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Halogenation of 1-Hexyne in Methanol[1]

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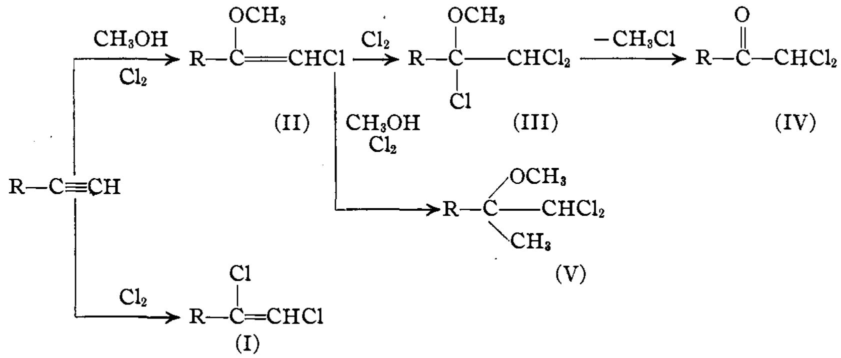
Introduction

Relatively little attention has been directed toward the halogenation of alkylacetylenes. It is generally accepted that di- and tetrahalogen addition products result from such reactions when conducted in inert solvents. However, there are numerous synthetic possibilities if a third reagent is present, *e. g.*, a reactive solvent such as methanol.

Goldschmidt, Endres and Dirsch[2] treated phenylacetylene with ethyl hypochlorite in carbon tetrachloride solution. They obtained dichloroacetophenone and not the anticipated diethoxydichloro addition product. Jackson[3] chlorinated phenylacetylene in methanol and obtained 1-phenyl-1,1-dimethoxy-2,2-dichloroethane. Similar studies with aliphatic acetylenes have not been reported. In the present investigation 1-hexyne has been chlorinated under a variety of conditions using both methanol and carbon tetrachloride as solvents. All likely addition products have been isolated or prepared by independent methods.

Chlorination of 1-hexyne in methanol at 0–5° yielded a mixture of 1,2-dichloro-1-hexene (I) and 1,1-dichloro-2,2-dimethoxyhexane (V). At 25–30°, 1,1-dichloro-2-hexanone (IV) was obtained in addition to the above products. The formation of these compounds may be represented by the following scheme of reactions (R is n-C_4H_9).



Compounds (II) and (III) were not isolated. The reactivity of (II) precludes the possibility of isolation from the chlorinated mixture. Compounds of type (III) spontaneously decompose, as has been shown previously.[4] During these experiments the formation of methyl chloride was observed, confirming the mechanism of dihaloketone (IV) formation.

The absence of (II) and the monochloro analogs of (IV) and (V) prompted us to synthesize these in another manner. The following reactions were employed, starting with 1-hexyne.

The 1-chloro-2-methoxy-1-hexene (II) thus obtained was dissolved in methanol and treated with chlorine at 25°. Compound (V) was ob-

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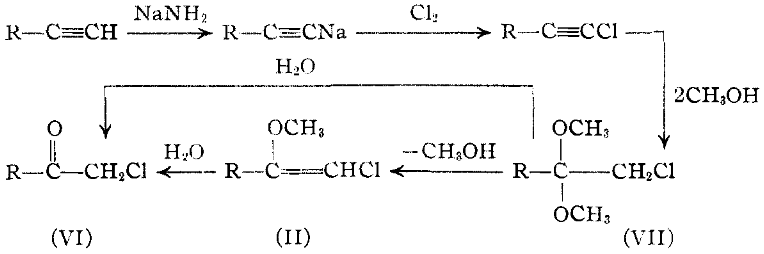
[1] Paper XXVI on the chemistry of the alkylacetylenes and their addition products; previous paper, THIS JOURNAL, **60**, 1159 (1938).

[2] Goldschmidt, Endres and Dirsch, *Ber.*, **58**, 572 (1925).

[3] Jackson, THIS JOURNAL, **56**, 977 (1934).

