

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	Trichloroethyl acetate, 15 g. Methyl chloride, ^e 15 g.

^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

BY ARTHUR A. BAUM, R. R. VOGT AND G. F. HENNION

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.

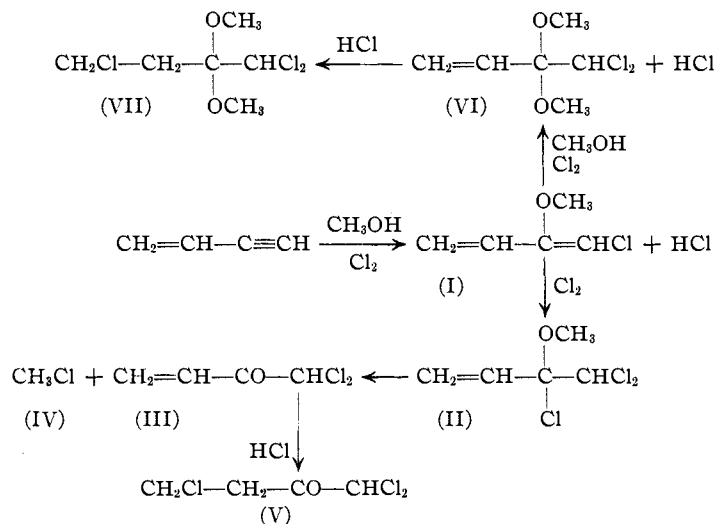
Of these many substances only the first inter-

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

(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).

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



tests, which we have observed to be typical of such compounds. It does undergo the haloform reaction, though slowly because of its insolubility. Due to its mode of formation and properties (V) might be formulated as either 1,1,3-trichloro-2-butanone or the 1,1,4-isomer. The former compound is recorded in the literature³ and boils considerably lower than the one isolated from this reaction. The assigned 1,1,4-trichloro structure also is the one which would be expected to result from the dichloro ketone (III).

Proof for the ketal structure (VII) is not so conclusive. Molecular weight determinations and analyses for methoxyl and chlorine agree with the anticipated values. It does not hydrolyze readily, which is characteristic of 1,1-dichloro-2,2-dimethoxy compounds.⁴ Heating with acetic acid containing a little water and sulfuric acid gave methyl acetate, indicative of a ketal structure. The last chlorine atom is provisionally assigned the 4-position by analogy with the ketone (V). The mechanism of such chlorination reactions has been discussed in previous papers.⁵

Experimental

Reaction of Chlorine with Vinylacetylene in Methanol.—

In a 3-liter 3-necked flask with a reflux condenser, mechanical stirrer, and gas-inlet tubes, was placed 2000 ml. of anhydrous methanol. The inlet tubes were so arranged that the vinylacetylene was led in beneath the surface of the methanol while the chlorine passed in over the surface.

The rate of addition of the two gases was so regulated that there was neither an appreciable excess of chlorine

(3) Schneider, *Monatsh.*, **20**, 411 (1899).

(4) Previous work showed that 1,1-dichloro-2,2-dimethoxyhexane could not be hydrolyzed.

(5) Verbanc and Hennion, *This Journal*, **60**, 1711 (1938); Weber, Hennion and Vogt, *ibid.*, **61**, 1457 (1939).

present, as evidenced by the absence of a greenish-yellow color in the liquid, nor gases escaping from the system due to incomplete reaction. These limitations required that a little less than two moles of chlorine be added per mole of vinylacetylene. In a typical experiment 3 moles of vinylacetylene and 5 moles of chlorine were added over a period of eleven hours. The reaction flask was cooled by a water-bath so that the temperature of reaction was maintained at 30°.

The reaction product was distilled through a glass-helix packed, total condensation, partial take-off column without any preliminary treatment. When all the methanol had been removed, the liquid in the still-pot separated into two layers. The upper layer was an aqueous solution of hydrogen chloride. The lower, organic layer was washed, dried and fractionally distilled.

Successive fractions were collected in 15-ml. vials. Indices of refraction and chlorine contents were determined for these samples. Fractions were recombined on this basis and refractionated by refractive index and boiling point. In addition to the compounds listed below, a considerable amount of a complex mixture boiling over the range of temperature between the ketone and ketal was obtained from which no definite compound could be isolated. The yields reported are the averages of several experiments and are based on the vinylacetylene used.

1-Chloro-2-methoxy-1,3-butadiene (I).—Obtained 35.6 g. (10% yield); b. p. 57.4–57.6° at 48 mm.; d^{20} 1.0807; n^{20}_D 1.4476; *MR* (calcd.), 30.86; *MR* (obsd.), 29.33.

Anal. Calcd. for $\text{C}_4\text{H}_7\text{ClO}$: Cl, 30.0; methoxy, 26.2; mol. wt., 118.5. Found: Cl, 33.8 (av. of three detns.); methoxy, 30.3 (av. of three detns.); mol. wt., cryoscopic in benzene, 118.3 (av. of four detns.).

1,1,4-Trichloro-2-butanone (II).—Obtained 42.1 g. (8% yield); b. p. 81.5–82.5° at 18 mm.; d^{20} 1.3356; n^{20}_D 1.4853; *MR* (calcd.), 35.28; *MR* (obsd.), 37.68.

Anal. Calcd. for $\text{C}_4\text{H}_5\text{Cl}_3\text{O}$: Cl, 60.7; mol. wt., 175.5. Found: Cl, 60.4 (av. of five detns.); mol. wt., cryoscopic in benzene, 178.7 (av. of four detns.).

1,1,4-Trichloro-2,2-dimethoxybutane (VII).—Obtained 133 g. (20% yield); b. p. 103° at 3 mm.; d^{20} 1.3785; n^{20}_D 1.4850; *MR* (calcd.), 47.79; *MR* (obsd.), 46.55.

