THE SATURATION
of
2 PENTENE WITH
HYDROGEN BROMIDE.

THESIS

by

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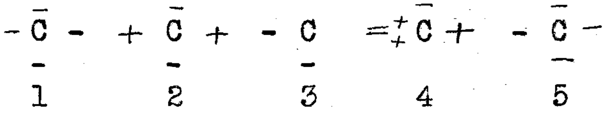
INTRODUCTION.

The purpose of this investigation was to determine whether 2 pentene upon saturation with hydrogen bromide, gave 2 brom pentene or 3 brom pentane or, in case some of both compounds was formed, to determine the relative proportion of the two compounds existing in the product.

There are two theories existent by which the position to which the entering hydrogen and brimine atoms will go, can be predicted.

1. The first of these two theories is the alternate polarity theory which states that the carbon atoms in a chain are alternately positive and negative. This theory as applied to the structure of 2 pentene will appear as follows:



$$\begin{array}{ccccc} -\overset{-}{\underset{-}{C}}- & +\overset{-}{\underset{-}{C}}+ & -\underset{-}{C} & =^{+}_{+}\overset{-}{C}+ & -\overset{-}{\underset{-}{C}}- \\ 1 & 2 & 3 & 4 & 5 \end{array}$$

The first carbon atom has four negative charges, three of which are neutralized by the positive charges of the three hydrogen atoms joined to it. The second carbon atom has two negative charges neutralized by hydrogen and two positive charges neutralized by the two negative charges of adjoining carbon atoms, etc.

From a study of the relation between the third and fourth carbon atoms, it is evident that the third carbon atom is much more negative than is the fourth carbon atom. Hence, in the addition of $H^+ Br^-$ to this compound, the prediction of the alternate polarity theory is that the hydrogen atom being positive would be attracted to the more negative of the two carbon atoms, and therefore, would go to the third carbon atom. On the other hand, the bromine being negative would go to the fourth carbon atom.

Thus we may see that in the saturation of 2 pentene with hydrogen bromide, the alternate polarity theory would predict that the compound formed would be 2 brom pentane. $CH_3\ CH_2\ CH_2\ CH\ Br\ CH_3$

The second of the two theories is known as the electron displacement theory and its theory as to the relation existing between carbon atoms in a chain, appears graphically as follows - only the electrons participating in the displacement will be illustrated:

$$C : C : C :: C : C$$

The above represents the relative position of the electron without any displacement. After the displacement of the electrons we have the following relationship.

1 2 3 4 5
C : C : C :: C : C

The reason for this shift may be stated as follows: The carbon atoms 1 and 2 constitute an ethyl group, which is more positive in its effect than is the single carbon atom 5.

As a result the two electrons between carbon atoms 2 and 3 are displaced toward carbon atom 3. This causes a shift of the four electrons between carbon atoms 3 and 4 toward carbon atom 4. This may be explained by saying that each carbon atom has a constant potential and, because of this, when the potential is increased on the one side by a displacement of the electrons toward a carbon atom, there must be a corresponding shifting away of the electrons on the other side of the atom.

From a consideration of carbon atoms 3 and 4, it is seen that carbon atom 4 is much more negative than is carbon atom 3, because of the displacement of the four electrons constituting the so-called double bond toward the fourth carbon atom.

Hence, in the addition of $H^+ Br^-$, the bromine being negative, will be attracted to the more positive of the two carbon atoms, which is the third carbon atom. The hydrogen atom, similarly, since it is positive, will be attracted to the fourth carbon atom which is the more negative of the two.

The prediction of the electron displacement theory then, is that upon the addition of hydrogen bromide to 2 pentene, 3 brom pentane, $CH_3\ CH_2\ CH\ Br\ CH_2\ CH_3$, will be formed.

Since the alternate polarity theory predicts the formation of 2 brom pentane and the electron displacement theory indicates that 3 brom pentane will be formed, the correctness of the two theories can be ascertained through the saturation of 2 pentene with hydrogen bromide.

METHOD OF ATTACK.

In the attempt to test the correctness of the alternate polarity and electron displacement theories, it was decided that the saturation of 2 pentene with hydrogen bromide would be used as a test reaction, because of the fact that the alternate polarity theory predicted that the bromine would be added to the second carbon atom of the chain, while the electron displacement theory predicted its addition to the third carbon atom.

In order to carry out the above reaction it was first necessary to synthesize 2 pentene involving the following steps, in the order mentioned:

(1) Preparation of ethyl formate from sodium formate and ethyl alcohol.

(2) Preparation of diethyl carbinol by use of Grignard's Reaction.

