tion for the ester, $C_{24}H_{24}O_6$, gave 15.31. Theory requires 15.20.

The ethyl ester was obtained on concentrating the ethanolic solution used to recrystallize the keto-acid. After recrystallization from chloroform, it had m.p. 133–134°. The Zeisel determination gave, for $C_{26}H_{28}O_6$, 20.71. Theory requires 20.64. Hydrolysis of the ester with aqueous ethanolic sodium hydroxide regenerated the keto-acid, m.p. 228–230°.

Ethyl Acetylenedicarboxylate.—Ruhemann and Beddow[28] report that this ester may be prepared in very high yield by direct esterification of acetylenedicarboxylic acid with ethanol and hydrogen chloride. Repetition of their procedure, however, furnished a product whose analysis and physical constants accorded very closely with those of ethyl chlorofumarate. Our product contained 15.95% Cl, had b.p. 96–100° at 6.0 mm., $n^{25}D$ 1.4600. Ethyl chlorofumarate[29] has b.p. 119° at 12 mm., $n^{24}D$ 1.4598, and contains 17.16% Cl. Clearly the main product from the above esterification was ethyl chlorofumarate.

The acetylenic ester was prepared in 65% yield by an adaptation of the azeotropic distillation method of Mitchovitch.[30] It had b.p. 106–107° at 12–13 mm.

Ethyl 1,1,2,2,3,4-Cyclobutanehexacarboxylate.—The method of Shibata[18] furnished this ester in about 5% yield. The method was very tedious, requiring manual separation of the hexaester from starting material and by-products. For the preparation of the cyclic ester in quantity, the following method was devised. Under anhydrous conditions and with stirring, a mixture of 34 g. (0.2 mole) of ethyl acetylenedicarboxylate, 66 g. (0.2 mole) of ethyl 1,1,2,2-ethanetetracarboxylate,[31] and 10 ml. of absolute ethanol was warmed to 45° to effect a clear solution. One and five-tenths grams (0.065 atom) of sodium dissolved in 24 ml. of absolute ethanol was added dropwise, with rapid stirring. After the addition of about 10 drops of the ethoxide solution, the internal temperature of the reaction mixture suddenly rose to 92° and then slowly subsided as the rest of the catalyst was added. As the temperature rose, the color of the solution changed to greenish-yellow and then to dark brown. The reaction mixture was poured into 100 ml. of 3 *N* hydrochloric acid and exhaustively extracted with ether. Evaporation of the ether left a mixture of solid and oil. The solid was collected and recrystallized from 80% ethanol. The deposition of crystals (typical square tablets) was slow. After one day, 28.5 g. of the hexaester, m.p. 78°, was obtained. A second crop (16 g.) was obtained four days later. The residual oil yielded about 4 g. of solid which was recrystallized. The total yield was about 48%. On slow recrystallization (two to four weeks), massive tablets, some with edges measuring 2 cm., were obtained, m.p. 78°.

Anal. Calcd. for $C_{22}H_{32}O_{12}$: C, 54.10; H, 6.56. Found: C, 54.07; H, 6.77.

Mixed m.p. determinations with material prepared by the method of Shibata (78°) showed no depression. With both ethyl ethanetetracarboxylate and ethyl ethylenetetracarboxylate mixed m.p. determinations showed considerable depression. In accord with the observation of Shibata, basic solutions rapidly attacked the ester, forming bubbles on the surface of the compound.

1,2,3,4-Cyclobutanetetracarboxylic Acid.—The hydrolysis of the cylic hexaester was carried out using 10 ml. of concentrated hydrochloric acid for each gram of ester. The mixture was refluxed until a clear solution resulted (about three days). Evaporation of the hydrolysis solution left a yellow oil which was dissolved in the minimum amount of concentrated hydrochloric acid. White amorphous acidic material slowly deposited, m.p. 204–210° (dec.). This material was immediately attacked by permanganate solution. After several slow recrystallizations from water pure compound was obtained in the form of a white microcrystalline powder. When heated at the rate of 2° per minute, the m.p. was 226–228° (dec.), but heating at the rate of one degree per three minutes caused the substance to melt at 216–217° (dec.). The product was stable to dilute permanganate solution for five to six hours. The yield of product was about 15%.

Anal. Calcd. for $C_8H_8O_8$: C, 41.38; H, 3.45; neut. equiv., 58. Found: C, 41.48; H, 3.56; neut. equiv. 59.2.

During the m.p. determinations a sublimate was observed to form above the decomposing sample. The identity of this sublimate, m.p. 75–85°, is unknown.

BALTIMORE 18, MARYLAND RECEIVED JULY 7, 1950

(28) Ruhemann and Beddow, *J. Chem. Soc.*, **77**, 1121 (1900).