Anal. Calcd. for $\text{C}_6\text{H}_{11}\text{Cl}_3\text{O}_2$: Cl, 48.1; methoxy, 28.0; mol. wt., 221.5. Found: Cl, 48.3; methoxy, 28.2; mol. wt., cryoscopic in benzene, 222.7 (av. of eight detns.).

Identification of Methyl Chloride.—In one experiment the methyl chloride formed was isolated and identified. During the primary distillation 68.1 g. of gas was condensed which on fractionation through a Davis column⁶ gave 58 g. (38.2% yield, based on one mole of methyl chloride from a mole of vinylacetylene) of methyl chloride, b. p. –24°. The methyl chloride was identified by its b. p. and vapor density. Calcd. mol. wt., 50.49; mol. wt. found by vapor density method, 50.66.

Reaction of 1,1,4-Trichloro-2,2-dimethoxybutane with Acetic Acid.—To a mixture of 100 ml. of glacial acetic

(6) Davis, *Ind. Eng. Chem., Anal. Ed.*, **1**, 63 (1929).

acid, 5 ml. of concd. sulfuric acid, and 5 ml. of water was added 22 g. of the ketal (VII). After a short period of refluxing the mixture was distilled through a short column, yielding 11 g. (75% yield) of methyl acetate. This treatment split hydrogen chloride from the molecule and polymerized the residue so that no ketone could be isolated.

Acknowledgment.—The authors acknowledge the kind assistance of the du Pont Company for furnishing the vinylacetylene used in this work.

Summary

Vinylacetylene has been chlorinated in methanol solution to yield a complex mixture from which methyl chloride, 1-chloro-2-methoxy-1,3-butadiene, 1,1,4-trichloro-2-butanone, and 1,1,4-trichloro-2,2-dimethoxybutane have been isolated. Water and hydrogen chloride are by-products of the reaction.

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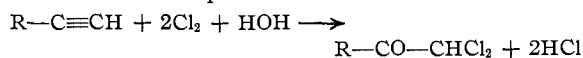
Chlorination of 1-Hexyne in Reactive Solvents¹

BY R. O. NORRIS, R. R. VOGT AND G. F. HENNION

Introduction

Continuing our studies of chlorination in reactive solvents, 1-hexyne has been chlorinated in various solutions and the products identified. Five media were used: water, *t*-butyl alcohol, acetic acid, acetic anhydride and methyl acetate. Of these only water, acetic acid and acetic anhydride gave products containing oxygen as well as chlorine. In the other cases only chlorinated products were obtained. In all experiments a mixture resulted which could be separated by fractional distillation.

Chlorination of a 1-hexyne emulsion in water gave *trans*-1,2-dichloro-1-hexene (I), 1,2,2-trichlorohexane (II), 1,1,2,2-tetrachlorohexane (III) and 1,1-dichloro-2-hexanone (IV). The first and third of these require only chlorine addition, the second chlorine and hydrogen chloride addition, while the fourth presumes reaction with water.

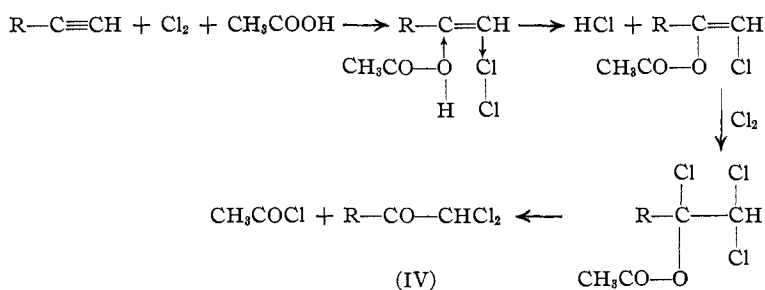


t-Butyl alcohol solution gave only *trans*-1,2-dichloro-1-hexene (I) and 1,2,2-trichlorohexane (II). The alcohol appeared to form *t*-butyl hypochlorite, thus furnishing the hydrogen chloride required for (II). Methyl acetate gave (I) and (II) and also some *cis*-1,2-dichloro-1-hexene (V) as well as higher chlorinated products.

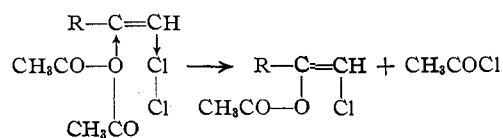
Solutions in either acetic acid or acetic anhydride afforded identical products: (II), (IV), (V),

(1) Paper XXXIII on the chemistry of substituted acetylenes and their derivatives; also paper No. 4 on halogenation in reactive solvents; previous paper in both series, *THIS JOURNAL*, **61**, 1458 (1939)

acetyl chloride, and hexyne polychlorides. The formation of (IV) and acetyl chloride may be explained on the following basis.



In acetic anhydride the first intermediate would give acetyl chloride rather than hydrogen chloride.



The formation of the *trans*-dichloride (I) in some instances and the *cis* isomer (V) in others presents a problem not understood at present. Methanol, like water and *t*-butyl alcohol, gave the *trans* compound.² The identification of these dichlorides (I and V) was by dipole moment. The lower boiling one (*trans*) showed a moment of 0.57×10^{-18} e. s. u., while the higher boiling one (*cis*) gave 1.993×10^{-18} e. s. u.³

The yields of products obtained and their properties are given in Tables I and II.

(2) Verbanc and Hennion, *ibid.*, **60**, 1711 (1938).

(3) The *cis* compound would be expected to be less compact in molecular structure than the *trans* isomer and therefore higher boiling. We are indebted to Dr. Harold Goebel for the dipole moment determinations.