was removed by distillation at 14 mm. The residue was dissolved in 200 cc. of water, an excess of freshly precipitated silver oxide added, and the mixture shaken for 18 hours in a machine. After filtration, the residue was again shaken with water for some time, and the extract added to the filtrate mentioned. The resulting solutions were concentrated under reduced pressure, the organic material taken up in alcohol, and an excess of phenylhydrazine added. The crystals obtained were purified from ethyl acetate. The yield of pure hydrazide was 1.9 g. (31%); m. p., 129.5°. Mixture with a known sample of the product[4] did not change the melting point.

Preparation of the Phenylhydrazide of α,γ-Dihydroxybutyric Acid from Diethyl 2-Bromocyclopropane-1,1-dicarboxylate.—Five g. of a fraction b_{15} 135–140° of the ester II, estimated by analysis as 97% pure, was warmed (without boiling) for four hours with 20 g. of 80% hydrobromic acid, and then refluxed for five hours more. After the removal of water and hydrobromic acid by distillation under reduced pressure, the residue, assumed to be α,γ-dibromobutyric acid, boiled at 130–131° under 15 mm. By a procedure similar to that described in the preceding paragraph, this was hydrolyzed with silver oxide, treated with phenylhydrazine, and a phenylhydrazide of α,γ-dihydroxybutyric acid obtained, identical by all tests with that described above.

Action of Bromine on Cyanocyclopropane and on 1-Cyanocyclopropane-1-carboxylic Acid.—After several hours' exposure to the light of a quartz-mercury vapor lamp, almost no bromine had reacted and the products were recovered practically unaltered.

Action of Bromine on Cyclopropane-1,1-dicarboxylic Acid.—Under the influence of ultraviolet light, the action of bromine on this acid is slow, but is completed in three to four hours. In CCl_4, the product was β-bromo-ethyl-bromomalonic acid,[11] of which 2.7 g. (76%) was isolated, melting at 111° and evolving carbon dioxide at 113°. The ammonium salt was precipitated from dry ether.

Anal. (Kjeldahl). Calcd. for $C_6H_{12}O_4N_2Br_2$: N, 8.66. Found: 8.68.

A similar bromination, with chloroform as solvent, took a different course. The product was a very viscous oil. On distillation at 20 mm. it lost carbon dioxide and gave a thick oil, boiling at 140° under 20 mm., which did not solidify at —14°. This was apparently 2-bromocyclopropane-1-carboxylic acid.

Anal. Calcd. for $C_4H_5O_2Br$: C, 29.09; H, 3.64. Found: C, 29.37; H, 3.57.

Action of Bromine on Ethyl 1-Cyanocyclopropane-1-carboxylate.—This ester behaves with bromine much as does I. Near its boiling point, it reacted vigorously with slowly added bromine and much hydrobromic acid was evolved. Two products, ethyl 2-bromo-1-cyanocyclopropane-1-carboxylate and ethyl α,γ-dibromo-α-cyano-acetate (V), were apparently formed, but a complete separation proved too tedious. After two careful fractionations at 11 mm. pressure, the following analyses were obtained.

Anal. (Carius). Calcd. for $C_7H_8O_2NBr$: Br, 36.7. Calcd. for $C_7H_9O_2NBr_2$: Br, 53.7. Found: (a) b_{11} 100–105°, Br, 45.8. (b) b_{11} 136–140°, Br, 52.6.

The latter fraction was apparently moderately pure V.

Action of HOCl and HOBr on Cyclopropane-1,1-dicarboxylic Acid and on 1-Cyanocyclopropane-1-carboxylic Acid.—The acid to be tested was dissolved in alkali and treated with a solution containing 1 mole of NaOCl or NaOBr. The solution was then cooled below 0°, carbon dioxide passed in to liberate the hypohalous acid, and the solution allowed to stand for some time (occasionally up to two days in the ice box). There was no evidence of reaction, and the unaltered acid was recovered in each case.

Action of ICl on Cyclopropane-1,1-dicarboxylic Acid and on 1-Cyanocyclopropane-1,1-carboxylic Acid.—Each acid was treated with 1 mole of ICl in glacial acetic acid solution, and the mixture allowed to stand for periods up to three weeks. There was no evidence of reaction, and titration showed a negligible decrease in the amount of ICl present. Even in ultraviolet light, no reaction could be detected.

Summary

1. Some new derivatives of cyclopropane have been described.

2. In the bromination of diethyl cyclopropane-1,1-dicarboxylate, the 2-bromo-derivative was isolated and shown to react with hydrobromic acid

[11] Marburg, *Ann.*, **294**, 125 (1897).

to give β-bromo-ethyl-bromomalonic ester. It is suggested that substitution, followed by splitting of the ring with addition of hydrobromic acid, may be the normal mechanism of the breaking of the cyclopropane ring by bromine.

3. A number of cyclopropane derivatives showed no reaction with HOCl, HOBr or ICl.

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

THE ADDITION OF ETHYL AND TERTIARY BUTYL HYPOCHLORITES TO CINNAMIC ACID

BY ERNEST L. JACKSON AND L. PASIUT

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The addition of methyl hypochlorite to cinnamic acid and other ethylene derivatives, by the reaction of chlorine with the unsaturated compounds in methyl alcohol solution, was reported in a previous paper.[1] The question of the applicability of this reaction to other alcohols led to the investigation of ethyl and *tert.*-butyl alcohols, the results of which are given in this paper.

Chattaway and Backeberg[2] have recently shown that in the chlorination of ethyl alcohol, ethyl hypochlorite and hydrogen chloride are the primary products and that in the presence of unchanged alcohol the ethyl hypochlorite quickly eliminates hydrogen chloride from its molecule with the formation of acetaldehyde, the chlorination of which follows. One would expect, therefore, the addition of ethyl hypochlorite to cinnamic acid, by the reaction of chlorine with the unsaturated compound in ethyl alcohol solution, to be complicated by a number of side reactions. The principal reactions follow.

$$CH_3CH_2OH + Cl_2 \longrightarrow CH_3CH_2OCl + HCl \quad (1)$$

$$C_6H_5CH{=}CHCOOH + CH_3CH_2OCl \longrightarrow C_6H_5CH(OC_2H_5)CHClCOOH \quad (2)$$

$$CH_3CH_2OCl \longrightarrow CH_3CHO + HCl \quad (3)$$

$$3CH_3CHO \xrightarrow{HCl} (CH_3CHO)_3 \xrightarrow{Cl_2} (CH_2ClCHO)_3 \longrightarrow, \text{ etc.} \quad (4)$$

$$C_6H_5CH{=}CHCOOH + Cl_2 \longrightarrow C_6H_5CHClCHClCOOH \quad (5)$$

By introducing a slow stream of dry chlorine into an efficiently stirred solution of cinnamic acid in absolute ethyl alcohol, we were able to add ethyl hypochlorite to the double linkage of the unsaturated compound. The chlorine concentration was kept as low as practicable and the temperature was either that of the Laboratory, or 0–10°, the results being about the same in both cases. Most of the chlorine went into the side

[1] Jackson, THIS JOURNAL, **48**, 2166 (1926).

[2] Chattaway and Backeberg, *J. Chem. Soc.*, **125**, 1097 (1924).