(3) Preparation of 3 brom pentane from diethyl carbinol.

(4) Unsaturation of 3 brom pentane to give 2 pentene.

The 2 pentene was then saturated with hydrogen bromide, forming brom pentane.

Since the boiling points of the 2 brom and 3 brom pentane are 113°C and 118°C respectively, it seemed advisable to have a method of analysis for the two compounds which was independent of the boiling points because of the small temperature difference existing between them.

Since no chemical method of analysis could be found to use in distinguishing between the two compounds, it was decided to ascertain whether there existed any appreciable difference in the refractive indices of the two compounds. Upon preparation of the two compounds a reading at 20°C for the 3 brom pentane of 1.4443 was obtained with an Abbé refractometer, while the reading of the 2 brom pentane was 1.4322 at 20°C. However, because of the difficulty of obtaining pure 2 pentanol the figure given for the index of 2 brom pentane may be slightly in error.

The large difference that was found to exist between the indices of refraction of the two compounds justified the use of the indices as a method of analysis and the results of the bromination of 2 pentene were interpreted by the use of this method of analysis in conjunction with that of the difference of the boiling points.

The first bromination of the 2 pentene was carried out at 60°C, in a pressure bottle containing glacial acetic acid saturated with an excess of hydrogen bromide and gave a brom pentane which, after washing and drying, was distilled using a fractionating column. The first drop of distillate came over at 117.2°C, but practically the whole of the distillate came over between the temperatures of 118° and 118.2°. The reading for the refractive index of the product of this run was 1.4430 at 20°.

The second bromination was carried out in the cold without the use of pressure by placing the pentene in an Erlenmeyer Flask containing glacial acetic acid saturated with an excess of hydrogen bromide. In the distillation of the washed and well dried product the first drop of the distillate came over at 117.4° and, as in the first run, the temperature immediately rose to 118° and stayed constant there for the remainder of the run.

The refractive index for the brom pentane obtained in this run was 1.4431 at 20° agreeing very closely with the value of 1.4430 from the first run.

DISCUSSION OF EXPERIMENTS.

In the preparation of some of the compounds involved in the synthesis of 2 pentene, the literature on the subject was found to be either unsatisfactory or totally lacking and for this reason original methods of preparation were used which may be of interest.

A new method of preparing ethyl formate was developed in which ethyl sulphuric acid (1 mol of ethyl alcohol + 1.15 mols of sulphuric acid, sp. G. 1.84) was added to 1 mol of C.P. Sodium formate and allowed to stand over night. Upon distillation the following day, water white ethyl formate was obtained. The whole of the ethyl formate upon redistillation came over within a temperature range of .4°. The yields using this method were very satisfactory varying from 87% to practically theoretical.

One method for the preparation of ethyl formate[1] which was found in the literature, involved the mixing of ethyl alcohol and glacial formic acid with a subsequent saturation with dry hydrochloric acid gas. It can easily be seen that the first mentioned method possesses several

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1. J. Chem. Soc. Vol 63. P 1202.

advantages, in that it does away with the necessity of obtaining glacial formic acid and also does not call for the saturation of the solution with hydrochloric acid gas.

In preparing this ester it is desirable to have all reagents as water-free as possible and because of the tendency of formic acid to form a constant boiling mixture containing about 30% water, it is advantageous to do away with the use of formic acid in the reaction.

The preparation of diethyl carbinol from ethyl formate was carried out by means of Grignard's reaction and conformed very closely with the methods mentioned in the literature,[1] with the exception perhaps of the relative quantities of material used and in minor points of technique, as for instance the dissolving of the solid matter in the bottom of the reactio flask with dilute sulphuric acid in order to form two layers of liquids in the flask, one of which, the ether layer, contained practically the whole of the product desired.

An extremely satisfactory method for brominating alcohol and unsaturated hydrocarbons was made use of in the experimental work of this research. Use was made of pressure bottles in all cases requiring bromination. The alcohol to be

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[1] Compt. Rend 132, 336, 1901
J. Chem Soc, 1901, 1,250
J. Chem Soc, 1901, 1,679
J. Chem Soc, 1900, 382

brominated is placed in the pressure bottle, preferably filling it about one-half full. The alcohol is next saturated with hydrogen bromide formed by dropping liquid bromine upon napthalene and removing bromine vapor by use of a drying tube filled with napthalene.

An excess of hydrogen bromide is dissolved, generally around 25%. The bottle is next closed, placed in a pressure frame and heated in a water bath. The heating serves not only to increase the rate of reaction by raising the temperature but also greatly increases the pressure of the hydrogen bromide gas in the bottle.

