

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

STUDIES OF CONJUGATED SYSTEMS. III. THE CHLORINATION OF VINYLACRYLIC ACID

BY IRVING E. MUSKAT AND BRUNNER C. BECKER

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In continuation of our studies¹ on the addition reactions of conjugated systems we have made an investigation on the chlorination of vinylacrylic acid. A review of previous work on the addition reactions of vinylacrylic acid has been reported in an earlier paper.^{1b}

Vinylacrylic acid was prepared according to the method of Muskat, Becker and Lowenstein,^{1b} by condensing acrolein with potassium bisulfite and treating the resulting addition product with malonic acid. The chlorination of vinylacrylic acid was then studied. It was found that vinylacrylic acid absorbed two atoms of chlorine to give a dichloride which boiled at 153° under 10-mm. pressure. The chlorination was carried out under varied experimental conditions, but in no case did we obtain a different dichloride. The dichloride is unstable, particularly toward heat and alkali, and readily loses hydrogen chloride.

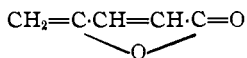
The structure of the dichloride was determined by ozonization. Three dichlorides are theoretically possible, depending on whether 1,2-, 1,4- or 3,4-addition takes place. On ozonizing the vinylacrylic acid dichloride, it was possible to isolate a 75% yield of oxalic acid, which was identified by its melting point and a melting point of a mixture with a sample of known origin. The second oxidation product, the α,β -dichloro propionic aldehyde was also isolated and identified. A number of ozonizations were made but in no case was it possible to obtain even the slightest indication of the presence of any of the aldehydes or acids to be expected from the oxidation of compounds resulting from the 1,2- or 1,4-addition of chlorine. This proves beyond any doubt that chlorine adds to vinylacrylic acid in the 3,4-position and not in the 1,4-position as is the case with hydrogen.²

We were not able to prepare a tetrachloride of vinylacrylic acid, even by allowing to stand with chlorine under pressure for several days. The dichloride can be reduced easily with zinc dust to the original vinylacrylic acid.

On distilling the dichloride under reduced pressure, decomposition occurred with the liberation of hydrogen chloride. A lower-boiling fraction distilled over which partially solidified on standing. This solid was identical with the one obtained by the distillation of vinylacrylic acid dibromide,^{1b} which was proved to be a γ -lactone having the structure

¹ (a) Muskat and Huggins, *THIS JOURNAL*, 51, 2496 (1929); (b) Muskat, Becker and Lowenstein, *ibid.*, 52, 326 (1930).

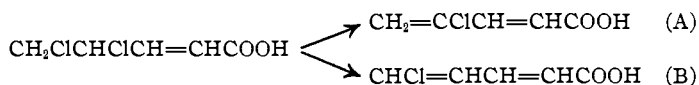
² Thiele, *Ber.*, 35, 2320 (1902); see also Doebner, *ibid.*, 35, 1136 (1902).



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

Chlorovinylacrylic acid is a light yellow, crystalline compound, very soluble in the ordinary organic solvents and rather unstable. It readily polymerizes to a light yellow 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 94° .

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



The structure of the monochloride was proved by further chlorinating it to the chlorovinylacrylic acid dichloride and studying the oxidation products of the trichloride formed.

Chlorovinylacrylic acid readily absorbed a molecule of chlorine to give a trichloro derivative, boiling at 162° under 8-mm. pressure. On standing it solidified to a solid melting at 132° . There are six trichlorides theoretically possible depending on the A or B structure of the monochloride and the type of addition, 1,2-, 1,4- or 3,4-, taking place.³

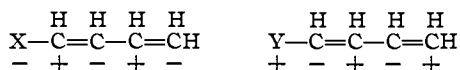
The chlorovinylacrylic acid dichloride was ozonized in the usual manner. It was possible to recover oxalic acid (53% yield), which was identified by its melting point and a melting point of a mixture with a sample of known origin, and also α,α,β -trichloropropionic aldehyde, which was also identified. This proves beyond any doubt that 3-4 addition of chlorine had again taken place, giving rise to a trichloride of structure, $\text{CH}_2\text{ClCCl}_2\text{-CH}=\text{CHCOOH}$, and therefore the structure of the monochloride must be as represented by (A), $\text{CH}_2=\text{CClCH}=\text{CHCOOH}$.

