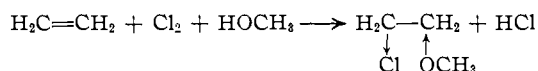


[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Addition of Halogen and Acetoxy to Ethylene¹

BY FRED C. WEBER, G. F. HENNION AND R. R. VOGT

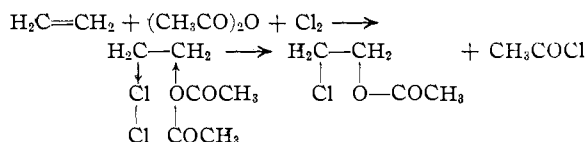
There are known a number of liquid phase reactions in which one atom of halogen and one other negative atom or group are added to an olefin. There is some evidence that the reactions of this type are often trimolecular,² that is, the two addenda appear to originate in separate molecules or ions. The halogen atom may be obtained from a molecule of a halogen or mixed halogen, from a trihalide anion,³ or from a compound in which a halogen atom is linked to oxygen,⁴ nitrogen,⁵ or a very negative organic radical.⁶ The second addendum apparently may be either an anion or a negative fragment taken from a neutral molecule. In these additions it is commonly assumed that one unsaturated carbon atom donates a pair of electrons to bind the electrophilic halogen,⁷ while the nucleophilic addendum supplies a pair of electrons to form a linkage with the other unsaturated carbon atom, *e. g.*



Francis has studied a few cases in which the nucleophilic addendum was the anion of a salt in water solution.⁸ In organic media Ushakov, Chistov and Zelinski⁹ have shown that the halogenation of an olefin in the presence of a silver salt resulted in the addition of an atom of halogen and the anion from the salt. Instances in which the nucleophilic addendum comes from a non-ionized molecule are neither so common nor so well proved. The formation of halohydrins by the halogenation of olefins in water solution and of β -chloroethers by the halogenations of olefins in alcoholic solutions are possible examples, but even in these cases it has been suggested that traces of hydroxyl

or alkoxy ions may be the active addenda. Other chemists have assumed that these additions proceed by the formation of hypochlorous acid or a hypochlorite which then adds to the olefin.

The present paper describes mixed chlorinations in which the nucleophilic fragment, the acetoxy group, was supplied by acetic acid, acetic anhydride, or methyl acetate, resulting in the formation of β -chloroacetates. In dry acetic anhydride or methyl acetate the existence of acetate ions appears improbable, and the presence of molecules of the hypochlorite type also is not to be expected. It is concluded that the molecules of acetic acid, acetic anhydride, or methyl acetate may enter the reaction as donors of electrons, *e. g.*



In all addition reactions of this general type some olefin dihalide appears along with the desired product of mixed addition. In the present work qualitative observations were made indicating the possibility of altering this ratio by changing the conditions of reaction.

As would be expected if the reactions are trimolecular, an increased proportion of the β -chloroethyl acetate should result if the chlorine concentration in the reaction mixture is kept very low. Since the ester was the desired product, this condition was observed in all reactions by making certain that no chlorine coloration became apparent. When ethylene was chlorinated in acetic acid, the presence of hydrogen chloride seemed to increase the proportion of ethylene dichloride formed. In an attempt to avoid this condition sodium acetate was added in order to throw sodium chloride from solution. This resulted in the formation of some glycol diacetate, possibly by the action of sodium acetate on the β -chloroethyl acetate. Sodium acetate, when introduced into the reaction with acetic anhydride, eliminated acetyl chloride as one of the products.

(1) Paper no. 2 on halogenation in reactive solvents; previous paper, *THIS JOURNAL*, **60**, 1711 (1938).

(2) Shilov and Kanyaev, *J. Phys. Chem. (U. S. S. R.)*, **5**, 654 (1934).

(3) Bartlett and Tarbell, *THIS JOURNAL*, **58**, 466 (1936).

(4) Conant and Jackson, *ibid.*, **46**, 1727 (1924); Likhosherstov and Alekseev, *J. Gen. Chem. (U. S. S. R.)*, **4**, 1279 (1934); Muskat and Hudson, *THIS JOURNAL*, **53**, 3178 (1931).

(5) Likhosherstov and Alekseev, *J. Gen. Chem. (U. S. S. R.)*, **3**, 927 (1933); Detouef, *Bull. soc. chim.*, **31**, 102 (1922); Petrov, *J. Gen. Chem. (U. S. S. R.)*, **4**, 1458 (1934); Tuot, *Compt. rend.*, **204**, 697 (1937).

(6) Schmidt, Ascherl and von Knilling, *Ber.*, **59B**, 1876 (1926).

(7) Ingold, *Chem. Rev.*, **15**, 268 (1934).

(8) Francis, *THIS JOURNAL*, **47**, 2340 (1925).

(9) Ushakov, Chistov and Zelinski, *Ber.*, **68B**, 824 (1935).