(29) Auwers and Harries, *Ber.*, **62**, 1678 (1929); Gladstone, *J. Chem. Soc.*, **59**, 290 (1891); Perkin, *ibid.*, **53**, 695 (1888).

(30) Mitchovitch, *Bull. soc. chim.*, [5] **4**, 1661 (1937).

(31) Bischoff and Rach, *Ber.*, **17**, 2781 (1884).

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Ketene Acetals. XXIV. The Preparation and Properties of Ketene Divinylacetal and Related Compounds

BY S. M. McELVAIN AND A. N. BOLSTAD

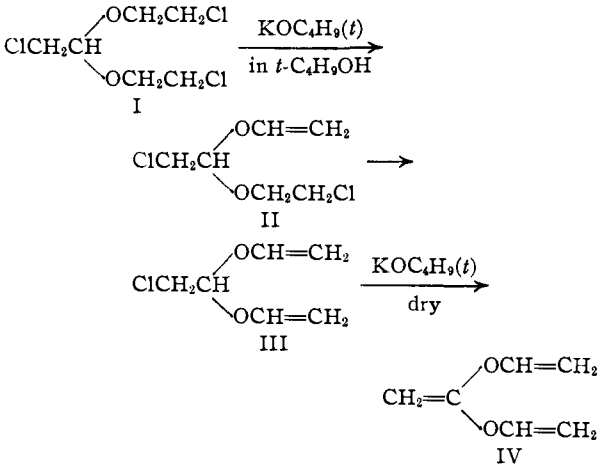
Ketene divinylacetal (IV) has been prepared by a stepwise dehydrochlorination of chloroacetaldehyde di-(β-chloroethyl)-acetal (I). The first dehydrochlorinations occur at the β-chloroethyl groups to yield the vinyl β-chloroethyl- and divinylacetals of chloroacetaldehyde (II) and III). While relatively stable to water and alcohols in the absence of acid, IV reacts vigorously with both in the presence of a trace of acid. IV is quite resistant to ionic polymerization, and to alkylation with benzyl bromide. At −70° IV reacts with hydrogen chloride to yield a stable addition product, $CH_3C(OCH{=}CH_2)_2Cl$ (VIII), the properties of which lead to the conclusion that a similar structure reported recently by Vogel and Schinz (ref. 4) is erroneous. With ethylene chlorohydrin, IV yields an orthoester that undergoes dehydrochlorination to trivinyl orthoacetate (VII). The relationships of the structures to the boiling points of this orthoester, ketene divinylacetal (IV), and their more saturated analogs is discussed.

In paper XV of this series the preparation and properties of ketene diphenylacetal were described.[1] The lower anioniod reactivity of this compound at the methylene carbon, as compared to that of ketene diethylacetal, was ascribed to a loss in the activating effect of the oxygens of the former compound through their polarization into the phenyl groups. To further extend the study of the effect of unsaturated groups attached to the acetal oxygens the preparation of ketene divinylacetal was undertaken.

Ketene divinylacetal (IV) was prepared by the step-wise dehydrochlorination of chloroacetaldehyde di-(β-chloroethyl)-acetal (I). The initial dehydrochlorinations, which were carried out in *t*-butyl alcohol solution with potassium *t*-butoxide, occur at the β-chloroethyl groups; the two intermediate vinylacetals (II and III) were separated and characterized by analyses and by the amount of acetaldehyde liberated when each was refluxed

(1) S. M. McElvain and B. Fajardo-Pinzon, THIS JOURNAL, **67**, 650 (1945).

with acidic *n*-butyl alcohol. The final dehydrochlorination of chloroacetaldehyde divinylacetal (III) to ketene divinylacetal (IV) was effected by dry, *sublimed* potassium *t*-butoxide. The use of this reagent was found expedient in order to facilitate the separation of the ketene acetal from the *t*-butyl alcohol. Even though there is a difference of 20° in the boiling points of these compounds, it was found impracticable, if not impossible, to separate IV from large amounts of *t*-butyl alcohol; however, the relatively small amount of the alcohol produced when the dry potassium *t*-butoxide was used could be separated from the ketene divinylacetal simply by washing with water.



The acetal II could be isolated in 45% yield, together with a 17% yield of III, from the reaction of one equivalent of potassium *t*-butoxide with I. However, if the reaction mixture from this initial dehydrochlorination were treated with an equivalent of sodium hydride, the second molecule of hydrogen chloride could be removed without the isolation of II. In this manner a 56% yield of III was obtained directly from I along with a 16% yield of II and a 6% yield of IV. The final dehydrochlorination of III to the ketene acetal (IV) was effected in 74% yield.

