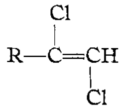
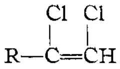
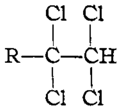
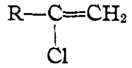
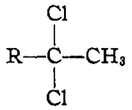
Table I

Physical Properties of Chlorides and Hydrochlorides of 1-Hexyne

Compound		 $R{-}\overset{Cl}{C}{=}\underset{Cl}{CH}$	 $R{-}\overset{Cl}{C}{=}\overset{Cl}{CH}$	 $R{-}\underset{Cl}{\overset{Cl}{C}}{-}\underset{Cl}{\overset{Cl}{CH}}$	 $R{-}\underset{Cl}{C}{=}CH_2$	 $R{-}\underset{Cl}{\overset{Cl}{C}}{-}CH_3$
Boiling point	°C.	63–65	88	99–101	113	68
	Mm.	32	30	14	740	49
d^{25}_4		1.1167	1.0812	1.3096	0.8886	1.0150
n^{25}D		1.4576	1.4631	1.4888	1.4278	1.4353
Mol. wt.	Calcd.	153	153	224	119	155
	Obsd.	152	156	226	118	156
MR	Calcd.	39.2	39.2	49.4	34.3	39.8
	Obsd.	39.2	39.0	49.2	34.3	39.8
Cl, %	Calcd.	46.4	46.4	63.4	29.9	45.8
	Obsd.	46.1	46.1	63.6	29.4	46.2

Addition of Hydrogen Chloride to 1-Hexyne.—A solution of 82 g. (1.0 mole) of 1-hexyne in 350 ml. of benzene was placed in a one-liter, three-necked flask equipped with an efficient stirrer reflux condenser, and a hydrogen chloride inlet tube. To the solution was added 3 g. of bismuth chloride. Dry hydrogen chloride gas was then bubbled beneath the surface of the liquid, at a temperature of 80–85°, until no more was absorbed. The increase in weight during the addition of hydrogen chloride was 37 g. The solution was then washed twice with water, with dilute sodium carbonate solution, again with water, dried over calcium chloride, and fractionally distilled: yield, 24 g. (20%) of 2-chloro-1-hexene and 62 g. (40%) of 2,2-dichlorohexane.

Preparation of 2-Chloro-1-hexene by Desaturation.—A solution of 78 g. (0.5 mole) of 2,2-dichlorohexane in 200 ml. of *n*-propyl alcohol was placed in a 500-ml. three-necked flask equipped with an efficient stirrer, and a reflux condenser. The solution was heated to 95° and a slight excess of solid potassium hydroxide added. After heating for five hours the reflux condenser was replaced with a short Vigreux column and the contents of the flask distilled to dryness. The distillate was washed three times with water, the organic layer separated and dried over anhydrous magnesium sulfate: yield, 35 g. (60.5%) of 2-chloro-1-hexene.

Addition of Chlorine to 2-Chloro-1-hexene.—The same procedure was followed as in the chlorination of 1-hexyne, except that the temperature was maintained at 35–40°: yield, 20.3 g. (26.7%) of *cis*-1,2-dichloro-1-hexene and 28.5 g. (25.4%) of 1,1,2,2-tetrachlorohexane.

Summary

Chlorination of 1-hexyne in inert solvents in the presence of antimony pentachloride gives *trans*-1,2-dichloro-1-hexene and 1,1,2,2-tetrachlorohexane as the sole products.

Bismuth chloride is an effective catalyst for the addition of hydrogen chloride to 1-hexyne.

The reaction of chlorine with 2-chloro-1-hexene in the presence of antimony pentachloride leads to *cis*-1,2-dichloro-1-hexene and 1,1,2,2-tetrachlorohexane.

Hydrogen chloride could not be added to either *cis*- or *trans*-1,2-dichloro-1-hexene.

Notre Dame, Indiana Received March 15, 1940

[Contribution from the Chemical Laboratories of the University of Notre Dame]

Chlorination of the Acetylenic Alcohols Derived from Acetone[1]

By G. F. Hennion and G. M. Wolf

Introduction

In general, chlorination of acetylenes in oxygen-containing solvents gives mixtures of chlorinated compounds.[2] Continuing these studies the action of chlorine on two acetylenic alcohols has been investigated. Dimethylethynylcarbinol (I) and 2,5-dimethyl-3-hexyne-2,5-diol (II) were selected for this work because they are easily obtainable in large quantity.[3] Carbon tetrachloride, methanol, and water were used separately as solvents. Methanol and water function also as reagents in the chlorination reactions, thus affording products not obtainable when carbon tetrachloride is used.

