

way for the production of large fluorinated molecules by condensation of several small fluorinated molecules.

### Experimental

The preparation of dichlorides by interaction of an aldehyde or a ketone with phosphorus pentachloride was first attempted by the method previously described.<sup>6</sup>

However, it was promptly found that one could not generalize as to the advisability of adding the organic material to the phosphorus chloride, or *vice versa*, because resinification and ease of handling had to be reckoned with. The procedures finally adopted after pilot trials were as follows.

**Preparation of  $\text{CH}_3\text{CCl}_2\text{C}_2\text{H}_5$ .**—Phosphorus pentachloride (521 g.) was added in small portions to the ketone (190 g.), to give 126 g. of olefinic material and 76 g. of the desired dichloride. Resinification was small and did not interfere with the handling.

**Preparation of  $\text{CH}_3\text{CCl}_2\text{C}_3\text{H}_7$ .**—Same procedure as above, with 430 g. of phosphorus chloride and 182 g. of ketone, to obtain 72 g. of dichloride and about 150 g. of olefinic material. Not much resinification was observed, and the handling of the reaction products was not interfered with.

**Preparation of  $\text{CH}_3\text{CH}_2\text{CHCl}_2$ .**—Propionaldehyde (108 g.) was added slowly to phosphorus pentachloride (310 g.). After completion of the addition and standing overnight, the mixture was heated slowly to 100°, cooled, and poured slowly into water. This water was brought to its boiling point, which caused the organic chlorides to be steam-distilled. After decantation, drying and rectification 22 g. of olefinic chloride and 77 g. of the desired dichloride were obtained. As the latter was obtained in good purity, the following physical constants are recorded: b. p. 88.3°,

(6) THIS JOURNAL, **59**, 2434 (1937).

$d_{20}^{20}$ , 1.1321,  $n_D^{20}$  1.42887, molecular refraction observed 25.73, calculated 25.78.

**Preparation of  $\text{CH}_3(\text{CH}_2)_2\text{CHCl}_2$ .**—Same procedure as above. The aldehyde (200 g.) added to the phosphorus pentachloride (416 g.) yielded 129 g. of dichloride, and a small amount of ethylenic monochloride.

**Preparation of  $\text{CH}_3(\text{CH}_2)_3\text{CHCl}_2$ .**—Commercial enanthaldehyde (127 g.) was added very slowly to cooled phosphorus chloride (250 g.). After completion of the addition and standing overnight, the mixture was progressively heated to 150°, which caused most of the phosphorus oxychloride to distil off. Then the distillation was pursued at reduced pressure, to give 81 g. of dichloride. The phosphorus oxychloride was poured slowly into water to permit the recovery of about 30 g. of organic dichloride.

**Fluorinations.**—They followed the procedures indicated in the articles referred to hereabove.

### Summary

The differences between the fluorination of  $\text{RCHX}_2$  compounds to  $\text{RCHF}_2$  on the one hand, and of  $\text{RCX}_2\text{R}'$  to  $\text{RCF}_2\text{R}'$  on the other hand, are described. The following new compounds were prepared:  $\text{CH}_3\text{CH}_2\text{CHF}_2$ ,  $\text{CH}_3(\text{CH}_2)_5\text{CHF}_2$ ,  $\text{CH}_3\text{CF}_2\text{CH}_3$ ,  $\text{CH}_3\text{CF}_2\text{C}_2\text{H}_5$ , and  $\text{CH}_3\text{CF}_2\text{C}_3\text{H}_7$ , together with the compounds resulting from the complete replacement of their hydrogen by chlorine. Their properties are tabulated. Directions are given to prepare 1,1-dichlorides and 2,2-dichlorides from an aldehyde or a ketone, respectively, and phosphorus pentachloride. The physical constants of  $\text{CH}_3\text{CH}_2\text{CHCl}_2$  are given.

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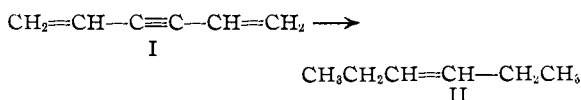
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[CONTRIBUTION FROM JACKSON LABORATORY, E. I. DU PONT DE NEMOURS AND CO.]

## Reactions of 3-Hexene. I. Reactions with Sulfuric Acid, Halogens and Halogen Acids

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3-Hexene (II) which has been described previously by Lespieau and Wiemann<sup>1</sup> and Schmitt and Boord<sup>2</sup> recently has become available through the catalytic hydrogenation of divinylacetylene<sup>3</sup> (I)



The present work was undertaken with the view of studying the behavior of this relatively unknown olefin in addition reactions with sulfuric acid, halogenating agents and halogen acids.

