ELECTRON DISPLACEMENT IN CARBON COMPOUNDS II. HYDROGEN BROMIDE AND 2-PENTENE

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Introduction

In a previous article[1] it was shown that much of the evidence advanced by Cuy[2] in favor of alternate polarity of carbon atoms in open-chain compounds is not valid, and that the data regarding the addition of hydrogen bromide to ethylene homologs are still inconclusive, since the results obtained by earlier investigators[3,4] have not been correctly interpreted. Moreover, when the work of Wurtz,[5] which has been considered[6] a reaction of hydrogen bromide and 2-pentene, is examined carefully, it is obvious that he was working not with 2-pentene, but with a mixture of pentenes obtainable from a mixture of *iso*-amyl and active amyl alcohols. The work here presented has the purpose of definitely determining the composition of the product resulting from the action of 2-pentene and hydrogen bromide.

On the basis of alternate polarized carbon atoms, the reaction between 2-pentene and hydrogen bromide should yield 2-bromopentane mostly, since the reaction would be: H_3C—+CH^+_-=CH—+CH_2+—CH_3 + H^+Br^- = H_3C—+$CHBr$+—CH_2—+CH+—CH_3. On the basis of the theory of electron displacement,[7] however, the reaction should yield 3-bromopentane as the main product. Methyl exerts a stronger pull on electrons than ethyl does, as shown by the relative ionization constants of organic acids and bases,[8] and therefore 2-pentene, where a methyl and an ethyl radical are situated on opposite sides of the double bond, should have the electrons of this bond closer to the methyl. Therefore when hydrogen bromide adds, the bromine should go largely to the middle carbon atom: CH_3—+CH=CH—+C_2H_5 + H^+Br^- = CH_3+—CH_2+—$CHBr$—+CH_2—+CH_3.[9]

[1] Lucas and Jameson, THIS JOURNAL, **46**, 2475 (1924).

[2] Cuy, *ibid.*, **42**, 503 (1920).

[3] Morgan, *Ann.*, **177**, 304 (1874).

[4] Wagner and Saytzeff, *Ann.*, **179**, 321 (1875).

[5] Wurtz, *ibid.*, **125**, 118 (1863).

[6] Beilstein, "Handbuch der Organischen Chemie," fourth ed., I, 131, Julius Springer, Berlin, **1918**. See also Cuy, Ref. 2.

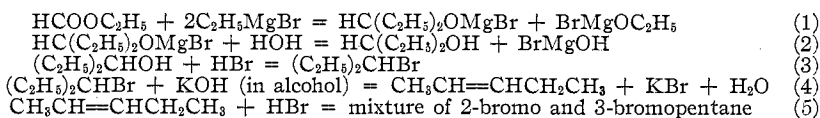[7] Ref. 1. Lewis, THIS JOURNAL, **38**, 762 (1916).

[8] Thus K_A of acetic acid is 1.86×10^{-5} and of propionic acid is 1.45×10^{-5}; K_B of methylamine is 5.0×10^{-4} and of ethylamine is 5.6×10^{-4}; of dimethylamine K_B is 7.4×10^{-4} and of diethylamine is 1.3×10^{-3}.

[9] This method of representing the chemical bond has been proposed by Williams, THIS JOURNAL, **45**, 1272 (1923), in order to show differences in the polarities of atomic linkages. It is well adapted for representing the polar conditions associated with electron displacements.

Since the result predicted by electron displacement differs from that predicted by alternate polarity, the course of this reaction should furnish evidence in favor of one of the two hypotheses.

The product of the reaction would be presumably a mixture of the two bromides.   These cannot be separated by means of fractional distillation, since the boiling point of 3-bromopentane is 118.0–118.2°, and that of 2-bromopentane is 117.5–118.5°.[10]   However, it was found that there is a difference in the refractive indices which makes possible the analysis of the mixture.

The following reactions illustrate the steps involved in the experimental work.

$$HCOOC_2H_5 + 2C_2H_5MgBr = HC(C_2H_5)_2OMgBr + BrMgOC_2H_5 \qquad (1)$$
$$HC(C_2H_5)_2OMgBr + HOH = HC(C_2H_5)_2OH + BrMgOH \qquad (2)$$
$$(C_2H_5)_2CHOH + HBr = (C_2H_5)_2CHBr \qquad (3)$$
$$(C_2H_5)_2CHBr + KOH \text{ (in alcohol)} = CH_3CH=CHCH_2CH_3 + KBr + H_2O \quad (4)$$
$$CH_3CH=CHCH_2CH_3 + HBr = \text{mixture of 2-bromo and 3-bromopentane} \quad (5)$$

Preparation of 3-Bromopentane

Ethyl formate was prepared in 90% yield by adding ethyl hydrogen sulfate (1 mole of C_2H_5OH + 1.15 mole of concd. sulfuric acid) to 1 mole of sodium formate.   The mixture was allowed to stand overnight, and the following day the ethyl formate was distilled through a Hempel column.   After the product had been washed with sodium carbonate solution and dried with phosphorus pentoxide, it redistilled completely within a range of 0.4°.   The ethyl bromide used was shaken with cold, concd. sulfuric acid twice to remove alcohol, washed with dil. sodium hydroxide solution until neutral, dried and distilled.   The boiling point was practically constant at 38° throughout.