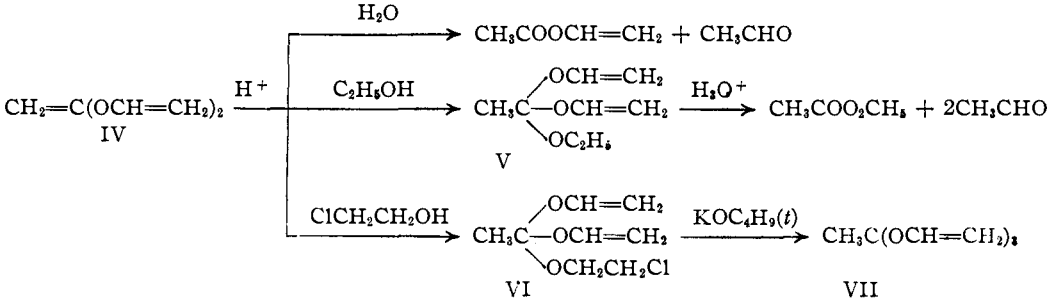
Ketene divinylacetal (IV) is a colorless liquid, which boils at 101.8–102°. It is not attacked by water, alcohols or dilute alkali and shows very little tendency to polymerization in the presence of ionic catalysts. After standing five months, 93% of the monomer could be distilled from a small amount of polymer. Cadmium chloride, which catalyzes the polymerization of ketene diethylacetal, and benzoyl peroxide, which induces the polymerization of most vinyl compounds, caused only 5 and 13% polymerization, respectively, in the same period of time at room temperature. At 100°, however, benzoyl peroxide produced 19% of the polymer within ten minutes. Hydrogen peroxide appears to be the most effective catalyst for the polymerization of ketene divinylacetal at room temperature, yielding 47% of the polymer after five months.

The polymer, which appears as a gel in the monomer, is obtained as a hard, brittle infusible residue after distillation of the monomer. In contrast of the polymers of ketene diethyl acetal,[2] the polymer of ketene divinylacetal is insoluble in organic solvents, dilute acids or alkalies, and concentrated sulfuric acid.

In the presence of a trace of acid, ketene divinylacetal (IV) reacts exothermically with both water and alcohols. Water converts IV to acetaldehyde and vinyl acetate (82 and 65%, respectively); ethyl alcohol gives an 80% yield of divinyl ethyl orthoacetate (V), which is converted by acid hydrolysis to ethyl acetate (90%) and acetaldehyde (90%). Ethylene chlorohydrin converts IV to the orthoester VI, which may be dehydrochlorinated to trivinyl orthoacetate (VII).

Ketene divinylacetal (IV) shows a similar behavior toward benzyl bromide as ketene diphenylacetal. When equimolar amounts of IV and benzyl bromide were heated at 145° for two hours, the reactants were recovered unchanged; ketene diethylacetal reacts completely with benzyl bromide in this time at 125°.[3] After heating IV with benzyl bromide at 155° for six hours, 80% of the bromide was recovered, but the ketene acetal was converted to a black, charcoal-like residue, the weight of which was equivalent to that of the ketene acetal used.

The reaction of ketene divinylacetal with hydrogen chloride is of particular interest. When these compounds were allowed to react in ethereal solution at −70°, the addition product VIII was formed and could be isolated in 70–83% yields as a clear liquid, boiling at 120–122°. This orthoacid chloride (VIII) reacts violently with both water and alcohol with the evolution of vapors of



acetaldehyde; on standing VIII changes to a brown resin. When treated with a cooled mixture of equimolar amounts of ethyl alcohol and pyridine,

$$\text{IV} + \text{HCl} \xrightarrow{-70^\circ} \underset{\text{VIII}}{\text{CH}_3\text{C(OCH=CH}_2)_2\text{Cl}} \xrightarrow[\text{C}_5\text{H}_5\text{N}]{\text{C}_2\text{H}_5\text{OH}} \text{V}$$

(2) P. R. Johnson, H. M. Barnes and S. M. McElvain, THIS JOURNAL, **62**, 964 (1940).

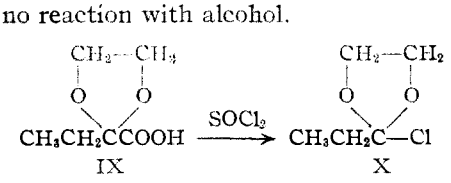
(3) S. M. McElvain and D. G. Kundiger, *ibid.*, **64**, 254 (1942).

VIII was converted to divinyl ethyl orthoacetate (V) in 83% yield.