A few hours of heating usually suffices to complete the reaction, whereupon the contents of the bottle are poured into water, the hydrobromic acid going over to the aqueous layer while the brominated alcohol forms a layer of its own. Any of the original alcohol remaining in the brominated layer may be removed by washing with concentrated sulphuric acid.

The unsaturating of brom pentane was carried out by dropping the brom pentane slowly into boiling alcoholic potassium hydroxide solution. A reflax condenser was placed above the reaction flask and was kept at 40°, at which temperature the vaporized alcohol would be condensed and returned to the flask, while the pentene was allowed to pass through the condenser.

The addition of hydrogen bromide to the 2 pentene was accomplished in much the same manner as was the bromination of the alcohol. The pentene was placed in glacial acetic acid and saturated with an excess of hydrogen bromide. In one case the reaction was carried out in a pressure bottle at about 50°, while in the second case, the abromination was allowed to take place in the cold. The addition proceeds very quickly even at low temperatures. The reaction was carried out at a low temperature in the second run to do **away** with any possibility of any 2 brom pentane changing over to 3 brom pentane upon heating. In both cases, however, the products were identical in all respects and varied by only 0.0001 in their indices of refraction at 20 C.

CONCLUSION.

From a consideration of the fact that in both cases where 2 pentene was saturated with hydrogen bromide, to give brom pentane, the product upon careful distillation with an efficient fractionating column, gave absolutely no distillate at 112°- 113°, or the boiling point of 2 brom pentane, but rose to practically 118°, the boiling point of 3 brom pentane before any distillate appeared and then continued to distill over at 118° till the whole of the charge had been distilled, we can conclude that little or no 2 brom pentane was present in the product formed by the saturation of the pentene.

This conclusion is further strengthened by the fact that the index of refraction of the brom pentane made by saturating 2 pentene with hydrogen bromide checked very closely the index of refraction of some 3 brom pentane made by brominating diethyl carbinol, 1.4430 as compared with 1.4443, while it varied by a very large amount from the index of refraction of 2 brom pentane whose index was 1.4322.

SIGNIFICANCE OF EXPERIMENTAL RESULTS.

As was stated earlier in this paper, the prediction of the alternate polarity theory was that, in the case of this reaction, the product formed would be 2 brom pentane, while, according to the electron displacement theory, the compound resulting from the saturation of 2 pentene with hydrogen bromide should be 3 brom pentane.

The experimental work connected with this investigation has shown, in the case of the reaction in question, that the product formed was 3 brom pentane. Hence, the following two conclusions may be made:

(1) That the alternate polarity theory is incorrect and does not give a satisfactory explanation of the relations between the carbon atom in a chain compound.

(2) That the predictions of the electron displacement theory are thoroughly in agreement with what has been found to take place in the case of this reaction and while this work does not serve as a final proof, it at least furnishes a partial substantiation for the electron displacement theory.

EXPERIMENTAL.

(1) Preparation of Ethyl formate ($H\ COO\ C_2H_5$)

($Na\ OOCH + H_2SO_4 = HOOCH + Na\ HSO_4$
($HOOCH + C_2H_5OH = HCOOC_2H_5 + H_2O$

Materials used:

NaOOCH	-100 gms	C.P.
C_2H_5OH	89 c.c.	-95%
H_2SO_4	81 c.c.	SP.G. 1.84

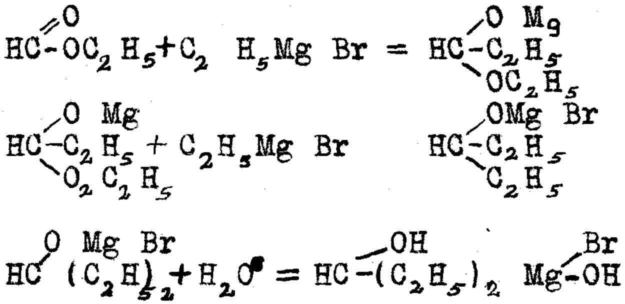
Method:

100 gms. of C. P. sodium formate were placed in a 1.5 litre flask to which was added ethyl sulphuric acid (89 c.c. ethyl alcohol+81 c.c. Sulphuric acid), while still warm from mixing.

The mixture was allowed to stand over night and then distilled from a water bath, using a Hempel column and coil condenser in series and catching the liquid in an ice colled flask. The distillate was then washed with sodium carbonate solution three times using a separatory funnel for separating the product from the aqueous layer. Phosphoric an hydrid was then added until no further hissing was heard on further addition. The solution was then cleared of the sludge by decantation and filtration and finally redistilled. Practically the whole of the liquid distilled over within a temperature range of 0.4°.