3-Hexene combined with 85–87% sulfuric acid and hydrolysis of this mixture produced the expected 3-hexanol in 50% yields, as well as some 3,4-hexylene oxide, and a mixture of olefinic polymers  $(\text{C}_6\text{H}_{12})_n$ , where  $n$  has a value of two to five. Chlorine, sulfuryl chloride or phosphorus pentachloride converted 3-hexene into 3,4-dichlorohexane and some higher chlorinated products which were not identified. Dry hydrogen bro-

(1) M. M. Lespieau and Wiemann, *Bull. soc. chim.*, [4] **45**, 627 (1929).

(2) C. G. Schmitt and C. E. Boord, *THIS JOURNAL*, **54**, 751–761 (1932).

(3) Du Pont Co., German Patent 649,000 (July 29, 1937).

mide combined with 3-hexene to give 3-bromohexane, but dry hydrogen chloride did not add. However, when aqueous hydrochloric acid was used, addition took place to give 3-chlorohexane.

### Experimental

(A) **Reaction with Sulfuric Acid.**—Nine hundred grams (500 cc.) of 87% sulfuric acid was cooled to 20°.

Three hundred forty-five grams (500 cc.) (4.1 moles) of 3-hexene was added dropwise to the acid over a one to two hour period. The temperature was kept below 20° by external cooling while stirring rapidly. The golden-yellow color of the mixture gradually changed to brown. After one to one and one-half hours, the charge was poured into 8000 cc. of water, heated to the reflux temperature and boiled for three to four hours under a reflux condenser.

The charge was then distilled to obtain a mixture of oil and water as distillate. This was saturated with potassium carbonate in order to separate out (A) 345 g. of crude 3-hexanol. In the still as residual oil floating on dilute acid there remained (B) 40–50 g. of a product which was not volatile with steam. Portion (A) was fractionally distilled employing a Vigreux type column of 2.5-cm. diameter and 25.4-cm. length packed with carborundum. Fractions collected were (1) 66–68° (16.5%) which was identified as 3-hexene; (2) 75–130° (8%) which on redistillation gave some 3-hexene; some 3,4-hexylene oxide, b. p. 105–106° and some 3-hexanol; (3) 134–138° (60%) which was identified as 3-hexanol; (4) 95–150° (30–35 mm.) (9%) which proved to be mainly an olefin dimer of 3-hexene.

*Anal.* Calcd. for  $C_{12}H_{24}$ : mol. wt., 168; iodine no., 150. Found: mol. wt., 172; iodine no., 149.

Table I gives the constants found for 3,4-hexylene oxide and 3-hexanol, and also the constants which have been reported previously for these compounds. Molecular weight determinations shown in Tables I and II were made by the Menzies-Wright boiling point method and by the depression of freezing point in benzene (cryoscopic method).

TABLE I

CONSTANTS FOR 3,4-HEXYLENE OXIDE AND 3-HEXANOL

Compound	3,4-Hexylene oxide	3-Hexanol
B. r., °C. { Observed	105–106	134–138
{ Literature	107–108 <sup>4</sup>	134–135 <sup>5</sup> 133–134 <sup>6</sup> 134 <sup>7</sup>
$d^{20}_D$ , observed	0.862	0.810
$d^{20}_D$ , literature	....	0.8182 <sup>5</sup> 0.8213 <sup>6</sup> 0.8550 <sup>7</sup>
$n^{20}_D$ { observed	1.5012	1.4138
{ literature	....	1.4141 <sup>6</sup> 1.4482 <sup>7</sup>
Mol. wt.	Calcd. 102, found 100	....

The non-volatile oil (B) was dried azeotropically with distillation with anhydrous benzene. It was found to be an olefinic mixture of polymers of 3-hexene,  $(C_6H_{12})_3$ ,  $(C_6H_{12})_4$ , and  $(C_6H_{12})_5$ , whose average composition was  $(C_6H_{12})_4$ .

*Anal.* Calcd. for  $C_{24}H_{48}$ : C, 86; H, 14; mol. wt., 336. Found: C, 84.7; H, 12.1; mol. wt., 339; S, 0.23.

(4) P. W. Zubow and W. Swietoslowski, *Bull. soc. chim.*, [4] **37**, 271–274 (1925).

(5) Oechsner de Coninck, *ibid.*, [2] **25**, 7 (1876).

(6) R. H. Picard and J. Kenyon, *J. Chem. Soc.*, **103**, 1942 (1913).