A structure of the type of VIII has been postulated as an intermediate in the reaction of ketene diethylacetal with hydrogen chloride to yield ethyl chloride and ethyl acetate.[3] Inasmuch as this reaction was run at room temperature, it seemed advisable to repeat this experiment at −70° to determine if the intermediate $CH_3C(OC_2H_5)_2Cl$ is indeed formed. When cooled ethereal solution of hydrogen chloride was added to a similar solution of ketene diethylacetal ethyl chloride, ethyl acetate and ethyl β-ethoxycrotonate were the reaction products; when the order of addition of the reactants was reversed, these same products were obtained, but with noticeably higher yields of the ethyl acetate. Since these results parallel those obtained at room temperature,[3] it appears that the unique stability of VIII is due to the greater strength of its oxygen–vinyl bonds. These results raise a question as to the even fleeting existence of such an intermediate as VIII in the reaction of the diethylacetal. The formation of the ethoxycrotonate in the presence of an excess of the ketene acetal indicates that the active intermediate is the carbonium ion, $CH_3C^+(OC_2H_5)_2$, which may react with another molecule of the ketene acetal to yield the crotonate or lose an ethyl cation to the chloride anion to yield ethyl acetate and ethyl chloride.

When ethereal solutions of ketene diphenylacetal and hydrogen chloride were mixed at −70°, there was a noticable evolution of heat, but distillation of the reaction mixture gave 76% of the hydrogen chloride (in the ether) and 83% of the ketene acetal. At room temperature, this ketene acetal absorbed one equivalent of hydrogen chloride with the evolution of considerable heat. If this product were treated with ether and the resulting solution distilled, hydrogen chloride and the ketene acetal were recovered, indicating that the initial complex was destroyed by the more basic oxygen of the ether. If, however, the hydrogen chloride–ketene acetal complex were distilled directly, hydrogen chloride together with 81% of one equivalent of phenol were the volatile products. The residue, amounting to 56% of the original ketene diphenylacetal, was an undistillable tar.

The properties of VIII are of special interest in connection with the structure (X) of a compound recently reported by Vogel and Schinz,[4] to result from the action of thionyl chloride on the acid (IX) or its sodium salt. X was reported to be stable to cold water and alkali solutions and to show no reaction with alcohol.



It is apparent that X has the same type structure as VIII and represents the addition product of hydrogen chloride and 2-ethylidene-1,3-dioxolane, methylketene dimethyleneacetal. While this particular ketene acetal has not as yet been prepared, a number of the corresponding 2-methylene-1,3 dioxolanes have been found in this Laboratory to react with hydrogen chloride to yield the corresponding β-chloroethyl esters.[5] There is no reason to expect a ketene cyclic acetal to yield a more stable addition product with hydrogen chloride than does ketene diethylacetal. This, together with the demonstrated vigorous reactivity of VIII with both water and alcohol, lead to the conclusion that the compound isolated by Vogel and Schinz was the isomeric β-chloroethyl propionate, $CH_3CH_2COOCH_2CH_2Cl$, rather than X. Indeed, this ester was prepared and found to have the same boiling point (86–88° (60 mm.)), the only property reported by the Swiss authors, as that recorded for X.

Attention should be drawn to the relationships of structure to boiling points among the vinyl orthoesters and ketene divinylacetal and their more saturated analogs. Trivinyl orthoacetate (VII), divinyl ethyl orthoacetate (V) and the completely saturated ethyl orthoacetate, $CH_3C(OC_2H_5)_3$, all boil within the range 144–147°, showing that the vinyloxy and ethoxy groups have similar effects on the boiling point. Ketene divinylacetal (IV) has the same boiling point (102°) as the completely saturated acetal, $CH_3CH(OC_2H_5)_2$, but ketene diethylacetal, $CH_2{=}C(OC_2H_5)_2$, boils at 126°. The relatively high boiling point of this latter compound reflects the large permanent polarization of its molecule due to the conjugation of the oxygen of the two ethoxyl groups with the carbon to carbon double bond. The lower boiling point of ketene divinylacetal (IV) points to the neutralization of this type of polarization by the attached vinyl groups, a condition which is also demonstrated by the depressed chemical activity of IV.

Experimental

Chloroacetaldehyde Di-(β-chloroethyl)-acetal (I).—In a flask fitted with a 30-cm. Vigreux column, a mixture of 373.5 g. (3 moles) of chloroacetaldehyde dimethylacetal and 495 g. (6.15 moles) of ethylene chlorohydrin was heated sufficiently to maintain a temperature of 64 to 69° at the head of the column. After 12 hours, when 70% of the methanol had distilled, an additional 50 ml. of ethylene chlorohydrin was added to complete the reaction. After 24 hours the temperature at the column head was raised to 100°, and then after 30 hours the reaction mixture was distilled under reduced pressure using a modified Claisen flask. The product (558 g.) distilled at 120–130° (5 mm.). The forerun was heated another 12 hours to distil more methanol and on redistillation an additional 66 g. of I was obtained; the total yield amounted to 94% of the theoretical. On refractionation through a 20-cm. Widmer column, I boiled at 134–135° (10 mm.); $n^{25}D$ 1.4757; d^{25}_4 1.320.