The yield obtained using the above method were extremely good, varying from 87% to practically theoretical.

Preparation of Di - Ethyl Carbinol.



$$HC\overset{O}{=}OC_2H_5 + C_2H_5MgBr = HC\left\langle\begin{array}{l}O\,Mg\\ C_2H_5\\ OC_2H_5\end{array}\right.$$

$$HC\left\langle\begin{array}{l}O\,Mg\\ C_2H_5\\ O_2C_2H_5\end{array}\right. + C_2H_5MgBr \quad HC\left\langle\begin{array}{l}OMg\,Br\\ C_2H_5\\ C_2H_5\end{array}\right.$$

$$HC\overset{O\,Mg\,Br}{}(C_2H_5)_2 + H_2O = HC\overset{OH}{-}(C_2H_5)_2 \quad Mg\overset{Br}{-}OH$$

Materials used.

C_2H_5Br	294 c c
C_2H_5OOCH	162 c c
Mg	96 gms
$(C_2H_5)_2O$	416 c c

Method:

The first step was to cover 96 gms of Magnesium ribbon with 416 c c's of absolute ethyl ether, using a 3 litre flask. 294 c c. of ethyl bromide were then added thru a refluxing column, care being taken to keep the reaction flask well cooled. Following the addition of the ethyl bromide, 162 c c of ethyl formate were added to the ethyl magnesium bromide. Upon completion of the reaction sufficient dilute sulphuric acid was added to dissolve up the magnesium bromide and form magnesium sulfate.

There were two layers in the flask at this point, one being the aqueous layer and the other the ether layer containing the diethyl carbinol. The layers were separated by use of a separatory funnel. The ether solution was then distilled, the ether passing off quickly, leaving the diethyl carbinol, which later distilled over. The diethyl carbinol was then well washed, dried over calcium chlorid and redistilled over a range of 117° - 119°. (Cor.)

(Method of Prepartion)

A yield of approximately 75% was obtained.

Preparation of 3 Brom Pentane from Diethyl Carbinol.

The bromination of diethyl carbinol was carried out by placing the carbinol in a pressure bottle, saturating the alcohol with hydrogen bromide gas and then subjecting to pressure by putting the bottle into a pressure bottle frame and heating by immersing in water at 60°.

This process of saturation and compression was repeated until the relative size of layers in the pressure bottle underwent no change upon further treatment, requiring about ten hours in all.

The product was then poured into a separatory funnel and washed four times with water to remove any hydrobromic acid that might be present in excess. The next washing was done with cold, concentrated sulphuric acid and served to remove any alcohol remaining. This was followed with two washings with water and two with sodium carbonate solution. The product was then dried over calcium chloride and distilled. The distillate came over entirely between 117.5° and 119°. (cor.)

Preparation of 2 Pentene from 3 Brom Pentane and Bromination of 2 Pentene.

In the first run the 3 brom pentane was unsaturated by using boiling alcoholic potassium hydroxide solution and the 2 pentene was caught in a pressure bottle containing glacial acetic acid saturated with hydrogen bromide.

The second run was changed in a few details. The vapors from the reaction flask were caught in xylene cooled with a salt and ice cooling bath. The pentene was distilled from the xylene into a flask containing glacial acetic acid saturated with hydrogen bromide. The hydrogen bromide and pentene were allowed to react in the cold. In the first run the pressure bottle was used and the reaction carried on under pressure.

Run #1.

$CH_3\ CH_2\ CHBr\ CH_2\ CH_3 + KOH\ (alc) \rightarrow CH_3\ CH_2\ CH{=}CH -$

$CH_3 + KBr + H_2O$.

$CH_3\ CH_2\ CH = CH\ \ CH_3 + HBr \rightarrow CH_3\ CH_2 - CH\ Br\ CH_2\ CH_3$ or CH_3

$CH_2\ CH_2\ CH\ Br\ \ CH_3$.

Materials.

$(C_2H_5)_2\ CH\ Br$	60 gms.
KOH	60 gms.
$C_2H_5O\ H$	90 gms.

Method.

60 gms. of 3 brom pentane were added, drop by drop, to a boiling solution of 60 gms. of potassium hydroxide in 90 gms. of ethyl alcohol. Connected to the flask was a reflux condenser kept at 40° which allowed the pentene to pass but refluxed the alcohol. From the reflux condenser the vapor passed to a bottle of water at 40° through which it bubbled. This bottle served to catch any alcohol that might have passed over. The vapor next passed through a calcium chloride drying tube, also at 40°, and finally was condensed in a pressure bottle cooled by a salt and ice cooling mixture. The pressure bottle contained approximately 60 gms. of glacial acetic acid to which 40 gms. of

hydrogen bromide were added by bubbling the gas through the acetic acid. The pressure bottle was then removed, closed and placed in the pressure frame where it was allowed to remain three hours at 50°. The contents of the bottle were then poured into water and the brom pentane layer separated by use of a separatory funnel. This layer was washed twice with water, once with sodium carbonate solution, three times with cold, concentrated sulphuric acid, once with water and twice with sodium carbonate solution, in the order named.

