methylene carbonate has been prepared by thermal decomposition of its usual polymeric form. Hexamethylene carbonate is tough and elastic.

WILMINGTON, DELAWARE

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

STUDIES OF CONJUGATED SYSTEMS
II. THE BROMINATION OF VINYLACRYLIC ACID

BY IRVING E. MUSKAT, BRUNNER C. BECKER AND JOEL S. LOWENSTEIN

RECEIVED JULY 25, 1929 PUBLISHED JANUARY 8, 1930

The abnormal addition reactions of conjugated systems have been the subject of a great deal of experimental work ever since Fittig[1] and Baeyer[2] found that compounds containing two double bonds in conjugation were reduced in the 1,4- rather than in the 1,2- or 3,4-positions, and did not exhibit the properties common to ordinary ethylenic double bonds. In 1899 Thiele[3] proposed his "partial valence" theory to interpret these 1,4-addition reactions to conjugated systems and brought a great deal of experimental evidence in its favor. According to this theory the type of addition taking place in a conjugated system depends solely on the valence relations of that system. Later work[4] proved this general theory to be incorrect, and it was modified by Hinrichsen[4] to take into consideration the electrochemical nature of the entering atoms or groups, as well as the nature of the original unsaturated compound in which the addition is taking place. More recent work,[5] carried out with greater precision and more refined technique, has shown that in many addition reactions where 1,4-addition is found, it is not due primarily to 1,4-addition but rather to an isomerization of the 1,2- or 3,4-addition compounds. Such isomerizations are common in three-carbon systems containing a double bond

Because of the theoretical importance of the addition reactions of conjugated systems, it was considered desirable to make a thorough investigation of such addition processes, particularly in simple conjugated systems. It was hoped that such studies would also throw some light on the mecha-

[1] Fittig, *Ann.*, **227**, 46 (1888).

[2] Baeyer, *ibid.*, **251**, 271 (1889); **256**, 1 (1890).

[3] Thiele, *ibid.*, **306**, 87 (1899).

[4] Michael, *J. prakt. Chem.*, **60**, 467 (1899); Erlenmeyer, Jr., *Ann.*, **316**, 43 (1901); Vorländer, *Ber.*, **36**, 2339 (1903); Kohler, *Am. Chem. J.*, **31**, 642 (1904); **33**, 153, 333 (1905); Hinrichsen, *Ann.*, **336**, 174 (1904); Strauss, *Ber.*, **42**, 2866 (1909); Ingold, *J. Chem. Soc.*, **121**, 329, 1306 (1921); and many others.

[5] Ingold and Shoppee, *J. Chem. Soc.*, **129**, 1477 (1926); Farmer, *ibid.*, 172 (1929); Prevost, *Ann. chim.*, [10] **10**, 113 (1928); Claisen, *J. prakt. Chem.*, **105**, 65 (1922).

nism of addition reactions and directive influence in the aromatic series. The present paper, the second of the series, contains the results of an investigation on the bromination of vinylacrylic acid.

Thiele[6] proved that vinylacrylic acid adds hydrogen in the 1,4 (or 1,6)-position. Kohler and Butler,[7] while studying the relative ease of 1,4- and 1,6-addition, showed that sodium malonic ester combines with the esters of vinylacrylic and sorbic acids to give 1,6-addition products, while phenylmagnesium bromide reacts with the same esters to give first the corresponding ketones, which react further to give 1,4-addition products.

In a recent publication by Farmer and Healy[8] on "Addition to Butadiene Esters," the authors also report the bromination of vinylacrylic acid. They found that bromine adds to vinylacrylic acid in the 3,4-position to give a liquid dibromide from which they were able to separate a solid dibromide melting at 47°. They treated the dibromide with diethylamine and obtained a monobromide which polymerized so rapidly that they were unable to determine its structure or even its melting point. Quite independent of this work we have studied the bromination of vinylacrylic acid but have carried the work much further and proved the structures of our products.

Vinylacrylic acid was prepared according to a modification of Nottbohm's[9] method. The pure acid melted at 72°, the same melting point reported by Nottbohm. Doebner,[10] using a somewhat different method, had previously prepared vinylacrylic acid, reporting its melting point as 80°. Auwers[11] and Kohler[7] repeated the preparation of vinylacrylic acid: the former used Nottbohm's method while the latter used Doebner's method; both reported its melting point as 72°. Recently Farmer[8] reported the preparation of vinylacrylic acid according to Doebner's method, confirming his melting point as 80°. We prepared vinylacrylic acid according to both methods. Both preparations melted at 72° as did a mixture of the two. It is possible that there are two vinylacrylic acids which are either physical or geometric isomers of each other.

