

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.

NOTRE DAME, INDIANA

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

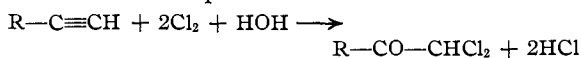
Chlorination of 1-Hexyne in Reactive Solvents¹

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.

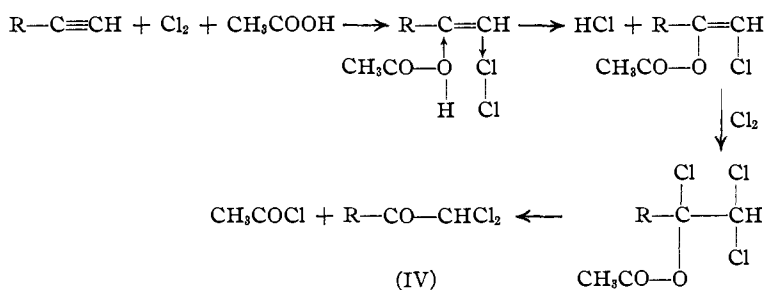


t-Butyl alcohol solution gave only *trans*-1,2-dichloro-1-hexene (I) and 1,2,2-trichlorohexane (II). The alcohol appeared to form *t*-butyl hypochlorite, thus furnishing the hydrogen chloride required for (II). Methyl acetate gave (I) and (II) and also some *cis*-1,2-dichloro-1-hexene (V) as well as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

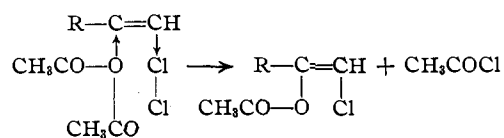
Solutions in either acetic acid or acetic anhydride afforded identical products: (II), (IV), (V),

(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.

TABLE I
WEIGHTS OF REAGENTS AND PRODUCTS IN THE CHLORINATION OF ONE MOLE OF 1-HEXYNE AT 40-50°

Reagents			Products (R = n-C ₅ H ₁₁)						
Solvent	Vol., ml.	Cl ₂ , g.	$\begin{array}{c} \text{Cl} \ \text{Cl} \\ \ \ \\ \text{RC}=\text{CH} \end{array}$	$\begin{array}{c} \text{Cl} \\ \\ \text{RC}=\text{CH} \\ \\ \text{Cl} \end{array}$	$\begin{array}{c} \text{Cl} \ \text{Cl} \\ \ \ \\ \text{RC}-\text{CH}_2 \end{array}$	$\begin{array}{c} \text{Cl} \ \text{Cl} \\ \ \ \\ \text{RC}-\text{CH} \\ \ \ \\ \text{Cl} \ \ \text{Cl} \end{array}$	$\begin{array}{c} \text{Cl} \ \text{Cl} \\ \ \ \\ \text{RC}-\text{C}-\text{Cl} \\ \ \ \\ \text{Cl} \ \ \text{Cl} \end{array}$	$\begin{array}{c} \text{Cl} \\ \\ \text{RCO}-\text{CH} \\ \\ \text{Cl} \end{array}$	CH ₂ COCl
HOH	300	150	..	20	20	28	..	20	...
<i>t</i> -BuOH	190	180	..	102	23
MeOAc	250	250	35	7	19	28	48
AcOH	300	112	23	...	18	7	..	34	20
Ac ₂ O	285	142	5	...	12	26	..	43	100

TABLE II
PROPERTIES OF COMPOUNDS PREPARED BY CHLORINATION OF 1-HEXYNE IN VARIOUS SOLVENTS

Compd.	B. p., °C.	Mm.	<i>d</i> ²⁵	<i>n</i> ^{25D}	Mol. wt.		% Cl		<i>MR</i>	
					Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.
$\begin{array}{c} \text{Cl} \ \text{Cl} \\ \ \ \\ \text{R}-\text{C}=\text{CH} \\ \\ \text{Cl} \end{array}$	80-82	25	1.076	1.4629	153	155	46.4	47.5	39.2	38.8
$\begin{array}{c} \text{Cl} \\ \\ \text{R}-\text{C}=\text{CH} \\ \\ \text{Cl} \end{array}$	55-57	25	1.051	1.4543	39.2	39.4
$\begin{array}{c} \text{Cl} \ \text{Cl} \\ \ \ \\ \text{R}-\text{C}-\text{CH}_2 \end{array}$	90-93	10	1.225	1.4760	189	190	56.0	55.2	44.5	43.7
$\begin{array}{c} \text{Cl} \ \text{Cl} \\ \ \ \\ \text{R}-\text{C}-\text{CH} \\ \ \ \\ \text{Cl} \ \ \text{Cl} \end{array}$	108-110	10	1.320	1.4890	224	222	63.4	63.0	49.4	49.2
$\begin{array}{c} \text{Cl} \ \text{Cl} \\ \ \ \\ \text{R}-\text{C}-\text{C}-\text{Cl} \\ \ \ \\ \text{Cl} \ \ \text{Cl} \end{array}$	129-131	10	1.370	1.4980	258	253	68.6	68.8	54.2	54.1
$\begin{array}{c} \text{Cl} \\ \\ \text{R}-\text{CO}-\text{CH} \\ \\ \text{Cl} \end{array}$	63-65	11	1.134	1.4532	169	167	42.0	41.8	39.6	40.0

Experimental

General Procedure.—In a 2-liter 3-necked flask equipped with mechanical stirrer, reflux condenser, thermometer and gas inlet tube, was placed the desired solvent and 82 g. (one mole) of 1-hexyne. A moderately rapid stream of chlorine was introduced over the surface of the rapidly agitated mixture. Absorption of chlorine was quite rapid and the reaction was accompanied by marked rise in temperature. Occasional cooling permitted controlling the temperature at 45 ± 5°. Admission of chlorine was stopped when the solution acquired a permanent greenish-yellow color. Stirring was continued for one hour and the product poured into water, except when either acetic acid or acetic anhydride was the solvent, in which cases the acetyl chloride was distilled off first. The washed product was treated successively with

sodium carbonate solution and water and then dried over anhydrous sodium sulfate. The dried materials were fractionated repeatedly through an efficient column, collecting 5-10 ml. samples for refractive index determinations. Fractions were recombined on the basis of boiling point and refractive index and redistilled. The yields cited in Table I are lower than actually obtained because of distillation losses.

Summary

1-Hexyne has been chlorinated in five media: water, *t*-butyl alcohol, methyl acetate, acetic acid and acetic anhydride. Use of water, acetic acid or acetic anhydride gave 1,1-dichloro-2-hexanone. Chlorides and polychlorides were obtained in all cases. This work is being continued.