The experimental results recorded here lend support to the Hinrichsen view of addition to conjugated systems as contrasted with the Thiele view. That is, the type of addition—1,2-, 1,4- or 3,4—to conjugated systems is a function not only of the conjugated compound itself, but also depends on the nature of the addendum. Thus vinylacrylic acid adds hydrogen in the 1,4-position, while it adds bromine and chlorine in the 3,4-position. It seems very likely in the light of more recent work by Ingold, Prevost, Farmer, Claisen, and others, that even in those cases

³ See Muskat, Becker and Lowenstein, *THIS JOURNAL*, 52, 328 (1930), for the six possible structures.

where the substituents are found in the 1,4-position, it is not necessarily due to 1,4-addition, but rather to a condition of equilibrium in three-carbon systems containing a double bond.

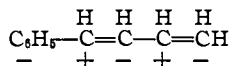
The elimination of the chlorine atom from the vinylacrylic acid dichloride from the 4-position rather than from the 3-position could be readily interpreted if it were assumed that the conjugated system has an electronic arrangement similar to that suggested by Stieglitz⁴ for the aromatic nucleus. Thus, we could develop the following electronic structures for conjugated systems.⁵



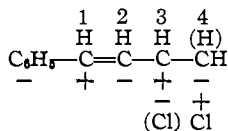
The plus and minus signs do not imply a complete transfer of an electron from one atom to another. They merely indicate the polarities of the atoms relative to one another and represent the resultant nuclear charge on each atom. The nuclear charge on each atom depends on the displacement of the octet of electrons surrounding each atom as influenced by the directing group X⁻ or Y⁺. The displacement of the electrons, it is believed, may be best expressed by the Lewis-Langmuir theory of electron shift. However, the resultant nuclear charge on each atom, and therefore the relative polarity of each atom, is not governed solely by the displacement of any single pair of electrons but rather by the displacement of the octet electrons surrounding one atom as compared to another.

Now let us consider the experimental facts so far obtained in our study of addition reactions to conjugated systems in the light of these electronic structures.

Muskat and Huggins^{1a} have studied the chlorination of phenylbutadiene and found that chlorine adds in the 3,4-position to give 1-phenyl-3,4-dichloro- Δ^1 -butene. They further showed that hydrogen chloride could be eliminated from the dichloride to give 1-phenyl-4-chlorobutadiene. These facts find a ready interpretation in the electronic structure proposed. The phenyl radical, the directing group, is usually considered to be relatively electronegative and we should therefore expect the following electronic arrangement in the molecule of phenylbutadiene



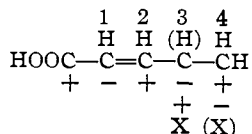
The structure of the dichloride would then be represented as



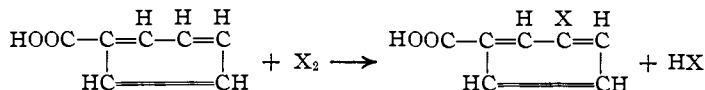
⁴ Stieglitz, *THIS JOURNAL*, **44**, 1299 (1922).

⁵ Lowry, *J. Chem. Soc.*, **123**, 822 (1923); Rodebush, *Chem. Reviews*, **5**, 528 (1928).

The dihalide could then be represented as



in which the 4-halogen atom would be relatively electronegative with respect to the 3-chlorine atom and would be expected to be eliminated as hydrogen halide as indicated by the (), which is in agreement with the experimentally determined facts. This might be regarded as meta-substitution, similar to the meta-substitution of halogen in benzoic acid.