The bromination of vinylacrylic acid was then studied. It was found that vinylacrylic acid absorbed two atoms of bromine to give a dibromide which distilled at 156° under 3-mm. pressure. On standing it partially solidified to a solid melting at 47°. Farmer[8] apparently obtained the same dibromide (but does not give its boiling point) starting with the vinylacrylic acid melting at 80°. He proved its structure, 3,4-dibromo-Δ^1-pentenic

[6] Thiele, *Ber.*, **35**, 2320 (1902); see also Doebner, *ibid.*, **35**, 1136 (1902).

[7] Kohler and Butler, THIS JOURNAL, **48**, 1036 (1926).

[8] Farmer and Healy, *J. Chem. Soc.*, **130**, 1060 (1927).

[9] Nottbohm, *Ann.*, **412**, 49 (1916).

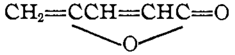
[10] Doebner, *Ber.*, **35**, 1136 (1902).

[11] Auwers, *Ann.*, **432**, 46 (1923).

acid, by ozonization. We confirmed his structure in every particular. Thus we see that vinylacrylic acid adds bromine in the 3,4-position and not in the 1,4-position as postulated by Thiele. This stands in variance with the hydrogenation of vinylacrylic acid, which takes place in the 1,4-position.[6]

Vinylacrylic acid dibromide readily absorbed two atoms of bromine to give the tetrabromide. It melted at 156° and was identical with the tetrabromide described by Nottbohm.[9] The vinylacrylic acid dibromide was reduced with zinc dust to give the original vinylacrylic acid melting at 72°.

On distilling the dibromide under reduced pressure, decomposition occurred with the liberation of hydrogen bromide. A lower-boiling fraction distilled over and solidified partially on standing. The solid was removed; it melted at 143° and solidified again at 162°. Its structure was finally proved by converting it into aceto-acrylic acid. This, with its analysis ($C_5H_4O_2$), showed that it was a γ-lactone having the structure

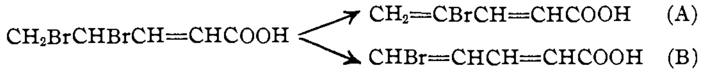


$$CH_2{=}\underbrace{CCH{=}CHC}_{O}{=}O$$

When vinylacrylic acid dibromide was treated with two molar equivalents of sodium hydroxide, the temperature being kept at about zero degrees, the soluble sodium salt of monobromo-vinylacrylic acid was formed in almost theoretical yield. The free acid was obtained by acidifying the alkaline solution with cold dilute acids.

Bromovinylacrylic acid is a white crystalline compound, very soluble in all ordinary organic solvents and very unstable. It readily polymerizes to a white solid which is insoluble in all ordinary organic solvents with the exception of acetone. Due to its ease of polymerization it was not possible to obtain a sharp melting point. It melted at about 106°.

It may be seen readily from the structure of the vinylacrylic acid dibromide that hydrogen bromide may be eliminated in either of two ways



$$CH_2BrCHBrCH{=}CHCOOH \to CH_2{=}CBrCH{=}CHCOOH \quad (A)$$

$$CH_2BrCHBrCH{=}CHCOOH \to CHBr{=}CHCH{=}CHCOOH \quad (B)$$

The structure of the monobromide was proved by further brominating it to the bromovinylacrylic acid dibromide and studying the oxidation products of the tribromide formed.

Bromovinylacrylic acid readily absorbed a molecule of bromine to give a tribromo derivative boiling at about 172° under 10-mm. pressure. There are six tribromides theoretically possible depending on the A or B structure of the monobromide and the 1,2-, 1,4- or 3,4-type of addition taking place

(A)	$CH_2{=}CBrCH{=}CHCOOH$	(B)	$CHBr{=}CHCH{=}CHCOOH$
(1–2)	$CH_2{=}CBrCHBrCHBrCOOH$	(1–2)	$CHBr{=}CHCHBrCHBrCOOH$
(1–4)	$CH_2BrCBr{=}CHCHBrCOOH$	(1–4)	$CHBr_2CH{=}CHCHBrCOOH$
(3–4)	$CH_2BrCBr_2CH{=}CHCOOH$	(3–4)	$CHBr_2CHBrCH{=}CHCOOH$

The bromovinylacrylic acid dibromide was ozonized in the usual manner. It was possible to recover oxalic acid (40% yield), which was identified by its melting point and a melting point of a mixture with a sample of known origin; and also α,α,β-tribromopropionic aldehyde, which was identified by the melting point of the α,α,β-tribromopropionic aldehyde hydrate and a melting point of a mixture with the synthesized product. This proves that 3,4-addition of bromine had again taken place, giving rise to a tribromide of structure $CH_2BrCBr_2CH{=}CHCOOH$, and therefore the structure of the monobromide must be as represented by (A).