[4] Baum and Hennion, *ibid.*, **60**, 568 (1938).



tained in 60% yield, thereby confirming, in part, the mechanism proposed above.

Chlorination of 1-hexyne in carbon tetrachloride yielded only the anticipated 1,2-dichloride.

Bromination of 1-hexyne yielded the 1,2-dibromide, irrespective of whether the reaction was conducted in carbon tetrachloride or methanol. Neither methoxy bromides nor bromo ketones could be prepared under the conditions employed.

Experimental

Reagents.—1-Hexyne[5,6] and 1-chloro-1-hexyne[7] were prepared as previously described. All other materials were C. P. stock reagents.

Reaction of Chlorine with 1-Hexyne in Methanol.—Into a two-liter three-necked flask with a reflux condenser, mechanical stirrer and a gas inlet tube, was placed 400 cc. of anhydrous methanol and 82 g. of 1-hexyne. A moderately rapid stream of chlorine, measured by a flowmeter, was introduced over the surface of the rapidly agitated mixture. The absorption of chlorine was quite rapid and the reaction was accompanied by a moderate rise in temperature. The initial temperature, 25–30°, was maintained by moderate cooling. After the theoretical amount of chlorine had been added the mixture was allowed to stir for an additional hour after which it was washed with water, dilute carbonate solution and again with water. The organic layer was dried over calcium chloride and fractionated. Distillation through an efficient column yielded the following compounds listed in order of increasing boiling point.

1,2-Dichloro-1-hexene (I).—Obtained 29 g. (18% yield); b. p. 60–61° at 34 mm.; d^{28} 1.0511; n^{28}_{D} 1.4535; *MR* (calcd.), 39.17; *MR* (obsd.), 39.10.

Anal. Calcd. for $C_6H_{10}Cl_2$: Cl, 46.4; mol. wt., 153.0. Found: Cl, 46.1; mol. wt., cryoscopic in benzene, 151.3.

1,1-Dichloro-2-hexanone (IV).—Obtained 60.3 g. (37% yield); b. p. 64–66° at 10 mm.; d^{26} 1.1344; n^{26}_{D} 1.4533; *MR* (calcd.), 39.65; *MR* (obsd.), 40.0.

Anal. Calcd. for $C_6H_{10}Cl_2O$: Cl, 42.0; mol. wt., 169.0. Found: Cl, 42.2; mol. wt., cryoscopic in benzene, 167.7.

1,1-Dichloro-2,2-dimethoxyhexane (V).—Obtained 75 g. (35% yield); b. p. 76–78° at 2 mm.; d^{29} 1.120; n^{29}_{D} 1.4530; *MR* (calcd.), 52.1; *MR* (obsd.), 51.8.

Anal. Calcd. for $C_8H_{16}Cl_2O_2$: Cl, 32.81; mol. wt., 216. Found: Cl, 32.7, 32.55, 32.50; mol. wt., cryoscopic in benzene, 215, 218.

A similar experiment was carried out employing a reaction temperature of 0–5°. This reaction resulted in a 20% yield of 1,2-dichloro-1-hexene and a 30% yield of 1,1-dichloro-2,2-dimethoxyhexane. Approximately 24% of 1-hexyne was recovered.

Bromination of 1-Hexyne in Methanol.—Into a two-liter three-necked flask with a reflux condenser, mechanical stirrer, and a gas inlet tube, was placed 500 cc. of anhydrous methanol, and 82 g. of 1-hexyne. Two hundred and forty grams of bromine was placed in a 250-cc. wide-mouthed bottle equipped with an inlet and outlet tube. The bromine bottle was connected by means of rubber tubing to the reaction flask and to a nitrogen tank. A slow stream of nitrogen was bubbled through the liquid bromine for four hours, sufficient to transfer all the bromine. The reaction flask was cooled in an ice-bath during the addition. The mixture was stirred for an additional hour, after which it was washed with water, dilute carbonate solution and again with water. The organic layer was dried over calcium chloride and distilled through an efficient column. The yield of 1,2-dibromo-1-hexene was 223 g. (92.5% yield). The compound had the following characteristics: b. p. 89–91° at 30 mm.; d^{22} 1.608; n^{22}_{D} 1.5080; *MR* (calcd.), 44.97; *MR* (obsd.), 44.80.

