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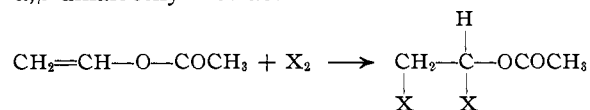
A New Synthesis of Acetals of Chloroacetaldehyde and Bromoacetaldehyde

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A variety of methods for the preparation of the acetals of chloroacetaldehyde and of bromoacetaldehyde has been reported. These may be summarized briefly as follows: (a) chlorination of ethyl alcohol^{2,3}; (b) the reaction of the α,β -dihalogenated ethyl ether with sodium ethylate⁴⁻⁷ or with ethyl alcohol⁸; (c) halogenation of the acetal⁹ preferably in the presence of calcium carbonate¹⁰⁻¹² or sodium ethylate¹³ and (d) the halogenation of paraldehyde followed by treatment with ethyl alcohol.¹⁴⁻¹⁶

Except for the process mentioned in the patent literature,¹³ the yields, where reported, were not highly satisfactory. A synthetic method from a readily available starting material, easily carried out, and resulting in good yields was the purpose of the present work.

There is described in the patent literature¹⁷ the addition of halogens to vinyl acetate yielding α,β -dihaloethyl acetate.

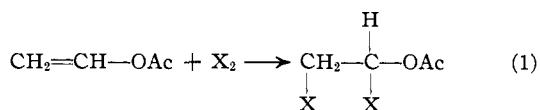


An inspection of this dihalide shows that it contains a very reactive halogen atom as well as an ester grouping that should undergo alcoholysis almost completely. Hence it is reasonable to expect the halogen and the acetoxy group to be replaced by alkoxy groups merely by treatment with the alcohol.

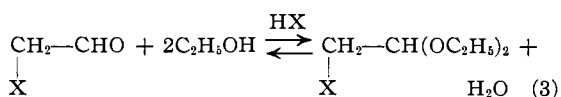
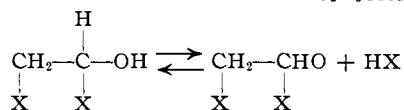
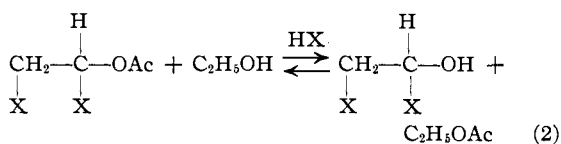
Such was found to be the case. Vinyl acetate dibromide was prepared by the addition of bromine to vinyl acetate. This was then mixed with ethyl alcohol. On standing they reacted and bro-

moacetal was formed. Ethyl acetate and hydrogen bromide were also among the products. In actual practice it was found more efficient to pass the halogen into a solution of vinyl acetate in the alcohol. The addition of halogen to the double bond is so rapid that halogenation of the alcohol is not extensive.

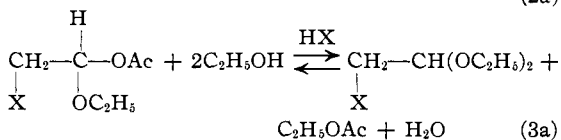
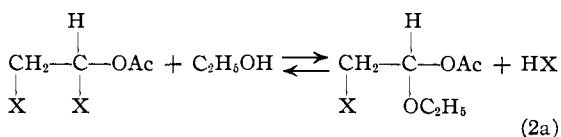
In any mechanism written, undoubtedly the first step is addition of halogen to the double bond.



The acetal may result from this by several paths which may be indicated as follows



or the following may represent the course of reaction



Reactions (2) and (3) are slow and do not occur at the low temperature of the halogen addition. By using methyl alcohol in place of ethyl alcohol, the methyl haloacetal is formed.

Experimental

Purification of Vinyl Acetate.—The practical grade vinyl acetate (purchased from Eastman Kodak Co.) was distilled and the fraction boiling at 69–71° was collected. Distillation gives an anhydrous ester since the water comes

- (1) Present address: Cornell University, Ithaca, N. Y.
- (2) Lieben, *Ann.*, **104**, 114 (1857).
- (3) Fritsch, *ibid.*, **279**, 300 (1894).
- (4) Lieben, *ibid.*, **146**, 193 (1868).
- (5) Wislicenus, *ibid.*, **192**, 112 (1878).
- (6) Natterer, *Monatsh.*, **3**, 444 (1882).
- (7) Kluger, *ibid.*, **26**, 881 (1905).
- (8) Paternò and Mazzara, *Gazz. chim. ital.*, **3**, 254 (1873).
- (9) Pinner, *Ber.*, **5**, 149 (1872).
- (10) E. Fischer and Landsteiner, *ibid.*, **25**, 2551 (1892).
- (11) Willstätter, *ibid.*, **35**, 602 (1902).
- (12) J. v. Braun, *ibid.*, **35**, 3388 (1902).
- (13) German Patent 639,507 (1936); *C. A.*, **31**, 3940 (1937).
- (14) Freundler, *Bull. soc. chim.*, [4] **1**, 70 (1907); Freundler and Ledru, *ibid.*, [4] **1**, 73 (1907).
- (15) Späth, *Monatsh.*, **36**, 4 (1915).
- (16) Rotbart, *Ann. chim.*, [11] **1**, 506 (1934).
- (17) British Patent 325,115 (1929); *C. A.*, **24**, 3800 (1930).

over in the first portion. Care was taken not to distill to dryness in case peroxides were present.