The experimental results recorded here lend support to the Hinrichsen view of addition to conjugated systems as contrasted to the Thiele view; that is, the mode of addition to conjugated systems is a function not only of the conjugated system itself, but also of the nature of the addendum.

Experimental Part

The Preparation of Vinylacrylic Acid.—The method of preparation described here is a modification of Nottbohm's[9] method. Nottbohm's method gives 15–20% of pure acid, while the Kohler[7] modification of Doebner's method gives 30% of pure acid. The following method gave about 55–65% of pure acid.

To a solution of 118 g. of potassium metabisulfite in about 200 cc. of water, cooled in a freezing mixture, 29 g. of acrolein was added, drop by drop, under continuous stirring. After all of the acrolein had been added, the stirring was continued for two hours at room temperature. Malonic acid (52 g.) was then added and the solution was refluxed for two hours. The solution was then concentrated to a thick, sirupy mass on the water-bath until the evolution of carbon dioxide gas had ceased. During this time the viscous mass was stirred in order to avoid excessive frothing. The residue was then dissolved in about 100 cc. of water, which is contained in an iron dish, and 300 g. of coarsely ground sodium hydroxide was gradually added with continuous stirring. It was then heated on the water-bath for four hours, after which it was allowed to cool. The semi-crystallized mass was placed in a large enamel dish to which was added about 500 g. of ice and 500 g. of chloroform. The mixture was then slowly neutralized with 25% hydrochloric acid under continuous stirring. During the neutralization ice was added to keep the temperature at about zero degrees. The chloroform layer was separated and the acidic layer was twice extracted with chloroform. The chloroform extract was dried and the chloroform removed under reduced pressure. The yellow residue (about 40 g.) was recrystallized from ligroin. The pure acid (about 30 g.) melted sharply at 72°.

Vinylacrylic acid was also prepared according to Doebner's method[10] by the direct condensation of acrolein and malonic acid in the presence of pyridine. The purified acid thus prepared also melted at 72°, as did a mixture of the acids prepared by each method.

Vinylacrylic Acid Dibromide.—Vinylacrylic acid dibromide was prepared by the addition of the theoretical amount of bromine dissolved in chloroform to a solution of vinylacrylic acid in chloroform. Absorption took place fairly readily and the reaction mixture became warm. The reaction mixture was distilled under reduced pressure; a light yellow oil distilled over at 156° under 3 mm. pressure. On standing it partially crystallized to a solid melting at 47°, which is the same melting point recorded by Farmer for his dibromide, which he obtained from vinylacrylic acid melting at 80°.

Anal. Calcd. for $C_5H_6O_2Br_2$: Br, 61.98. Found: Br, 61.91, 62.01.

The conditions under which the vinylacrylic acid was brominated were varied considerably. Various solvents such as ligroin, carbon tetrachloride, carbon bisulfide and glacial acetic acid were used besides chloroform, and the temperature was varied from about −20° to about 50°. However, in all cases only one dibromide was obtained, regardless of the experimental conditions employed. The dibromide is unstable, particularly toward heat and alkali, and loses hydrogen bromide easily.

The pure vinylacrylic acid dibromide (4.2 g.), dissolved in chloroform, was subjected to ozonization and the ozonide thus formed was decomposed with water. To assure the complete decomposition of the ozonide it was warmed on the water-bath for a short time. The mixture consisted of aldehydes and acids and was separated by extracting the aqueous solution several times with ether. The aqueous solution was carefully evaporated to dryness and further heated in the oven to 110° for several hours. The residue (1.10 g.) melted at 187°, the melting point of anhydrous oxalic acid. A mixture with pure oxalic acid also melted at 187°. This corresponds to a 75% yield of oxalic acid. The aldehyde portion was distilled under reduced pressure. An oil distilled over at 80° under 5–6 mm. pressure, the boiling point of α,β-dibromopropionic aldehyde. This was further identified by treating with sodium acetate according to the method of Piloty and Stock,[12] which converted the dibromide into α-bromo-acrolein. This distilled over at 49–50° under 30 mm. pressure, the recorded boiling point of α-bromoacrolein. The α-bromo-acrolein gave a semicarbazone melting at 160° with decomposition. This proves beyond any doubt that bromine had added to vinylacrylic acid in the 3,4-position.