Anal. Calcd. for $C_6H_{10}Br_2$: Br, 66.1; mol. wt., 242. Found: Br, 65.9; mol. wt., cryoscopic in benzene, 239.

Chlorination of 1-Hexyne in Carbon Tetrachloride.—Into a one-liter three-necked flask with a reflux condenser, motor driven stirrer, and a gas inlet tube, was placed 82 g. of 1-hexyne and 500 cc. of carbon tetrachloride. An additional 100 cc. of solvent to which had been added 3 cc. of antimony pentachloride was added slowly to the agitated mixture. A moderate stream of chlorine was passed over the surface until the theoretical amount had been added. The reaction mixture was stirred for an additional hour after which it was washed with water, dilute carbonate solution and again with water. The organic layer was dried over calcium chloride and distilled. The yield of product was 38 g. (25% of the theoretical). Considerable polymer (tar) was also obtained. The 1,2-dichloro-1-hexene had the following characteristics: b. p. 62–65° at 36 mm.; d^{27} 1.0525; n^{27}_{D} 1.4540; *MR* (calcd.), 39.17; *MR* (obsd.), 39.10.

Proof of Structure of 1,1-Dichloro-2-hexanone.—Ten grams of 1,1-dichloro-2-hexanone and 20 g. of calcium hypochlorite were mixed with 100 cc. of distilled water. The mixture was refluxed for thirty minutes after which it was subjected to distillation. The following compounds were obtained: 3.5 g. of chloroform, b. p., 57–58° at 746 mm.; d^{25} 1.481; n^{25}_{D} 1.4438, and 1.5 g. of *n*-valeric acid, identified by its characteristic odor and *p*-bromophenacyl ester, m. p. 63°.

Identification of Methyl Chloride.—A solution of 82 g. of 1-hexyne in 500 cc. of methanol was chlorinated at 40–50° as described above. The exit gas was passed through two wash bottles containing 25% sodium hy-

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[5] Picon, *Compt. rend.*, **158**, 1346 (1914); **169**, 32 (1919).

[6] Vaughn, Hennion, *et. al.*, *J. Org. Chem.*, **2**, 1 (1937).

[7] McCusker and Vogt, This Journal, **59**, 1307 (1937).

droxide solution, then through a calcium chloride drying tube, and finally into a 500-cc. flask cooled to −75° with carbice and acetone. About 20 cc. of condensate was obtained, identified as methyl chloride by conversion to methylmagnesium chloride, then to acetic acid (b. p. 118–119°), in turn converted to acetanilide (m. p. 114°). The chlorinated methanol solution yielded 39 g. of 1,2-dichloro-1-hexene and 38 g. of 1,1-dichloro-2-hexanone.

Addition of Methanol to 1-Chloro-1-hexyne.—This reaction was carried out using the method previously reported.[8] From 116.5 g. of 1-chloro-1-hexyne there was obtained 150 g. (83% yield) of 1-chloro-2,2-dimethoxyhexane: b. p. 77–80° at 14 mm.; d^{25} 0.9873; n^{25}_{D} 1.4305; *MR* (calcd.), 47.30; *MR* (obsd.), 47.20.

Anal. Calcd. for $C_8H_{17}O_2Cl$: Cl, 19.65; mol. wt., 180.5. Found: Cl, 19.40; mol. wt., cryoscopic in benzene, 179.8.

Preparation of 1-Chloro-2-methoxy-1-hexene.—Employing the general procedure already reported,[9] 90.3 g. of 1-chloro-2,2-dimethoxyhexane was desaturated using *p*-toluenesulfonic acid as a catalyst. The yield of 1-chloro-2-methoxy-1-hexene was 68.5 g. (92.5% yield). The following characteristics were determined for this compound: b. p. 90–91° at 65 mm.; d^{23} 0.9725; n^{23}_{D} 1.4460; *MR* (calcd.), 40.57; *MR* (obsd.), 40.65.