Anal. Calcd. for $C_6H_{11}Cl_3O_2$: Cl, 48.1. Found: Cl, 48.0.

Dehydrochlorination of I: Chloroacetaldehyde Vinyl-(β-chloroethyl)-acetal (II) and Chloroacetaldehyde Divinylacetal (III).—A solution of potassium *t*-butoxide in *t*-butyl alcohol was prepared by dissolving 39.1 g. (1 g. atom) of potassium in 700 ml. of the alcohol. When the potassium had dissolved completely, this solution was added to 221.5 g. (1 mole) of I over a period of three to four hours with stirring and heating on a steam-bath. Then after 20 hours, 24 g. (1 mole) of sodium hydride was added over a period of three hours and the mixture heated for another 1.5 hours.

(4) E. Vogel and H. Schinz, *Helv. Chim. Acta*, **33**, 116 (1950).

(5) S. M. McElvain and M. J. Curry, THIS JOURNAL, **70**, 3781 (1948).

The mixture was allowed to cool and stand for 16 hours, after which it was washed three times with 1-l. portions of water. The water-insoluble material, which amounted to 225 ml., was dried over anhydrous potassium carbonate with 0.1 g. of hydroquinone added to reduce polymerization. On fractional distillation under reduced pressure 80 g. (53.8%) of III, b.p. 45–55° (11 mm.) and 30 g. (16.2%) of II, b.p. 88–105° (11 mm.) were obtained along with a recovery of 4 g. (1.8%) of I. The forerun and a small amount of liquid from the cold trap were combined and washed four times with 100-ml. portions of water. After drying the water-insoluble material with anhydrous potassium carbonate, it was separated into 7.4 g. (6.6%) of ketene divinyl acetal (IV) and 3.5 g. (2.3%) of III. Thus a total yield of III was 56.1%.

Chloroacetaldehyde vinyl-(β-chloroethyl)-acetal (II) on refractionation was obtained as a clear liquid b.p. 95–96° (10 mm.); $n^{25}D$ 1.4644; d^{25}_4 1.205.

Anal. Calcd. for $C_6H_{10}Cl_2O_2$: Cl, 38.4. Found: Cl, 38.3.

Chloroacetaldehyde divinylacetal (III) on refractionation was obtained as a clear liquid b.p. 48–49° (10 mm.); $n^{25}D$ 1.4483; d^{25}_4 1.060; m.p. *ca.* −25°.

Anal. Calcd. for $C_6H_9ClO_2$: Cl, 23.9. Found: Cl, 22.7.

Both II and III were hydrolyzed in a few minutes on warming with 5% hydrochloric acid to give homogeneous solutions, showing that the dehydrochlorinations occurred at the β-chloroethyl groups.

Alcoholysis of II and III.—To 4.00 g. of II was added 3.20 g. of *n*-butyl alcohol and a boiling chip moistened with sulfuric acid. This mixture was refluxed and the gas passing through the condenser was collected in a Dry Ice cold-trap. The amount of acetaldehyde obtained was 0.94 g. (99%), m.p. of 2,4-dinitrophenylhydrazone 166–167°.

A mixture of 4.00 g. of III and 4.00 g. of *n*-butyl alcohol was treated as above and 2.17 g. (91%) of acetaldehyde was obtained, m.p. of the 2,4-dinitrophenylhydrazone 167–168°.

Ketene Divinylacetal (IV).—To 50 g. (0.34 mole) of III was added 38 g. (0.34 mole) of sublimed potassium *t*-butoxide[6] in small portions with stirring in order to prevent local overheating and charring. The reaction mixture was cooled whenever the liberated *t*-butyl alcohol began to boil. After completing the addition of the base, the reaction mixture then was placed on a steam-bath and refluxed for two hours. After cooling, the reaction mixture was diluted with 200 ml. of water and the organic layer separated and dried with anhydrous potassium carbonate. Then it was treated with 1 g. of sodium hydride to remove the last traces of *t*-butyl alcohol. On distillation under reduced pressure, 28.07 g. (74%) of IV, b.p. 47–50° (100 mm.), and 2 g. (4%) of III, b.p. 90–93° (100 mm.), were obtained.

Ketene divinylacetal (IV) on refractionation through a 30 cm. McMahon packed column was obtained as a clear liquid with a pleasant odor, b.p. 101.8–102° (741 mm.); $n^{25}D$ 1.4360; d^{25}_4 0.898.

