[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF MOUNT HOLYOKE COLLEGE]

Addition of Hydrogen Bromide to Pentene-1 and Heptene-1

BY MARY L. SHERRILL, KATHERINE E. MAYER AND GERTRUDE F. WALTER

The general conclusions obtained from various investigations of the addition of the hydrogen halides to the normal primary gaseous olefins, ethylene, propylene, butene-1, have been that a given hydrogen halide adds more readily to the higher olefins than to the lower ones and that, of the hydrogen halides, hydrogen iodide reacts most readily, hydrogen bromide easily and hydrogen chloride with difficulty or not at all. Maass and co-workers[1] have found that gaseous ethylene and gaseous halide do not react even under pressure until the critical temperature is reached and a liquid phase appears, that the velocity of reaction of propylene with hydrogen chloride under high pressure increases with the temperature when the substances are in the liquid state but above the critical temperature the velocity of reaction becomes zero, that gaseous propylene and gaseous hydrogen bromide do not react at 100° but react rapidly in the liquid phase, the reaction in the liquid phase being catalyzed by the presence of water and excess acid, that butene-1 reacts easily with hydrogen chloride when the substances are in the liquid phase but that there is no measurable reaction when the reactants are in the gaseous state at atmospheric pressure. The explanation offered is that in the liquid state there is regional orientation and increased molecular attraction.

It has been found that with catalysts[2] gaseous hydrogen halides under atmospheric pressure, in the presence or absence of air, add to gaseous hydrocarbons, even ethylene, to give addition products in yields as high as 93%.

The addition product formed with ethylene has been in all cases ethyl halide and in some cases an additional small amount of a polymeric hydrocarbon has been indicated.[3] Propylene reacted with hydrogen halide to give as the main product isopropyl halide. A small amount of normal propyl iodide was identified by Michael[4] and a small high boiling fraction of halide has been found in the products from catalytic processes. Ingold and Ramsden[5] showed that the product of the addition of hydrogen iodide to propylene depended on the solvent and the concentration of the iodide, the maximum amount of normal propyl iodide being 24.8% in a propane solution and the minimum being 2.8% in a water solution. The halide formed from butene-1 has been 2-bromo- and 2-chlorobutane.[1a,6] The formation of the isopropyl halide and the 2-halobutane in these reactions is in accord with Markownikoff's rule of addition of a hydrogen halide to a double bond. It is especially worthy of note that Maass and his co-workers isolated higher halides and hydrocarbons of high molecular weight indicative of polymerization. From propylene they obtained a secondary hexyl halide equivalent to 50% of the propylene and with butene-1 they have obtained octyl chloride and octylene equivalent to 25% of the butene. Kharasch and his co-workers[7] have indicated that peroxide formation in hydrocarbons modifies the addition of hydrogen bromide to propylene and a larger amount of normal propyl bromide is formed. Hydrogen bromide was added to propylene (0.1 mole or less) in the presence of both antioxidants and oxidants including air. In the case of antioxidants isopropyl bromide was the only product, in the presence of air and other oxidants the amount of isopropyl bromide varied from 79 to zero per cent. The amount of each halide was determined by the index of refraction, assuming the composition a straight line function. The authors state that "the boiling ranges of the addition products were consistent with their composition as calculated by their indices of refraction." In most of the cases where the oxidizing agents were used the quantity of propylene was only 3.5 g. and the total yield of halide small due to separation of the added oxidant. It would seem that under these circumstances the yield of normal propyl bromide is not very significant.

Ingold and Ramsden[5] have studied the addition of hydrogen bromide and iodide to pentene-1. Only 2-bromopentane was obtained when the reaction

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(1) (a) Coffin and Maass, *Can. J. Research*, **3**, 525 (1930); (b) Sutherland and Maass, *ibid.*, **5**, 48 (1931).

(2) Wibaut, Dieckmann and Rutgers, *Proc. Royal Acad. Amsterdam*, **27**, 671 (1924); *Rec. trav. chim.*, **47**, 477 (1928); Wibaut, *Z. Elektrochem.*, **35**, 602 (1929).

(3) Maass and Wright, THIS JOURNAL, **46**, 2664 (1924); Wibaut, Dieckmann and Rutgers, *Proc. Royal Acad. Amsterdam*, **27**, 671 (1924).