Anal. Calcd. for $C_7H_{13}OCl$: Cl, 24.9; mol. wt., 148.5. Found: Cl, 24.8; mol. wt., cryoscopic in benzene, 147.1.

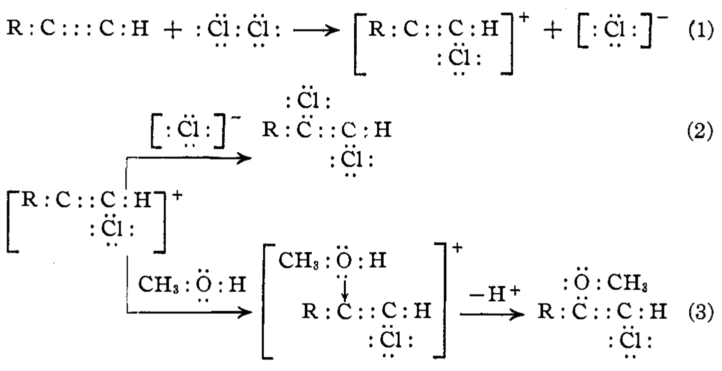
Chlorination of 1-Chloro-2-methoxy-1-hexene.—Forty grams of 1-chloro-2-methoxy-1-hexene was added dropwise (below the surface) to 200 cc. of methanol, while chlorine was passed over the surface. The temperature was maintained at 25–30°. At the completion of the reaction the excess chlorine and hydrogen chloride formed were exactly neutralized with sodium methylate–methanol solution, using phenolphthalein as an indicator. The sodium chloride was filtered off and the filtrate distilled. There was obtained 35 g. (60% yield) of 1,1-dichloro-2,2-dimethoxyhexane.

Hydrolysis of 1-Chloro-2-methoxy-1-hexene.—Fifteen grams of 1-chloro-2-methoxy-1-hexene was added to a mixture of 15 cc. of water and 50 cc. of methanol to which had been added 0.2 g. of *p*-toluenesulfonic acid. The solution was placed in a 250-cc. flask equipped with a reflux condenser and heated for a period of two hours. The excess water was removed by addition of anhydrous sodium sulfate and the clear supernatant liquid fractionated. The yield of 1-chloro-2 hexanone was 11 g. (82%). The ketone had the following properties: b. p. 73–74° at 20 mm.; d^{24} 1.007; n^{24}_{D} 1.4370; *MR* (calcd.), 34.79; *MR* (obsd.), 34.80.

Anal. Calcd. for $C_6H_{11}ClO$: Cl, 26.38. Found: Cl, 26.3.

Discussion

It is extremely unlikely that methoxychloro addition products of 1-hexyne result through direct addition of methyl hypochlorite. In accord with modern electronic concepts, we prefer to consider a series of repeated fragmentary additions as shown below with electronic formulas.



Equations (1) and (2) represent the normal course of halogenation in inert solvents. Equation (3) shows how a reactive solvent may coordinate with the "positive fragment" from (1), the complex then stabilizing by rejection of a hydrogen ion.

While direct proof of such mechanisms cannot be offered, these electronic concepts have proved extremely useful in predicting a number of other mixed addition reactions now under investigation.

Summary

1-Hexyne has been chlorinated in methanol and in carbon tetrachloride. Chlorination in methanol yielded 1,2-dichloro-1-hexene, 1,1-dichloro-2,2-dimethoxyhexane, and 1,1-dichloro-2-hexanone. In carbon tetrachloride 1,2-dichloro-1-hexene was formed. Bromination in methanol gave exclusively the 1,2-dibromide.

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[8] Hennion, Killian, *et. al.*, THIS JOURNAL, **56**, 1130 (1934).

[9] Killian, Hennion and Nieuwland, *ibid.*, **57**, 544 (1935).