Anal. Calcd. for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.40; H, 7.34.

Ketene divinylacetal (IV) and chloroacetaldehyde divinylacetal (III) showed a tendency to polymerize, becoming gels on standing four months. III was stabilized by the addition of a trace of hydroquinone and anhydrous potassium carbonate. Stabilization of IV was obtained by storing in a sealed glass-stoppered bottle and with either sodium hydride or potassium *t*-butoxide and a trace of hydroquinone; under these conditions it appeared cloudy only after three months. II showed little if any tendency to polymerization. The gelatinous polymers of III and IV showed adhesive properties toward glass and metal surfaces, and on distillation of the monomer left hard glassy residues which were difficult to remove from the flasks. A hot 10% solution of sodium hydroxide was found the most useful for loosening these polymers.

Reactions of Ketene Divinylacetal (IV). (a) Polymerization.—A series of tests were run using 5.00-g. samples of freshly distilled IV in clean, dry, alkali-washed Pyrex test-tubes, which were stoppered with paraffin covered corks. After standing for five months the monomer was removed under reduced pressure at room temperature into a Dry Ice and acetone cold trap until no further loss in weight occurred under prolonged evacuation.

The sample of pure IV showed some cloudiness in one month and after five months was a gel from which 4.65 g. (93%) of the monomer, $n^{25}D$ 1.4347, was recovered leaving only 0.34 g. (7%) of polymer. A sample of this polymer was refluxed for three days with dilute sulfuric acid. The surface became slightly brown and a faint odor of acetaldehyde was detected; on replacing the acid solution with a 5% sodium hydroxide solution and refluxing another day, no further change occurred. The polymer was insoluble in organic solvents and concentrated sulfuric acid and did not melt on heating over a flame.

Cadmium chloride (0.04 g.) was added to a second sample and 0.05 g. of aluminum *t*-butoxide to a third sample. The second sample was cloudy after one month and a gel in five months, but distillation yielded 4.65 g. (93%) of monomer, $n^{25}D$ 1.4354, and left only 0.26 g. (5%) of the polymer. The third sample after five months was a brown liquid, from which 4.73 g. (94%) of the monomer $n^{25}D$ 1.4350 was obtained on distillation.

Benzoyl peroxide (0.03 g.) was added to a fourth sample. After five months it was a gel, from which 4.32 g. (86%) of the monomer $n^{25}D$ 1.4353 was recovered leaving 0.66 g. (13%) of polymer. A 1-g. sample of IV, to which 0.01 g. of benzoyl peroxide had been added, became a firm gel after heating on a steam-bath for ten minutes. On distillation 0.80 g. (80%) of the monomer was recovered leaving a residue of 0.19 g. (19%) of the polymer.

Hydrogen peroxide (5 drops of 30%) was added to a fifth sample. A small amount of precipitate appeared after a few hours, and after four days the liquid turned to a firm white gel; after five months the material was hard and brittle. Distillation yielded 2.36 g. (47%) of the monomer, $n^{25}D$ 1.4240, and left 2.37 g. (47%) of the polymer.

(b) Hydrolysis.—To 5.00 g. of IV in a 10-ml. flask with a 15 cm. Vigreux column was added 0.90 ml. of 1% sulfuric acid solution. Gentle refluxing was maintained and care was used to keep the temperature below 35° in the head of the column. A 1.62-g. (82%) yield of acetaldehyde was obtained in a Dry Ice cold-trap over a period of two hours. Then on distillation a 2.49-g. (65%) yield of vinyl acetate (b.p. 64–69°) was obtained. A residue of 1.62 g. remained in the flask.

(c) With Ethanol. Divinyl Ethyl Orthoacetate (V).—To 15 g. (0.13 mole) of IV was added two drops of an ethanol solution containing 0.3 g. of hydrogen chloride per ml. Then 6.15 g. (0.13 mole) of ethanol was added slowly while the reaction mixture was stirred and cooled in an ice-bath. Pyridine (5 drops) was added to neutralize the hydrogen chloride. On distillation 17 g. (80%) of divinyl ethyl orthoacetate (V), b.p. 130–145°, was obtained leaving a colorless, rubber-like residue of 3.06 g. in the flask. On refractionation V was obtained as a colorless liquid b.p. 144–145.4°: $n^{25}D$ 1.4221; d^{25}_4 0.924.

Anal. Calcd. for $C_8H_{14}O_3$: C, 60.73; H, 8.92. Found: C, 60.80; H, 8.97.

The orthoester V polymerizes on standing, becoming quite viscous within a week; however, the addition of a small amount of hydroquinone and anhydrous potassium carbonate kept the sample in the liquid state. The polymer is obtained as a clear rubbery residue after distillation of the monomer.