The product was then dried over night using calcium chloride. Upon distillation, using a fractionating column, the first of the distillate came over at 117.2° (cor.) but raised immediately to 118° (cor.) where it remained constant until only a very small quantity of liquid remained in the flask.

The final product weighed 28.2 gms., a yield of 46.7% from the 3 brom pentane and had a refractive index of 1.4430 at 20°.

Run #2

The generation of the pentene was carried out exactly as in the first run. The vapor was caught in an ice-cooled flask of xylene from which it was later distilled, the pentene coming over at 36° - 37°. The pentene distilled was caught in a cooled Erlenmeyer flask containing 60 gms. of glacial acetic acid saturated with 43.2 gms. of hydrogen bromide.

The yield of pentene from 57.5 gms. of 3 brom pentane was 20.8 gms., corresponding to a yield of 78.2%.

The reaction mixture of pentene and hydrogen bromide in acetic acid was kept for two hours at 0° to 5° and then allowed to stand over night in an ice box at a temperature of 10° to 15°. The following day it was worked up as described in the first run, the final distillation giving a distillate whose first drop came over at 117.4° (cor.). The temperature rose quickly to 118° (cor.) where it remained for practically the whole of the distillation. The last part of the distillation gave a gradual temperature rise up to 118.8° (cor.).

The weight of brom pentane was 33.3 gms, a yield of 74.3% from the pentene and 57.9% from 3 brom pentane. The refractive index at 20° was 1.4431. Indices of Refraction of 3 Brom Pentane at Various Temperatures.

The 3 brom pentane which was used in obtaining the following readings was the fraction which distilled over a range of 118° - 118.2° (cor.). The 3 brom pentane used for the refractometer reading was some that had been made by brominating diethyl carbinol. The fraction boiling at 118° - 118.2° (cor.) was considered the purest because it was at this temperature that the largest portion of the distillate came over. This fraction gave the following refractive indices as measured with an Abbé refractometer using white light.

$d_{20} = 1.4443$

$d_{25} = 1.4427$

$d_{30} = 1.4400$

$d_{40} = 1.4351$

$d_{45} = 1.4322$

Preparation of 2 Brom Pentane.

An effort was made to prepare 2 brom pentane from 2 pentanol put out by the Standard Oil Company. The procedure was the same in all respects as was the bromination of diethyl carbinol, 3 pentanol.

2 brom pentane boils at 113° but upon distillation of the brominated alcohol no satisfactory results were obtained in that the boiling point rose gradually from about 110° to 125° with no period where it seemed as though a pure product were coming over.

The fraction boiling from 112° - 114° (cor.) had the following refractive indices:

d_{20}	1.4405
d_{25}	1.4382
d_{30}	1.4354
d_{40}	1.4297
d_{45}	1.4269

Because of the fact that there is only a 1° or 2° difference in the boiling points of 2 pentanol and 3 pentanol, there is no surety in the correctness of the above readings. There is a distinct possibility that the brominated product was a mixture of 2 and 3 brom pentane. A second attempt was made to obtain 2 brom pentane by first carefully fractionating the alcohol. Following the procedure mentioned before in this paper, the product was prepared and gave a refractive index reading of 1.4322. at 20°. This value is probably much closer to the correct value than are the readings for 2 brom pentane made from the 2 pentanol not fractionated.

Summary,

Ethyl formate was produced by a new method which, from the standpoint of yields and purity of product, was exceptionally good.

Diethyl carbinol was synthesized from ethyl formate by use of Grignard's reaction with minor changes.

3 brom pentane was made from diethyl carbinol by use of a pressure bottle containing diethyl carbinol saturated with an excess of hydrogen bromide.

2 pentene was obtained from 3 brom pentane by adding the 3 brom pentane to a boiling solution of alcoholic potassium hydroxide.

Brom pentane was made from 2 pentene by allowing the 2 pentene to react with hydrogen bromide.

Boiling points and refractive indices indicated that the brom pentane mentioned above was 3 brom pentane. This fact serves to disprove the correctness of the predictions of the alternate polarity theory and also serves to substantiate the election displacement theory.