Anal.[10] Calcd. for $C_{12}H_{12}O_4$: C, 65.42; H, 5.50. Found: C, 64.87, 65.10; H, 5.82, 5.91.

Reaction of Phenylmagnesium Bromide with Methyl Dihydrocoumarin-4-acetate.—A solution of 2.1 g. of the redistilled ester in 20 cc. of dry ether was added to an excess of phenylmagnesium bromide in ether. A vigorous reaction occurred with the formation of a white precipitate which quickly dissolved. The solution was refluxed for thirty minutes and decomposed with ice–ammonium chloride solution. The product, after steam distillation and recovery with ether, was a viscous oil which could not be induced to crystallize.

The addition of a trace of sulfuric acid to a solution of the oil in acetic acid transformed it quickly into a white crystalline material. Recrystallized from acetic anhydride this product formed soft white needles, m. p. 216–218°. Mixed with a sample of VIII, m. p. 218–219°, the melting point was 216–218°.

Summary

1. It has been shown that the compounds produced by the reaction of phenylmagnesium bromide with *o*-hydroxybenzaldiacetophenone do not have the structures proposed for them by Gomm and Hill.[3]

2. The structure of one of these compounds has been established by a different method of synthesis, and a structure for the other proposed on the basis of its properties and its relationship to compounds of known structure.

LOS ANGELES, CALIFORNIA RECEIVED JANUARY 26, 1940

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[10] Analysis by Dr. J. Haagen-Smit, California Institute of Technology, Pasadena, Calif.

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

Chlorides and Hydrochlorides from 1-Hexyne[1]

BY G. F. HENNION AND CHARLES E. WELSH

Introduction

When 1-hexyne is chlorinated in various oxygen-containing media a complex mixture of products results, some of which contain oxygen as well as chlorine.[2] Various chlorine derivatives of 1-hexyne are thus obtained together and may be separated by fractional distillation. It was thought advisable to prepare these separately, by chlorination in inert solvents, in order to obtain pure substances for the determination of reliable physical data. It was desired also to prepare the mono and dihydrochlorides of 1-hexyne for comparison with the chlorides. During this investigation certain observations were made which may be of interest, and hence are recorded here.

Chlorination of 1-hexyne in either carbon tetrachloride or *n*-heptane containing a small amount of antimony pentachloride gave a mixture of *trans*-1,2-dichloro-1-hexene and 1,1,2,2-tetrachlorohexane only. When the antimony pentachloride was omitted the product was much less tractable and boiled over a wide range.

Direct addition of hydrogen chloride to 1-hexyne, with or without a solvent, was unsuccessful in the absence of a catalyst. Numerous metal chlorides were studied for catalytic activity. Of these bismuth chloride appeared to be best and with its use hydrogen chloride added readily to 1-hexyne to yield both 2-chloro-1-hexene and 2,2-dichlorohexane. By heating with potassium hydroxide in propyl alcohol the latter product could be reverted to the former.

Chlorination of 2-chloro-1-hexene in carbon tetrachloride containing antimony pentachloride was of particular interest because the reaction did not lead to 1,2,2-trichlorohexane, as anticipated. Instead a mixture of *cis*-1,2-dichloro-1-hexene and 1,1,2,2-tetrachlorohexane was obtained. Attempts to prepare 1,2,2-trichlorohexane by the addition of hydrogen chloride to both *cis*- and *trans*-1,2-dichloro-1-hexene likewise were unsuccessful. No reaction was observed in either case, even when bismuth chloride was present.

Physical data for the compounds prepared are given in Table I.

Experimental

Chlorination of 1-Hexyne.—A solution of 41 g. (0.5 mole) of 1-hexyne in 200 ml. of carbon tetrachloride was placed in a one liter, three-necked flask equipped with an efficient stirrer, a reflux condenser, and a chlorine inlet tube. To the solution was added slowly, with stirring, 50 ml. of carbon tetrachloride containing 1.5 ml. of antimony pentachloride. Chlorine was then passed over the solution in a fairly rapid stream, at a temperature of 45 ± 5°, until 35.5 g. (0.5 mole) was absorbed. The solution was washed with water, dilute sodium carbonate solution, again with water, dried over calcium chloride, and fractionally distilled: yield, 15 g. (19.6%) of *trans*-1,2-dichloro-1-hexene and 39.3 g. (30.6%) of 1,1,2,2-tetrachlorohexane.

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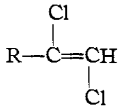
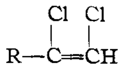
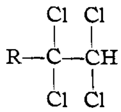
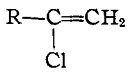
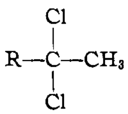
[1] Paper XXXVIII on the chemistry of substituted acetylenes and their derivatives; previous paper, THIS JOURNAL, **62**, 653 (1940).

[2] Norris, Vogt and Hennion, *ibid.*, **61**, 1460 (1939); **62**, 449 (1940).

TABLE I

PHYSICAL PROPERTIES OF CHLORIDES AND HYDROCHLORIDES OF 1-HEXYNE

Compound	 $R\text{—}CCl\text{=}CHCl$	 $R\text{—}CCl\text{=}CHCl$	 $R\text{—}CCl_2\text{—}CHCl_2$	 $R\text{—}CCl\text{=}CH_2$	 $R\text{—}CCl_2\text{—}CH_3$
Boiling point °C.	63-65	88	99-101	113	68
Boiling point 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
Mol. wt. Obsd.	152	156	226	118	156
MR Calcd.	39.2	39.2	49.4	34.3	39.8
MR Obsd.	39.2	39.0	49.2	34.3	39.8
Cl, % Calcd.	46.4	46.4	63.4	29.9	45.8
Cl, % 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).