Chlorine added directly to (I) in carbon tetra-

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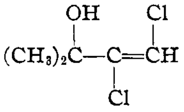
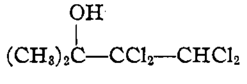
(1) Paper XXXIX on substituted acetylenes and their addition products; previous paper, This Journal, **62**, 1367 (1940). Also paper No. 6 on halogenation in reactive solvents; *cf.* This Journal, **62**, 449 (1940).

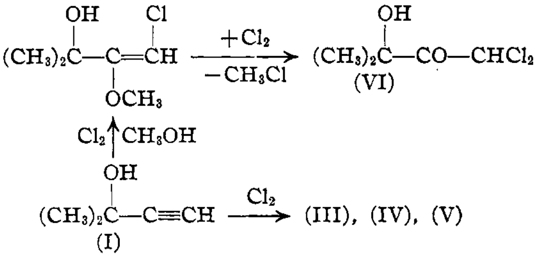
(2) Hennion, *et al.*, *ibid.*, **60**, 1711 (1938); **61**, 1458, 1460 (1939); **62**, 449 (1940).

(3) Froning and Hennion, *ibid.*, **62**, 653 (1940).


$$(CH_3)_2\overset{OH}{C}-\underset{Cl}{C}=\overset{Cl}{C}H$$
(III)

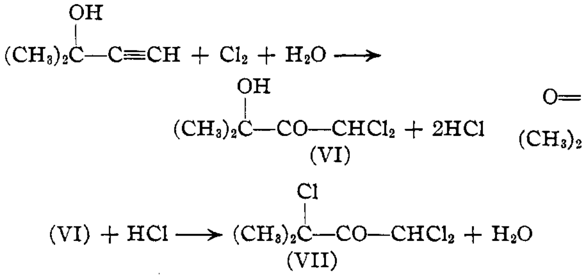

$$(CH_3)_2\overset{OH}{C}-CCl_2-CHCl_2$$
(IV)

chloride to yield only *trans*-1,2-dichloro-3-methyl-1-butene-3-ol (III) and 1,1,-2,2-tetrachloro-3-methyl-3-butanol (IV). A methanol solution of (I) reacted at 25–30° to give (III), (IV), *cis*-1,2-dichloro-3-methyl-1-butene-3-ol (V) and 1,1-dichloro-3-methyl-3-hydroxy-2-butanone (VI). These products may be explained according to the following mechanism, based on previous work.[2]

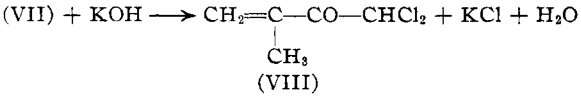

$$(CH_3)_2\overset{OH}{C}-\underset{OCH_3}{C}=\overset{Cl}{C}H \xrightarrow[-CH_3Cl]{+Cl_2} \underset{(VI)}{(CH_3)_2\overset{OH}{C}-CO-CHCl_2}$$
$$Cl_2\uparrow CH_3OH$$
$$\underset{(I)}{(CH_3)_2\overset{OH}{C}-C\equiv CH} \xrightarrow{Cl_2} (III), (IV), (V)$$

When the reaction in methanol was carried out at 60–65°, (V) was eliminated and the yield of (IV) was increased.

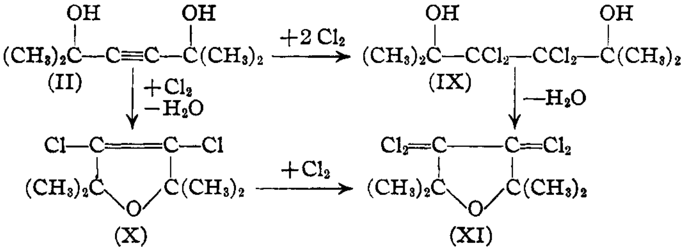
Chlorination of (I) in aqueous solution gave (V) and considerable quantities of 1,1,3-trichloro-3-methyl-2-butanone (VII). No doubt (VII) was formed by reaction of hydrogen chloride with the tertiary hydroxyl group of (VI).


$$(CH_3)_2\overset{OH}{C}-C\equiv CH + Cl_2 + H_2O \longrightarrow \underset{(VI)}{(CH_3)_2\overset{OH}{C}-CO-CHCl_2 + 2HCl}$$
$$(VI) + HCl \longrightarrow \underset{(VII)}{(CH_3)_2\overset{Cl}{C}-CO-CHCl_2 + H_2O}$$

Attempts to revert (VII) to (VI) by treatment with potassium hydroxide resulted in desaturation and gave 1,1-dichloro-3-methyl-3-butene-2-one (VIII).