The formation of the ethylmagnesium bromide was carried out in a large flask provided with a mechanical stirrer, and to the reaction product ethyl formate was added during continuous stirring.   The 3-pentanol obtained in 75% yield boiled at 117–119° (corr.) at 745 mm.

The conversion of 3-pentanol to the bromide was carried out at a temperature not exceeding 60° by passing hydrogen bromide into the alcohol to saturation, heating under pressure in a water-bath kept at a temperature of 55–60°, cooling, resaturating and continuing the process until there was no change in the relative volumes of the two layers, requiring about ten hours' heating.   It was thought at first that a comparatively low temperature was desirable in order to eliminate the possibility of rearrangement of the bromide.[11]   The crude product was washed four times with water to remove hydrobromic acid, then twice with cold, concd. sulfuric acid to remove unchanged alcohol, then twice each with water and sodium carbonate solution to remove acid, dried over calcium chloride and distilled.   The 3-bromopentane distilled completely between 117.5° and 119° (corr.) at 745 mm., the largest portion coming over at 118–118.2° (corr.) at 745 mm.[12]

[10] Lucas, Simpson and Carter (following article); THIS JOURNAL, **47**, 1462 (1925).

[11] Later, the tendency of 2-bromopentane to rearrange at 140° was found to be nil (Ref. 10).

[12] Rozanov [J. Russ. Phys. Chem. Soc., **48**, 168 (1916); C. A., **11**, 454 (1917)] gives the boiling point of 3-bromopentane as 118.5–119.5° (745 mm.) and $n_D^{20} = 1.44299$. Since the cycloparaffin, from which he obtained this bromide by the action of fuming hydrobromic acid gave isopentane when reduced, it is doubtful that his product was pure 3-bromopentane.

This fraction gave for the D lines the following refractive indices: at 20°, 1.4443; at 25°, 1.4427; at 30°, 1.4400; at 35°, 1.4351; at 40°, 1.4322. In order to make certain that no carbinol remained, the bromide was again shaken with cold, concd. sulfuric acid, washed and dried, this time by shaking with anhydrous potassium carbonate which removes traces of acid as well as water. The refractive index, n_D^{20}, was still 1.4443.

Preparation of 2-Pentene and its Reaction with Hydrogen Bromide

Since olefins sometimes isomerize when heated with acids, it was thought best to prepare 2-pentene by the action of alcoholic potassium hydroxide on 3-bromopentane, rather than by heating 3-pentanol with acidic dehydrating agents.[13] Of the bromide, 60 g. (0.4 mole) was dropped slowly into a boiling solution of 60 g. (1 mole) of potassium hydroxide in 90 g. of ethyl alcohol, heated in an oil-bath at 125–130°. The vapors passed through a reflux condenser kept at 40°, which served to condense ethyl alcohol, then passed into about 50 cc. of xylene, b. p. 135–140°, which was kept cold by means of ice and salt. This xylene solution of the 2-pentene was washed carefully with cold water in order to remove alcohol, and then dried with calcium chloride.

The pentene was distilled between 35° and 37° through a Hempel column into a cold solution of 43 g. (0.5 mole) of hydrogen bromide in 60 g. of glacial acetic acid. The gain in weight was 20.8 g., indicating a yield of 78.2% of pentene from 3-bromopentane. The reaction mixture was allowed to stand for two hours at 0° to 5° and then put into an ice box overnight, where the temperature was slightly higher (10–15°). The following day it was poured into water, the bromide layer was washed twice with water, once with sodium carbonate solution, thrice with cold, concd. sulfuric acid, once with water and twice with sodium carbonate solution. The product, after standing for several hours over anhydrous calcium chloride, was distilled in a flask of the Eastman type. A few drops came over at 117.4° (corr.) and then the temperature rose to 118.0° (corr.) where it remained constant until practically all of the liquid had distilled. Toward the last, the temperature rose gradually to 118.8° (corr.). The distillate weighed 33.3 g., a yield of 74.3% from the pentene, and 57.9% from the 3-bromopentane; n_D^{20}, 1.4431. It was put through the same process of purification twice more, but dried with potassium carbonate, instead of with calcium chloride. The refractive index was 1.4437 the first time, and 1.4437 the second time. Since the refractive index of 3-bromopentane is 1.4443 and that of pure 2-bromopentane is 1.4416,[10] the value found corresponds to a composition of 78% of the former and 22% of the latter.[14] The actual composition may vary as much as 8% from these values.

The result obtained is, therefore, in harmony with the hypothesis of electron displacement, but not with that of alternately polarized carbon atoms.

Summary

1. Hydrogen bromide and 2-pentene react to give a mixture of isomeric bromides consisting of approximately 78% of 3-bromopentane and 22% of 2-bromopentane.

2. This result is in agreement with the prediction made on the basis of electron displacement, but not with that made on the basis of alternately polarized carbon atoms in open chains.

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[13] Risseghem [*Compt. rend.*, **158**, 1694 (1914)] used *p*-toluene-sulfonic acid.

[14] The refractive index is a linear function of the composition. (Ref. 10.)