In studying the addition reactions of conjugated systems we have a marked advantage over the study of similar reactions in the aromatic nucleus for it is possible to isolate the intermediate addition compound prior to its breakdown to the substitution derivative; in the reactions of aromatic compounds, only substitution products can as yet be isolated. The experimental work so far obtained, in the light of the electronic structures postulated, suggests that conjugated systems may act as an intermediate group between the true aromatic and aliphatic groups.

Experimental Part

Vinylacrylic Acid Dichloride.—To prepare vinylacrylic acid dichloride a stream of dry chlorine was allowed to pass into a chloroform solution of pure vinylacrylic acid. Absorption took place readily and the reaction mixture became warm. When the theoretical quantity of chlorine was absorbed, the reaction product was distilled under reduced pressure. A light yellow oil distilled over at 153° under 10 mm. pressure.

Anal. Calcd. for C₅H₆O₂Cl₂: Cl, 41.97. Found: Cl, 41.85, 41.83.

The conditions under which the vinylacrylic acid was chlorinated 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 dichloride was obtained regardless of the experimental conditions employed. The dichloride is unstable, particularly toward heat and alkali, and loses hydrogen chloride easily.

The pure vinylacrylic acid dichloride (5 g.), dissolved in chloroform, was subjected to ozonization, and the ozonide thus formed was decomposed with water. To assure complete decomposition 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 (2.00 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 (from the ether extract) was distilled under reduced pressure. An oil distilled over at 73° under 50 mm. pressure, the boiling point of α,β-dichloropropionic aldehyde. This was further identified by treating with sodium acetate according to

the method of Piloty and Stock,⁸ which converted the dichloride into α -chloro-acrolein. This distilled over at 40° under 30 mm. pressure, the recorded boiling point of α -chloro-acrolein. This proves that chlorine had added to vinylacrylic acid into the 3,4-position.

Vinylacrylic acid dichloride would not absorb any more chlorine. Even after standing for several days under a pressure of chlorine no addition of chlorine took place. The vinylacrylic acid dichloride was reduced with zinc dust to the original vinylacrylic acid. The yield was low due to polymerization of the vinylacrylic acid during the reduction.

When vinylacrylic acid dichloride was distilled under reduced pressure, decomposition occurred with the liberation of hydrogen chloride. A lower-boiling fraction distilled over which partially solidified on standing. The solid melted at 143° and solidified again at 162°. It was identical with the γ -lactone, $\text{CH}_2=\text{CCH}=\text{CHC}=\text{O}$, obtained by the distillation of vinylacrylic acid dibromide.^{1b}

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

Anal. Calcd. for $\text{C}_5\text{H}_5\text{O}_2\text{Cl}$: Cl, 26.76%. Found: Cl, 26.83, 26.81%. It was also titrated with standard sodium hydroxide: 0.3965 g. of sample required 28.1 cc. of 0.1063 *N* NaOH. Found: mol. wt., 132.7. Calcd. for $\text{C}_5\text{H}_5\text{O}_2\text{Cl}$: mol. wt., 132.5.

Chlorovinylacrylic acid is a light yellow, crystalline compound, very soluble in the ordinary organic solvents and rather unstable. It readily polymerizes to a light yellow solid which is insoluble in all ordinary organic solvents with the exception of acetone. Due to its ease of polymerization it is not possible to get a sharp melting point. It melts at about 94°. The structure of the monochloride was established by further chlorinating it to the chlorovinylacrylic acid dichloride and determining the oxidation products of the trichloride formed.

Chlorovinylacrylic Acid Dichloride.—To prepare chlorovinylacrylic acid dichloride a stream of dry chlorine was allowed to pass into a chloroform solution of pure chlorovinylacrylic acid. Absorption took place readily and the reaction mixture became hot. After the theoretical quantity of chlorine was absorbed, the reaction mixture was distilled under reduced pressure. A light yellow oil distilled over at 162° under 8-mm. pressure. On standing it solidified. The solid melted at 132°.