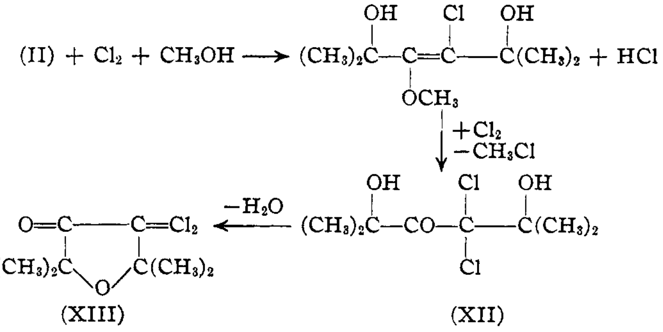

$$(VII) + KOH \longrightarrow \underset{(VIII)}{CH_2=\underset{CH_3}{C}-CO-CHCl_2 + KCl + H_2O}$$

Chlorination of the acetylenic glycol (II) invariably was accompanied by considerable cyclodehydration and thus gave rise to furan derivatives as well as direct addition products. In carbon tetrachloride solution (II) gave (IX), (X) and (XI).



These results are in accord with those of Kruglov,[4] who obtained a 30% yield of 2,5-dimethyl-3,4-dibromo-3-hexenediol and nearly a 70% yield of 2,2,5,5-tetramethyl-3,4-dibromodihydrofuran by the action of bromine on a chloroform solution of (II).

Chlorination of (II) in methanol solution also gave (XI). In addition small amounts of 2,5-dimethyl-2,5-dihydroxy-3,3-dichloro-4-hexanone (XII) were obtained as well as considerable quantities of 2,2,5,5-tetramethyl-3,3-dichlorotetrahydro-4-furanone (XIII). There was evidence also for small amounts of a methoxyl-containing product, b. p. 47–49° at 6 mm., not identified for lack of sufficient material.



Aqueous solutions of (II) absorbed chlorine readily and gave preponderantly (XIII) and low yields of its precursor (XII).

Yield data for the various experiments are given in Tables I and II. Physical constants and analytical data are given in Table III. Parachor values were determined to establish structures for the products. Practically all of the compounds enumerated are unstable and darken upon standing. The dichloroketones are

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[4] Kruglov, *J. Gen. Chem.* (U. S. S. R.), **6**, 925 (1936); *C. A.*, **31**, 682 (1937).

TABLE I

CHLORINATION OF ONE-MOLE LOTS OF DIMETHYLETHYNYLCARBINOL IN 500 ML. OF SOLVENT AT 25–30°

Solvent	Cl_2, g. absorbed	Yields of products, %[a] (III)	(IV)	(V)	(VI)	(VII)
CCl_4	148	22.0 (7.7)[a]	44.6 (38.5)	.....	.....	.....
CH_3OH	160	20.6 (7.2)	35.6 (32.1)	6.9 (3.1)	10.5 (4.9)	.....
H_2O	134	.....	.....	15.5 (8.0)	.....	30.0 (21.2)

[a] Values in parentheses are for purified compounds. Other values are for crude samples obtained on first distillation.

TABLE II

CHLORINATION OF HALF-MOLE LOTS OF 2,5-DIMETHYL-3-HEXYNE-2,5-DIOL IN 500 ML. OF SOLVENT AT 60–65°

Solvent	Cl_2, g. absorbed	Yields of products, %[a] (IX)	(X)	(XI)	(XII)	(XIII)
CCl_4	135	16.9 (4.6)[a]	20.5 (8.6)	45.8 (26.8)	.....	.....
CH_3OH	123	.....	.....	46.6 (30.1)	1.7 (1.5)	40.5 (14.6)
H_2O	106	.....	.....	.....	3.5 (3.2)	80.5 (57.5)

[a] Values in parentheses are for purified compounds. Other values are for crude samples obtained on first distillation.