The products of hydrolysis of V were determined by treating 6.74 g. (0.043 mole) of V with 0.80 g. (0.044 mole) of water containing 1% of sulfuric acid in a flask provided with a 15-cm. Vigreux column. By gentle heating, 3.40 g. (91% of two equivalents) of acetaldehyde was collected in a Dry Ice cold-trap. Then on distillation 3.36 g. (90%) of ethyl acetate b.p. 72–76° was obtained; 0.35 g. of residue remained. The ethyl acetate contained no unsaturation as determined by treatment with bromine.

(d) With Ethylene Chlorohydrin. Trivinyl Orthoacetate (VII).—To 16 g. (0.14 mole) of IV was added two drops of ethylene chlorohydrin solution containing 0.2 g. of hydrogen chloride per ml. Then 11.5 g. (0.14 mole) of ethylene chlorohydrin was added slowly while the reaction mixture was stirred and cooled in an ice-bath. The resulting ortho-

(6) The sublimed potassium *t*-butoxide was prepared by dissolving potassium in *t*-butyl alcohol and distilling the alcohol. The pressure was then reduced to 0.1 mm. and the dry salt heated in an oil-bath to 200–220°. The product, a granular, white, crystalline solid collected on the top cooler half of the flask; it showed a neutral equivalent of 111.8 (mol. wt. 112.2).

ester formed was dehydrochlorinated by adding 1 g. of sublimed potassium *t*-butoxide and warming the reaction mixture to 100°; then, with continued stirring, the remainder of the base (18.5 g. or a total of 0.17 mole) was added over the period of one-half hour and the reaction mixture refluxed for two hours. The precipitated potassium chloride was separated by centrifuging and the liquid fractionally distilled. A forerun of 12.26 g., b.p. 81–120°, was mainly *t*-butyl alcohol; then 8.15 g. (37%) of VII, b.p. 120–148°, was obtained. On refractionation trivinyl orthoacetate (VII) was obtained as a clear liquid b.p. 145–147°; $n^{25}D$ 1.4328; d^{25}_4 0.941.

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.51; H, 7.74. Found: C, 61.67; H, 7.82.

This orthoester also polymerized on standing, but was stabilized satisfactorily in the monomeric form by trace amounts of hydroquinone and anhydrous potassium carbonate.

(e) **With Benzyl Bromide.**—A mixture of 20 g. (0.18 mole) of IV and 30.6 g. (0.18 mole) of benzyl bromide was sealed in a heavy Pyrex tube and heated at 145° in an oil-bath for two hours. After cooling no pressure was apparent upon opening the tube. On distillation in a system connected to a Dry Ice cold-trap, 25.8 g. (83%) of the benzyl bromide, b.p. 30–48° (0.3 mm.), was recovered; 15.3 g. (75%) of IV, $n^{25}D$ 1.4335 collected in the cold-trap; a residue of 3.68 g. remained in the flask.

Under more strenuous conditions (155° for six hours) with the same amounts of reactants, the reaction mixture turned black. Pressure was apparent upon opening the tube after it had cooled. A black rubbery tar amounting to 48.3 g. (96% of reaction mixture) was scraped out of the tube and placed in a distilling flask. Distillation under reduced pressure yielded 24 g. (80%) of benzyl bromide and left a charcoal-like residue amounting to 23 g.

(f) **With Hydrogen Chloride. 1,1-Divinyloxy-1-chloroethane (VIII).**—To 10.75 g. (0.096 mole) of freshly distilled ketene divinylacetal, cooled to −70° in a Dry Ice-bath, was added with stirring 42.5 ml. of a 2.26 *N* solution of hydrogen chloride in ether. The reaction mixture was allowed to warm to room temperature and the ether was distilled. The pressure then was reduced and 11.65 g. (82%) of VIII b.p. 58–65° (54 mm.) was collected; a residue of 1.24 g. remained. On distillation at atmospheric pressure VIII was obtained as a colorless liquid, b.p. 120–122°; $n^{25}D$ 1.4422; d^{25}_4 1.03.

Anal. Calcd. for $C_6H_9ClO_2$: Cl, 23.9. Found: Cl, 20.9.

As the analysis indicates, VIII as obtained was somewhat impure and it was not sufficiently stable to permit further purification by fractionation. This compound darkens within 24 hours and turns to a brown resin on longer standing. It reacts with explosive violence with both water and alcohol to evolve acetaldehyde.

To 10.42 g. (0.07 mole) of freshly distilled VIII, cooled in a Dry Ice-bath, was added dropwise a mixture of 3.23 g. (0.07 mole) of ethanol and 5.55 g. (0.07 mole) of pyridine with stirring. A white precipitate of pyridine hydrochloride separated; after filtering and washing with ether, it weighed 7 g. (87%). The ether solution was distilled to yield 8.2 g. (83%) of divinyl ethyl orthoacetate (V), b.p. 129–145°, which was identified by its hydrolysis products, acetaldehyde and ethyl acetate.