(7) R. Lespieau and R. Lombard, *Compt. rend.*, **198**, 2179–2180 (1934).

Table II gives the results which were obtained by vacuum distillation of the mixture.

TABLE II  
PROPERTIES OF DISTILLATION FRACTIONS

Fraction b. r., °C. (3 mm.)	90–136	136–200	200–250	
% of total	31	21.4	21.4	
Mono-olefin compn. for 3-hexene	Trimer	Tetramer	Pentamer	
$d^{20}_D$	0.824	0.841	0.868	
$n^{20}_D$	1.4605	1.4700	1.4847	
Analytical figures	Formula			
	Mol.	$C_{18}H_{36}$	$C_{24}H_{48}$	$C_{30}H_{60}$
	wt.	252	336	420
	Iodine no.	100	75	60
	Calcd.			
	Found			
	91.4	87.6	39	

It was necessary to preheat the above described polymer mixture at 240–250° for a period of eight to twelve hours in order to expel sulfur dioxide before it could be vacuum distilled successfully. Of the total, 26.2% remained in the still as residual hydrocarbon. This displayed no evidences of decomposition and showed an average molecular weight of 1104.

**Influence of Conditions on the Reaction.**—It was observed in a number of experiments that prolonged operation of the reaction mass, after mixing of the 3-hexene and 87% sulfuric acid prior to dilution and hydrolysis, tended to give lower yields of 3-hexanol and higher yields of the olefinic polymers. For example, while one hour of mixing as already described produced 50% of 3-hexanol and 12% of 3-hexene polymers, a fifteen hour mixing resulted in 1% of 3-hexanol and 58% of polymers.

The introduction of peroxides such as ascaridole or anti-oxidants such as hydroquinone was observed to have little or no effect upon the course of the reaction and on the relative quantities of the products formed. In one experiment, the introduction of 0.25% of potassium ferricyanide resulted in a low yield of hexanol and a high yield of 3-hexene polymer.

(B) **Chlorination of 3-Hexene with Chlorine.**—Eighty-four grams of 3-hexene and 215 g. of chloroform were mixed and cooled to –30 to –40°. Chlorine gas was bubbled in until a weight increase of 71 g. was obtained. The chlorine was absorbed without any evolution of hydrogen chloride. The reaction mass was distilled fractionally under diminished pressure. A carborundum-packed Vigreux type column of 2.5 cm. diameter and 20-cm. length was employed for distillation. A water aspirator was employed for this operation since small amounts of hydrochloric acid were evolved when the mass was warmed up above room temperature. The 3,4-dichlorohexane distilled over at 69–70° under 30 mm. of mercury pressure. The product, a colorless liquid with a sweetish odor, has a density of 1.055 at 20° and a refractive index of 1.4490 ( $n^{20}_D$ ); yield 105 g. or 67%.

*Anal.* Calcd. for  $C_6H_{12}Cl_2$ : Cl, 45.8. Found: Cl, 45.76. Forty grams of material boiling above 70° at 30 mm. containing 55.6% chlorine remained in the still.

**With Sulfuryl Chloride.**—Eighty-four grams of 3-hexene was warmed to 40–45°. One hundred and forty grams of sulfuryl chloride ( $SO_2Cl_2$ ) was then added dropwise over a period of four hours so that the temperature did not exceed 50–55°. Vigorous evolution of sulfur dioxide occurred with practically no evidence of hydrogen chloride.

The reaction mass was held at 50–55° for three to four hours after adding all of the sulfuryl chloride until no further evolution of sulfur dioxide was noted. Fractional distillation under diminished pressure yielded 13 g. of unreacted 3-hexene and 91 g. of 3,4-dichlorohexane. Thirty-six grams of residual material remained in the still. This contained more highly chlorinated bodies.

**With Phosphorus Pentachloride.**—Two hundred and eight grams of phosphorus pentachloride (1 mole) was suspended in 600–700 g. of carbon tetrachloride. The agitated mixture was warmed to 50–60° and 84 g. of 3-hexene (1 mole) was slowly dropped in over a period of four to five hours. As the reaction proceeded the suspended phosphorus pentachloride gradually dissolved. A clear solution of phosphorus trichloride and 3,4-dichlorohexane in carbon tetrachloride was obtained. Fractional distillation yielded phosphorus trichloride dissolved in carbon tetrachloride, b. r. 73–79° (760 mm.); 95 g. of 3,4-dichlorohexane, b. r. 66–68° (27 mm.); and 18 g. of residual chlorinated material in the still.

The phosphorus trichloride solution in carbon tetrachloride can be chlorinated to phosphorus pentachloride and reused for reaction with further quantities of 3-hexene.