Vinylacrylic acid dibromide readily absorbed two atoms of bromine to give the tetrabromide. It melted at 156° and was identical with the tetrabromide described by Nottbohm. The dibromide was reduced with zinc dust to the original vinylacrylic acid, which was identified by its melting point, 72°. The yield was low, due to the polymerization of the vinylacrylic acid.

If vinylacrylic acid dibromide was distilled under reduced pressure, a great deal of decomposition occurred at about 140° with the liberation of hydrogen bromide. A lower-boiling fraction distilled over which solidified on standing. The solid is characterized by a marked insolubility in ether and could thus be freed easily from impurities by washing with ether. It is insoluble in all ordinary organic solvents with the exception of acetone, from which it can be recrystallized in pure white crystals. It melts at 143° and solidifies again at 162°, which may indicate that polymerization has occurred. It contained no halogen and dissolved slowly in alkali to give a reddish colored solution.

Anal. Calcd. for $C_5H_4O_2$: C, 62.5; H, 4.2. Found: C, 62.6, 62.6; H, 4.4, 4.4.

The molecular weight was determined by the boiling point method in acetone, which was erratic under the conditions of the experiment. Subs., 0.3134 g.; acetone, 100 g.; ΔT, 0.063°. Calcd. for $C_5H_4O_2$: mol. wt., 96. Found: mol. wt., 86.

The titer value of the substance was then determined by dissolving it in pure acetone, diluting with water, and titrating in the usual manner with standard alkali. Subs., 0.1003: 9.8 cc. of 0.1063 N sodium hydroxide. Calcd. for $C_5H_4O_2$: mol. wt., 96. Found: mol. wt., 96.3.

This proved that the substance contained one carboxyl group, but its slow solubility in alkali indicated that it was a lactone. From the fact that it was formed as a result of the elimination of two molecules of hydrogen bromide from vinylacrylic acid dibromide, it is at once clear that it could be either a δ- or a γ-lactone. The δ-lactone is known. It melts at 5° and has entirely different properties from those shown by our

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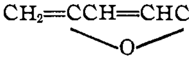
[12] Piloty and Stock, *Ber.*, **31**, 1385 (1898).

compound. It was proved to be the γ-lactone,  $\mathrm{CH_2{=}\underbrace{CCH{=}CHC}_{O}{=}O}$, by hydrolyzing it with alkali to the corresponding aceto-acrylic acid. The hydrazone of aceto-acrylic acid melts at 160° with decomposition; the hydrolysis product of our lactone also formed a hydrazone melting at 160° with decomposition. The isolation and proof of the structure of this lactone stand in good agreement with the proof of the structure of the monobromide that follows.

Bromovinylacrylic Acid.—When vinylacrylic acid dibromide was treated with one molar equivalent of aqueous sodium hydroxide, the soluble sodium salt of the dibromide was formed. If another molar equivalent of sodium hydroxide was added, the temperature being kept at about 0° during this operation, the dibromide easily lost a molecule of hydrogen bromide and was thus converted into the soluble sodium salt of the monobromovinylacrylic acid, with an almost theoretical yield. It is of the utmost importance to keep the temperature very low, otherwise the monobromide polymerizes. The free acid was precipitated as a voluminous crystalline mass by acidifying the alkaline solution with cold dilute acids.

Anal. Calcd. for $C_5H_5O_2Br$: Br, 45.16. Found: Br, 45.07, 45.15.

The bromovinylacrylic acid is a white, crystalline compound, very soluble in the ordinary organic solvents and very unstable. It readily polymerizes to a white solid which is insoluble in all ordinary organic solvents with the exception of acetone. Due to its ease of polymerization it was not possible to obtain a sharp melting point. It melted at about 106°. The structure of the monobromide was established by further brominating it to the bromovinylacrylic acid dibromide and determining the oxidation products of the tribromide formed.