Experimental

Procedure.—The apparatus used in these experiments consisted of a one-liter, three-necked flask fitted with a reflux condenser, a motor-driven liquid-sealed stirrer, and two gas inlet tubes extending below the surface of the liquid. From the top of the condenser a tube led to two gas bottles connected in series, one of which contained water to permit estimation of the amount of escaping gases by means of the rate of flow of bubbles in this bottle. In all cases, unless stated differently, the reaction flask was cooled in running water, keeping the reaction temperature between 10–15°. About 200 ml. of solvent was used in all reactions and the ethylene and chlorine were added simultaneously at a rate such that the bubble bottle connected to the reflux condenser showed a very slow flow of exit gases with no chlorine color apparent in the reaction flask at any time. At completion of the reaction the mixtures were given a rough separation by distillation. The various fractions were then washed with water, if methyl acetate was the solvent, or with sodium carbonate solution if acetic acid or acetic anhydride had been used, and were then refractionated. The results of the various experiments are given in Table I.

TABLE I

Expt.	Solvent, g.	Dichloride G.	% ^a	Chloroacetate G.	% ^a	Molar ratio	By-products, g.
Acetic acid							
1	240	70	65.7	45	34.3	0.522	Glycol diacetate 6 g.
2 ^c	240	23	46.7	27	44.7	.957	
3 ^d	240	85	62.0	60	38.0	.611	
Acetic anhyd.							
1	152	55	83.1	13	16.9	0.195	AcCl, 22 g.
2 ^c	204	3	12.9	25	87.1	6.770	

Methyl acetate

1 182 63 62.1 37 29.6 0.476 $\left\{ \begin{array}{l} \text{Trichloroethyl} \\ \text{acetate, 15 g.} \\ \text{Methyl chloro-} \\ \text{ride, }^e \text{ 15 g.} \end{array} \right.$

^a Molar percentage based upon amount of ethylene appearing in the products. ^b Molar ratio of β -chloroethyl acetate/1,2-dichloroethane. ^c Forty-one grams of sodium acetate was suspended in the reaction mixture. ^d This reaction was run at 40–43° to illustrate a favorable increase in the molar ratio with an increase in temperature. ^e The methyl chloride was condensed by washing the exit gases during the distillation with concd. potassium hydroxide, concd. sulfuric acid and then condensing in a flask cooled in liquid ammonia.

PHYSICAL DATA

Compound	B. P., °C.	Mm.	n_D	d	Calcd.	MR Obsd.
β -Chloroethyl acetate	142–144	743	1.4234 ²⁰			
	54–56	25	1.4216 ²⁷	1.1455 ²⁷	27.19	27.18
Ethylene dichloride	83–86	743	1.4420 ²⁷	1.2403 ²⁷	21.17	21.12
Glycol diacetate	70–74	10	1.4198 ²⁰			
			1.4181 ²⁸	1.1032 ²⁸	33.22	33.27
Trichloroethyl acetate ^a	88–91	9	1.4691 ²⁸	1.4239 ²⁸	36.92	37.46
Acetyl chloride ^b	48–55	743				

^a Anal. Calcd. for $C_4H_5Cl_3O_2$: Cl, 55.62. Found: Cl, 54.84. ^b Anilide, m. p. 113–114°.

Summary

It has been shown that β -chloroethyl acetate and ethylene dichloride are the chief products when ethylene is chlorinated in acetic acid, acetic anhydride, or methyl acetate.

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Chlorination of Vinylacetylene in Methanol¹

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Chlorination of vinylacetylene in methanol solution gives excellent yields of chlorinated material containing oxygen. The product, however, is a complex mixture of wide boiling range and it was found difficult to isolate pure compounds of known structure. In such a reaction it is possible to have addition of various addenda ($-\text{Cl}$, $-\text{OCH}_3$, $=\text{O}$, $-\text{H}$) in many ways due to the high degree of unsaturation of vinylacetylene. On the basis of compounds isolated it appears that the main reactions proceed as indicated.

Of these many substances only the first inter-

(1) Paper XXXII on the chemistry of substituted acetylenes and their derivatives; previous paper, *THIS JOURNAL*, **61**, 887 (1939). Also paper No. 3 on halogenation in reactive solvents; *cf. ibid.*, **61**, 1457 (1939).

mediate (I) and the end-products (IV, V, VII) were isolated. Even in these cases it was difficult to obtain pure compounds. The groups $-\text{OCH}_3$ and $-\text{Cl}$ have about the same weight, refraction and influence on the boiling point. Difficulty in separating methoxy compounds from the corresponding chlorides has been experienced by others.² Nevertheless the physical properties and analytical data for the various compounds agree sufficiently well to determine their composition. In addition it was necessary to establish the structures of (V) and (VII).

The ketone (V) failed to give carbonyl group

(2) Likhosherstov and Alekseev, *Acta Univ. Voronegiensis*, **8**, No. 2, 64 (1935).