Reaction of Ketene Diethylacetal with Hydrogen Chloride.—(a) To 11.6 g. (0.1 mole) of this ketene acetal cooled in a Dry Ice-bath was added 15.4 g. of an ether solution containing 3.65 g. of hydrogen chloride similarly cooled. Distillation of the resulting solution gave 6.35 g. (72%) of ethyl acetate, b.p. 69–75°, and 2.03 g. (26%) of ethyl β-ethoxycrotonate, b.p. 86–91° (20 mm.); 3.33 g. (52%) of ethyl chloride was collected in a cold-trap, after it was passed through sulfuric acid to remove ether.

(b) To 92.4 g. of an ether solution containing 23.3 g. (0.64 mole) of hydrogen chloride cooled in a Dry Ice-bath was added dropwise and with stirring 74 g. (0.64 mole) of ketene diethylacetal over the period of 30 minutes. When warmed, ethyl chloride was collected in a cold-trap and on continued distillation 47.5 g. (84%) of ethyl acetate, b.p. 65–75°, and 6.87 g. (13%) of ethyl β-ethoxycrotonate, b.p. 86–92° (20 mm.), were obtained. Distillation of the material in the cold-trap yielded 36 g. (88%) of ethyl chloride.

Reaction of Ketene Diphenylacetal with Hydrogen Chloride.—(a) To a cooled (−70°) solution of 10 g. (0.047 mole) of this ketene acetal in 10 ml. of ether was added dropwise 27.8 ml. of 1.7 *N* hydrogen chloride in ether over a period of one hour with stirring. Considerable heat of reaction was evident; the stirring was continued for an additional three hours. Then on applying reduced pressure the ether was collected in a cold-trap and 8.29 g. (83%) of the unchanged ketene acetal distilled, b.p. 95–105° (0.5 mm.). The ether from the cold-trap was diluted with water and titrated with 1.00 *N* sodium hydroxide to show the presence of 76% of the hydrogen chloride used in the reaction.

(b) Dry hydrogen chloride (1 equiv.) was dissolved in a gram sample of ketene diphenylacetal, m.p. 26–27°. None of the ketene acetal crystallized on adding a small amount of ether and cooling to the temperature of Dry Ice. On distillation the ketene acetal was recovered in 65% yield and 75% of the hydrogen chloride was found in the ether solution.

(c) When 20 g. (0.095 mole) of the ketene acetal, m.p. 26–27°, was treated with hydrogen chloride gas, 3.46 g. (0.095 mole) was absorbed exothermically. This mixture then was distilled in a system with an Ascarite tube and cold-trap placed beyond the receiver; 7.18 g. of phenol b.p. 62–66° (1 mm.) was collected in the receiver; this amounts to 81% of one mole of phenol per mole of the acetal. The Ascarite tube became hot and gained 1.93 g. in weight and the cold-trap contained 1.61 g. of water; these values account for all of the hydrogen chloride used in the reaction. A black, undistillable residue of 11.08 g. remained.

β-Chloroethyl Propionate.—A mixture of 370 g. (5 moles) of propionic acid, 402.5 g. (5 moles) of ethylene chlorohydrin, 150 ml. of benzene and 0.5 g. sulfosalicylic acid were refluxed using a Cope separator.[7] In 20 hours 101 g. of water layer containing 0.2 mole of acid was obtained. On fractional distillation of the reaction mixture, 445 g. (65%) of β-chloroethyl propionate, b.p. 87.5–88° (60 mm.), or 161–162° (740 mm.), $n^{25}D$ 1.4250, d^{25}_4 1.103, was obtained.

Anal. Calcd. for $C_5H_9ClO_2$: Cl, 26.0. Found: Cl, 25.9.

A 29.3-g. yield of the dipropionate of ethylene glycol, b.p. 93.8–94° (10 mm.) or 211–212° (740 mm.), $n^{25}D$ 1.4186, d^{25}_4 1.039, also was obtained from this reaction. Perkin[8] reports the following properties for this compound: b.p. 210.5–212°, d^{25}_{25} 1.04566.

β-Chloroethylpropionate forms a homogeneous solution with water after heating for three hours on a steam-bath; with aqueous alkali it dissolves in a few minutes at 60–70°. Vogel and Schinz[4] report similar behavior of the compound to which they assigned structure X.

MADISON, WISCONSIN RECEIVED OCTOBER 19, 1950

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(8) W. H. Perkin, *J. Chem. Soc.*, **45**, 505 (1884).