TABLE III

ANALYTICAL AND PHYSICAL DATA

Compd.	B. p., °C. at 6 mm.	$n^{20}D$	d^{20}	Mol. wt.[a] Calcd.	Mol. wt.[a] Obsd.	% Cl Calcd.	% Cl Obsd.	MR Calcd.	MR Obsd.	$[P]$[b] Calcd.	$[P]$[b] Obsd.
(III)	64–66	1.4778	1.213	155.0	156	45.74	45.4	36.08	36.22	312.6	304.6
(IV)	95–97	1.5086	1.488	225.9	223	62.78	62.8	46.28	45.24	398.0	389.6
(V)	76–78	1.4822	1.268	155.0	159	45.74	46.35	36.08	34.87	312.6	303.4
(VI)	58–60	1.4825	1.339	171.0	169	41.46	41.68	36.56	36.45	332.6	330.7
(VII)	61–63	1.4765	1.345	189.5	184	56.13	56.1	39.90	39.77	349.8	347.6
(VIII)	64–66	1.4752	1.261	153.0	154	46.34	46.4	34.57	34.18		
(IX)	82–84	1.5006	1.346	284.0	279	49.93	49.6	61.66	62.06	535.0	531.3
(X)	46–48	1.4638	1.125	195.1	190	36.35	37.7	47.85	47.80	403.9	404.8
(XI)	96–98	1.5110	1.354	266.0	261	53.32	53.8	58.05	58.85	489.3	481.4
(XII)	M. p. 99°			229.1	234	30.95	31.1				
(XIII)	84–86	1.4880	1.243	211.1	213	33.60	33.9	48.33	48.85	423.9	419.2

[a] Cryoscopic method in benzene. [b] Calculated from values of Sugden.

the least stable and turn almost black after several weeks.

Experimental

Reagents.—Dimethylethynylcarbinol (I) and 2,5-dimethyl-3-hexyne-2,5-diol (II) were prepared as previously described.[2] Further quantities of (II) were obtained by the method of Macullum.[5]

Chlorination of (I) in Methanol.—Into a 1-liter 3-necked flask equipped with a mechanical stirrer, reflux condenser and a gas inlet tube were introduced 500 ml. of anhydrous methanol and 84 g. (1 mole) of (I). A moderately rapid stream of chlorine was introduced below the surface of the agitated solution. The temperature was held at 25–30°, by occasional cooling, for seven hours, after which time the solution acquired a greenish-yellow color. Methanol was removed by distillation through a helix-packed total-condensation, partial take-off column. The residue separated into two layers. The upper layer was an aqueous solution of hydrogen chloride. The lower layer (165 g.) was fractionally distilled, *in vacuo*, and successive small fractions collected in 15-ml. vials. Fractions were recombined on the basis of boiling range and refractive index and refractionated.

Chlorination of (I) in Water.—After chlorination as described above the reaction mixture separated into two layers. The organic material was removed, washed with water, twice with 10% sodium bicarbonate solution, again with water, and dried over calcium chloride. Fractional distillation at 6 mm. gave (V) and (VII).

Haloform Reaction with (VI).—Ten grams of (VI) and 20 g. of bleaching powder were mixed with 100 ml. of distilled water, refluxed for thirty minutes and steam distilled. The distillate contained 3 g. of chloroform, b. p. 59–60°; d^{20} 1.485; $n^{20}D$ 1.4443.

Desaturation of (VII) to (VIII).—To 14 g. of (VII) in 30 ml. of methanol was added 10 ml. of 50% potassium hydroxide solution. There was an immediate exothermic reaction. The potassium chloride was removed by filtration and methanol distilled from the filtrate. The residue was dried and fractionated to obtain (VIII). The yield was 60% of the theoretical.

Chlorination of (II) in Methanol.—Seventy-one grams (0.5 mole) of (II) was dissolved in 500 ml. of methanol and chlorinated as described above. Temperature was held at 60–65°. After the chlorination reaction, methanol was distilled directly from the product. The organic layer was removed from the residue and fractionally distilled at 6 mm. Fractions boiling between 85–95° (6 mm.) deposited fine white crystals on standing. These fractions were filtered and the solid crystallized from petroleum ether to yield (XII), m. p. 99°. In addition (XI) and (XIII) were obtained as shown in Table II.

Other Chlorinations.—The above procedures were followed for the six chlorination reactions studied. Since

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(5) Macullum, U. S. Patent 2,162,676 (1939).

mixtures of products were obtained in all cases, it was necessary to fractionate repeatedly so as to obtain compounds sufficiently pure for analysis. All distillations were carried out at 6 mm., through suitable fractionating columns, and small fractions collected in 15-ml. vials. The yields of crude products were estimated from the first distillation. Ordinarily 10 to 20 fractions were collected. These were recombined for subsequent distillations on the basis of boiling range, refractive index, and chlorine content.