Anal. Calcd. for $\text{C}_5\text{H}_5\text{O}_2\text{Cl}_2$: Cl, 52.29. Found: Cl, 52.29, 52.09. It was also titrated with standard sodium hydroxide: 0.6947 g. of sample required 31.8 cc. of 0.1063 *N* NaOH. Found: mol. wt., 205.5. Calcd. for $\text{C}_5\text{H}_5\text{O}_2\text{Cl}_2$: mol. wt., 203.4.

The pure chlorovinylacrylic acid dichloride (2.1 g.) was subjected to ozonization and the ozonide thus formed was treated in a manner entirely analogous to that of the dichloride previously described. The acid and aldehyde portions were separated; the acid portion yielded 0.693 g. of calcium oxalate, which corresponds to a 53% yield, while the aldehyde portion was removed as such and distilled under reduced pressure. It distilled over at 63–65° under 45-mm. pressure, the boiling point of α, α, β -trichloropropionic aldehyde. We completely verified the α, α, β -structure of the trichloropropionic aldehyde by oxidizing it to the corresponding α, α, β -trichloropropionic acid with

⁸ Piloty and Stock, *Ber.*, 31, 1385 (1898).

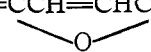
concentrated nitric acid according to the method of Berlande.⁹ It melted sharply at 60°. We repeated the preparation of α, α, β -trichloropropionic acid according to Berlande's method and found it to melt at 60° and not at 50–52° as he reports. We analyzed the α, α, β -trichloropropionic acid so prepared to prove its purity.

Anal. Calcd. for $C_3H_3O_2Cl_3$: Cl, 60.0. Found: Cl, 60.37, 60.17.

A mixture of the trichloropropionic acid obtained from the ozonization of chlorovinylacrylic acid dichloride with the synthesized α, α, β -trichloropropionic acid also melted at 60°. It was observed that the acid is very hygroscopic and if allowed to stand in a moist atmosphere for a short time the melting point is materially lowered. This proves beyond any doubt that chlorovinylacrylic acid dichloride has the structure $CH_2ClCCl_2CH=CHCOOH$, and therefore the chlorovinylacrylic acid has the structure $CH_2=CClCH=CHCOOH$.

Summary

1. By chlorination of vinylacrylic acid a dichloride is formed whose structure was proved by ozonization to be a 3,4-derivative and not a 1,4-derivative as required by Thiele's theory of addition to conjugated systems.
2. 3,4-Dichloro- Δ^1 -pentenic acid loses a molecule of hydrogen chloride to give 3-chlorovinylacrylic acid.
3. 3-Chlorovinylacrylic acid absorbs one molecule of chlorine in the 3,4-position to give 3,3',4-trichloro- Δ^1 -pentenic acid. Its structure was proved by ozonization.
4. On distilling 3,4-dichloro- Δ^1 -pentenic acid two molecules of hydrogen chloride are lost and a γ -lactone, $CH_2=CCH=CHC=O$ is formed.


5. The melting point of α, α, β -trichloropropionic acid is corrected.
6. An electronic structure for conjugated systems is suggested.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE JOHNS HOPKINS UNIVERSITY AND THE BUREAU OF CHEMISTRY AND SOILS]

PHENACYL, PARA-CHLOROPHENACYL AND PARA-BROMOPHENACYL ESTERS OF SOME HIGHER FATTY ACIDS

By RAYMOND M. HANN, E. EMMET REID AND GEORGE S. JAMIESON

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The utilization of phenacyl and para halogen phenacyl esters for the identification and separation of acids has been indicated by Rather and Reid¹ and by Judefind and Reid.² The successful employment of these reagents for fruit acids has suggested the possibility of quantitative differentiation of the fatty acids obtained from the saponification of the glycerides contained in fats and vegetable oils. The present accepted analytical procedure for substances of this nature consists in esterify-

⁹ Berlande, *Bull. soc. chim.*, [4] 37, 1385 (1925).

¹ Rather and Reid, *THIS JOURNAL*, 41, 75 (1919).

² Judefind and Reid, *ibid.*, 42, 1043 (1920).