Synthesis of the Acetals

Ethyl Chloroacetal.—A solution of 43 g. (0.5 mole) of vinyl acetate in 150 cc. (2.5 mole) of absolute ethyl alcohol was placed in a 3-necked flask and the flask immersed in a crock containing dry ice-acetone cooling mixture. The flask, where exposed to light, was wrapped with black cloth. Accompanied by vigorous stirring, a stream of dry chlorine, flowing at the rate of 0.4 g. per minute, was bubbled into the solution for ninety minutes, *i. e.*, till the theoretical amount had been added. The mixture was next allowed to warm to room temperature and then stand overnight. It was then poured into an equal volume of iced water, and the ethyl chloroacetal, which separated as an oil, was taken up with ether. The ether solution was washed twice with cold water, then with sodium bicarbonate solution until the ether layer showed no acid reaction to moist litmus, then washed once more with cold water, and finally dried with anhydrous calcium chloride. The ether was removed by distillation from a water-bath, and the residual ethyl chloroacetal was fractionated *in vacuo*. The yield was 62 g. (83% yield) of ethyl chloroacetal boiling at 53–54° (16 mm.); d_{20}^{20} 1.017; n_D^{20} 1.4171; M_D 37.7 (calculated 38.1); Cl, 23.38 (theoretical 23.23).

Further proof of the identity of this compound was obtained by hydrolysis. Ethyl alcohol was identified in the hydrolyzate through its 3,5-dinitrobenzoate, m. p. 92°. Chloroacetaldehyde was identified in the hydrolyzate by oxidation with hydrogen peroxide to chloroacetic acid, m. p. 60°.

An experiment identical to the above except that the chlorine was passed in at a higher temperature (–10 to –5°) resulted in a 70% yield of ethyl chloroacetal.

Methyl Chloroacetal.—This preparation was carried out exactly as above. From 86 g. (1 mole) of vinyl acetate in 200 cc. (5 moles) of methyl alcohol, there resulted 66 g. (53% yield) of methyl chloroacetal boiling at 124.5–126.5° (atmospheric pressure); d_{20}^{20} 1.094; n_D^{20} 1.4150; M_D 28.5 (calcd. 28.8).

Anal. Calcd. for $C_4H_9O_2Cl$: Cl, 28.48. Found: Cl, 28.47.

Hydrolysis of this acetal gave an hydrolyzate in which methyl alcohol was shown to be present by isolation of its 3,5-dinitrobenzoate, m. p. 106°. Hydrolysis followed by oxidation with hydrogen peroxide gave chloroacetic acid, m. p. 62°, showing the presence of chloroacetaldehyde.

Ethyl Bromoacetal.—Air was passed over the surface of 12.5 cc. (0.25 mole) of bromine, and the bromine laden stream of air was led into a solution of 21.5 g. (0.25 mole) of vinyl acetate in 75 cc. (1.3 moles) of absolute ethyl alcohol. During this addition (one and one-half hours) the

solution was stirred. Cooling was effected by a freezing mixture (about –10°). The resulting solution was worked up exactly as above. The yield was 33 g., or 68% of the theoretical, of ethyl bromoacetal boiling at 62–63° (15 mm.); d_{20}^{20} 1.276; n_D^{20} 1.4395; M_D 40.7 (calcd. 41.0).

Another experiment similar to the above except that liquid bromine was added dropwise to the ethyl alcohol solution of vinyl acetate gave a 58% yield of ethyl bromoacetal. This substance is a good lachrymator.

This acetal was characterized as above. Hydrolysis gave ethyl alcohol, identified through its 3,5-dinitrobenzoate, and bromoacetaldehyde, identified by oxidation with hydrogen peroxide to bromoacetic acid, m. p. 45°.

Methyl Bromoacetal.—A solution of 64.5 g. (0.75 mole) of vinyl acetate in 150 cc. (3.7 moles) of methyl alcohol was cooled in a dry ice-acetone mixture. To this was added, with stirring, a solution of 120 g. (38.5 cc., 0.75 mole) of bromine in 100 cc. of chloroform. (It was necessary to use a solution of bromine since liquid bromine solidified in the stem of the dropping funnel.) The addition required two hours, during which time the reaction mixture remained below –40°. The resulting solution was worked up as the others. Thus there was obtained 59 g. (a yield of 46%) of methyl bromoacetal boiling at 48–51° (18 mm.); d_{20}^{20} 1.467; n_D^{20} 1.4475; M_D 30.8 (calcd. 31.7). This compound is also lachrymatory.

As in the above cases, this acetal was characterized by its products of hydrolysis. These were shown to be methyl alcohol and bromoacetaldehyde.

Summary

A new synthesis of acetals of chloroacetaldehyde and bromoacetaldehyde has been investigated. The addition of chlorine to vinyl acetate in the presence of ethyl alcohol or in the presence of methyl alcohol resulted in good yields of the acetals, ethyl chloroacetal and methyl chloroacetal, respectively. Similarly, addition of bromine to vinyl acetate in the presence of methyl or ethyl alcohol formed the corresponding bromoacetals. The yields of the ethyl haloacetals were considerably higher than the yields of the corresponding methyl haloacetals.

As for the mechanism, undoubtedly the halogen first adds to the vinyl acetate, resulting in the α,β -dihaloethyl acetate, which subsequently reacts with the alcohol present in the mixture, giving rise to the acetal of the α -haloacetaldehyde.

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