Summary

Dimethylethynylcarbinol and 2,5-dimethyl-3-hexyne-2,5-diol have been chlorinated, each in three solvents: carbon tetrachloride, methanol, and water. The products have been identified and characterized.

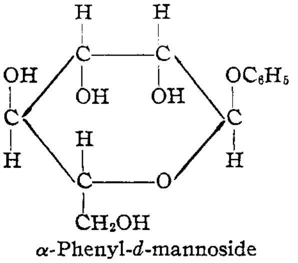
NOTRE DAME, INDIANA RECEIVED MARCH 2, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY, LEIPZIG, GERMANY]

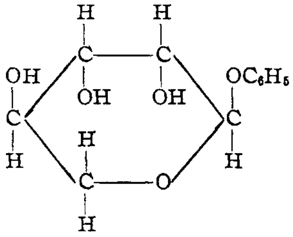
The Action of Almond Emulsin on α-Phenyl-*d*-lyxoside

BY WILLIAM WARD PIGMAN[1]

The occurrence in almond emulsin of enzymes which hydrolyze glycosides is well known. However, with very few exceptions, the previous work with these enzymes has been confined to glycosides of naturally occurring sugars. In an earlier paper,[2] the results of a study of the action of almond emulsin on a number of methyl glycosides of synthetic sugars were reported and in no instance was an hydrolysis observed which was larger than the experimental error. In general, the phenyl glycosides are much better materials for such studies since, when they are hydrolyzable, the rate of hydrolysis is much greater than that of the corresponding methyl glycosides. Also, a very sensitive method for the measurement of the degree of hydrolysis of the phenyl glycosides is available.[3] The negative results reported for α-methyl-*d*-lyxoside in the previous work[2] were somewhat surprising since α-phenyl-*d*-mannoside is known to be hydrolyzed by the enzymes in almond emulsin and as illustrated in the following formulas the pyranose rings of the phenyl-*d*-mannosides and lyxosides are identical except for the groups attached to the fifth carbon atom.



α-Phenyl-*d*-mannoside



α-Phenyl-*d*-lyxoside

In order to settle this question definitely α-phenyl-*d*-lyxoside was prepared according to the general method of Helferich and Schmitz-Hillebrecht.[4] The new substance which most probably has a pyranose structure and which has the expected rotation for the alpha isomer was found to be hydrolyzed by almond emulsin (the "Rohferment" of Helferich[5]). The rates of hydrolysis of β-phenyl-*d*-glucoside and α-phenyl-*d*-mannoside also were determined under the same conditions. The results are summarized in Table I.

TABLE I

Glycoside	$k \times 10^3$	Enzyme efficiency (Wertigkeit)
α-Phenyl-*d*-lyxoside	0.088[a]	9.4×10^{-4}
α-Phenyl-*d*-mannoside	3.5	0.15[b]
β-Phenyl-*d*-glucoside	7.3	.31[b]

[a] The enzyme concentration was four times as great for the lyxoside experiments as for the other experiments.

[b] The substrate concentrations were more dilute than those normally used but the values found are substantially the same as those reported by Helferich and Winkler.[6]

The value of 9.4×10^{-4} found for the α-phenyl-*d*-lyxoside is the smallest value reported for a hydrolyzable phenyl glycoside and compares with a value of 20×10^{-4} for β-phenyl-*d*-xyloside and a value of 3000×10^{-4} for β-phenyl-*d*-glucoside.

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[1] This work was made possible by a grant from the Lalor Foundation of Wilmington, Del. The present address of the author is National Bureau of Standards, Washington, D. C.

[2] B. Helferich, W. W. Pigman and H. S. Isbell, *Z. physiol. Chem.*, **261**, 55 (1939).

[3] B. Helferich, H. Appel and R. Gootz, *ibid.*, **215**, 282 (1933).

[4] B. Helferich and E. Schmitz-Hillebrecht, *Ber.*, **66**, 378 (1933).

[5] B. Helferich, S. Winkler, R. Gootz, O. Peters and E. Günther, *Z. physiol. Chem.*, **208**, 91 (1932).

[6] B. Helferich and S. Winkler, *ibid*,. **209**, 269 (1932).