Bromovinylacrylic Acid Dibromide.—Bromovinylacrylic acid dibromide was prepared by the addition of the theoretical amount of bromine dissolved in chloroform to a solution of bromovinylacrylic acid dissolved in chloroform. Absorption took place fairly readily and the mixture became warm. The reaction mixture was distilled under reduced pressure. A light yellow oil distilled over at about 172° under 10 mm. pressure.

Anal. Calcd. for $C_5H_5O_2Br_3$: Br, 71.19. Found: Br, 71.23, 70.58.

The pure bromovinylacrylic acid dibromide (1.1 g.) was subjected to ozonization and the ozonide thus formed was worked up in the manner previously described for the vinylacrylic acid dibromide. The acid and aldehyde portions were separated; the acid portion yielded 0.17 g. of calcium oxalate, which corresponds to a 40% yield, while the aldehyde was removed as such and distilled under reduced pressure. It distilled over at 104–106° under 30-mm. pressure, the boiling point of α,α,β-tribromopropionic aldehyde. We completely verified the α,α,β-structure of the tribromopropionic aldehyde by preparing the hydrate, which melted at 57° and did not lower the melting point of the synthesized α,α,β-tribromopropionic aldehyde hydrate when mixed with it. This proves that the bromovinylacrylic acid dibromide has the structure $CH_2BrCBr_2CH{=}CH$-$COOH$, and consequently the bromovinylacrylic acid has the structure $CH_2{=}CBr$-$CH{=}CHCOOH$.

Summary

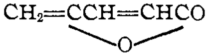
1. By bromination of vinylacrylic acid a dibromide is formed whose structure was proved by ozonization to be a 3,4-derivative, rather than a 1,4-derivative as required by Thiele's theory of addition to conjugated systems.

2. 3,4-Dibromo-Δ^1-pentenic acid loses a molecule of hydrogen bromide to give 3-bromovinylacrylic acid.

3. 3-Bromovinylacrylic acid absorbs one molecule of bromine in the 3,4-position to give 3,3′,4-tribromo-Δ^1-pentenic acid. Its structure was proved by ozonization.

4. An improved method for the preparation of vinylacrylic acid is given which doubles the best yield heretofore obtained.

5. On distillation 3,4-dibromo-Δ^1-pentenic acid loses two molecules of hydrogen bromide to give a γ-lactone whose structure was proved to be



$$\underbrace{CH_2{=}C\,CH{=}CH\,CO}_{O}$$

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

CARBITHIOIC ACID STUDIES. I. TOLYL-4-CARBITHIOIC ACID AND CERTAIN DERIVATIVES[1]

BY R. W. BOST AND W. J. MATTOX

RECEIVED JULY 25, 1929 PUBLISHED JANUARY 8, 1930

There are three methods by which the carbithioic acids are usually made, namely, hydrolysis of the corresponding thio esters with alcoholic potassium hydroxide,[2] the action of carbon disulfide on benzene in the presence of anhydrous aluminum chloride[3] and the Grignard reaction.[4,5] Sakurada[2] first isolated tolyl-4-carbithioic acid by the hydrolysis of ethyl dithio-*p*-toluate with alcoholic potassium hydroxide, the ethyl dithio-*p*-toluate being prepared by passing dry hydrogen sulfide into an ethereal solution of the corresponding thio-imino ester. However, none of its properties was studied and no derivatives were prepared other than the ethyl ester.

In this paper is described the preparation of tolyl-4-carbithioic acid by the action of carbon disulfide on tolyl-4-magnesium bromide. The acid is a viscous red oil having a disagreeable odor. Attempts to distil the acid resulted in decomposition. The sodium salt was more stable and was used in the preparation of the derivatives

Tolyl-4-carbithioic acid readily forms salts with the chlorides and acetates of inorganic metals. It is easily converted into thio esters by alkyl sulfates and alkyl halides. The thio esters are susceptible to ammonolysis, whereupon thio amides are obtained. In these respects the —CSSH group is similar to the —COOH group.

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[1] This paper is an abstract of a thesis submitted in June, 1929, to the Faculty of the University of North Carolina by W. J. Mattox in candidacy for the degree of Master of Arts.

[2] Sakurada, *Mem. Coll. Sci. Kyoto*, **10**, 79–83 (1926).

[3] Jörg, *Ber.*, **60**, 1466 (1927).

[4] Houben, *ibid.*, **39**, 3219 (1906).

[5] Wheeler and Thomas, THIS JOURNAL, **50**, 3106 (1928).