#### (C) Hydrohalogenation of 3-Hexene

**Reaction of 3-Hexene and Hydrogen Bromide.**—Into a mixture of 84 g. of 3-hexene and 250 g. of chloroform, cooled to –20° and stirred continuously, was introduced 87 g. of dry hydrogen bromide prepared by burning bromine in hydrogen.<sup>8</sup> This operation required three to three and a half hours. The reaction mass was then washed with cold water and the oil was distilled through a short carborundum packed column. After removal of chloroform, there was obtained 125 g. of 3-bromohexane (76% of theoretical) boiling from 53 to 55° at 35 mm.

Table III gives the constants found for 3-bromohexane, and also the values which have been reported previously for this compound, when prepared from 3-hexanol and hydrogen bromide.

TABLE III  
CONSTANTS OF 3-BROMOHEXANE

	Observed	Literature
Boiling { °C. at mm.	68 at 50	65.8–67 at 49 <sup>9</sup>
range { °C. at mm.	141–142 at 760	142 at 760 <sup>10</sup>
$d_{20}^{20}$	1.65	1.166 <sup>10</sup>
$n_D^{20}$	1.4450	1.4469 <sup>9</sup>

**3-Thiocyanohexane,** (CH<sub>3</sub>CH<sub>2</sub>CH(SCN)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), b. p. 121° at 40 mm.,  $d_{20}^{20}$  0.932,  $n_D^{20}$  1.5608, was obtained in 90% yield by the reaction of 3-bromohexane with sodium thiocyanate in alcoholic solution.

(8) *Org. Syntheses*, **15**, 24, 35 (1935).

(9) H. A. Shonle and J. H. Waldo, *THIS JOURNAL*, **55**, 4649 (1933).

(10) P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **91**, 687 (1931).

*Anal.* Calcd. for C<sub>6</sub>H<sub>13</sub>SCN: N, 9.8; S, 22.7. Found: N, 9.48; S, 21.7.

**3-Mercaptohexane.**—(CH<sub>3</sub>CH<sub>2</sub>CH(SH)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>) (b. p. 57° at 25 mm.,  $d_{20}^{20}$  0.832,  $n_D^{20}$  1.4428) was obtained from 3-bromohexane and sodium sulfhydrylate (anhydrous NaSH) in ethyl alcohol solution.

*Anal.* Calcd. for C<sub>6</sub>H<sub>14</sub>S: S, 27.1. Found: S, 26.5.

**Reaction of 3-Hexene and Hydrogen Chloride.**—Attempts to produce 3-chlorohexane by the action of dry hydrogen chloride gas upon 3-hexene were unsuccessful. Little or no reaction was observed from –20° to room temperature. The product, however, formed satisfactorily by reaction of concentrated aqueous hydrochloric acid at room temperature. The procedure employed follows.

Eighty-four grams of 3-hexene dissolved in 225 g. of chloroform was stirred or shaken vigorously with 300 cc. (350 g.) of 36.5% hydrochloric acid for forty-eight hours at room temperature, while saturating hourly with dry hydrogen chloride. The reaction mass was then settled and the oily portion separated. This was washed two times with cold water and then subjected to distillation under diminished pressure employing a short carborundum-packed column for fractionation. There was thus obtained 55 g. of 3-chlorohexane, b. r. 59.5–60° (95 mm.),  $d_{20}^{20}$  0.870;  $n_D^{20}$  1.4163.

*Anal.* Calcd. for C<sub>6</sub>H<sub>13</sub>Cl: Cl, 29.5. Found: Cl, 30.3.

**Acknowledgment.**—The writers are indebted to Mr. E. L. Korb and Mr. W. T. Granger for their assistance in the experiments on the reaction of 3-hexene and sulfuric acid.

#### Summary

Addition reactions of 3-hexene with sulfuric acid, halogenating agents and hydrogen halides are described.

3-Hexene, combined with 85% sulfuric acid and hydrolyzed, formed 3-hexanol, 3,4-hexylene oxide and olefinic polymers of 3-hexene.

With chlorine, sulfuryl chloride or phosphorus pentachloride, 3,4-dichlorohexane (b. r. 69–70° at 30 mm.) was produced.

3-Hexene and anhydrous hydrogen bromide yielded the expected 3-bromohexane. From the latter compound, 3-thiocyanohexane (b. p. 121° at 40 mm.) and 3-mercaptohexane (b. p. 57° at 25 mm.) were prepared. 3-Hexene and aqueous concentrated hydrogen chloride yielded 3-chlorohexane (b. r. 59.5–60° at 95 mm.).

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