(4) Michael, *J. prakt. Chem.*, [2] **60**, 445 (1899).

(5) Ingold and Ramsden, *J. Chem. Soc.*, 2752 (1931).

(6) Lucas, Dillon and Young, THIS JOURNAL, **52**, 1952 (1930).

(7) Kharasch, McNab and Mayo, *ibid.*, **55**, 2531 (1933).

took place either in water or without a solvent. With hydrogen iodide only 2-iodopentane was obtained from a water solution but 1.7% of 1-iodopentane was isolated when no solvent was present.

With the exception of the catalytic processes all these addition reactions have been carried out by cooling the reactants to very low temperatures (liquid air), sealing them in tubes and then allowing them to mix and come to 0° or room temperature. The reactions have therefore taken place under considerable pressure.

For several years a study of the olefin hydrocarbons with five and seven carbon atoms has been in progress in this Laboratory. The ultimate purpose was to measure the ultraviolet absorption spectra of these highly purified compounds and special emphasis has therefore been directed toward methods of preparation and purification. This paper reports the results of a special investigation of the addition reactions of hydrogen bromide to pentene-1 and heptene-1. In the early work when the gaseous halide was added to pentene-1 in a solvent, glacial acetic acid or hexane, the product, contrary to expectation, was found to be almost entirely 1-bromopentane.[8] A thorough investigation of this addition reaction has confirmed the fact that 1-bromopentane is the only product obtained under these conditions. Similarly hydrogen bromide has been added to heptene-1 in hexane, glacial acetic acid and carbon tetrachloride and in each case the product has been found to be exclusively 1-bromoheptane. The conditions under which the primary halide has formed differ from those used by previous investigators mainly in that the hydrocarbon was liquid at ordinary temperature and was dissolved in an organic solvent, that dry hydrogen bromide was passed into the solution at atmospheric pressure, and that the reactants were kept at atmospheric pressure during the entire reaction period. An entirely different result was obtained when aqueous hydrobromic acid was added to each of the hydrocarbons. Since the reaction in water solution is so slow, the mixture was shaken in closed bottles for a long period of time and the product was found to be exclusively the 2-bromo derivative.

Experimental

Preparation of the Hydrocarbons.—Pentene-1 and heptene-1 were prepared[9] by the action of allyl bromide on ethylmagnesium bromide and butylmagnesium bromide, respectively, using butyl ether as a solvent for the Grignard reagent, and by the reduction of 1-bromo-2-ethoxypentane and 1-bromo-2-ethoxyheptane with zinc.[10] The hydrocarbons were purified first by azeotropic fractionation through a Crismer[11] column with absolute alcohol, methyl or ethyl. The Crismer column used for pentene-1 was 1.5 m. in length and 15 mm. in diameter; that for heptene-1 was 60 cm. in length and 15 mm. in diameter. Two distinct fractions were obtained in the pentene-1–methyl alcohol fractionation, a very small amount boiling at 19.2–20.0° at 754 mm. and the other large fraction (92% pentene-1) boiling at 25.8–26.0° at 754 mm. The hydrocarbon obtained from the low boiling azeotropic fraction had a refractive index n^{15}_{D} 1.3680, n^{20}_{D} 1.3650, which would indicate this to be isopropylethylene (b. p. 20.0 ± 0.05° at 760 mm., n^{15}_{D} 1.3675).[12] The amount of material was insufficient, less than 10% of the distillate, for boiling point and density determinations. In the final distillation the azeotropic mixture of heptene-1 and ethyl alcohol (57% heptene-1) boiled at 70.4 ± 0.1° at 754 mm. The hydrocarbons were freed from alcohol by washing repeatedly with water and dried over lime. Calcium chloride is to be avoided as a drying agent for olefins as it catalyzes peroxide formation. The dried hydrocarbon was refluxed over sodium and distilled two or three times from sodium through a Crismer column, the surface of the sodium remaining clean after the first distillation. In no case was there any high boiling fraction or residue indicative of peroxide or polymeric compounds and the index and density of the product showed no change after the first distillation.

The ultraviolet absorption spectrum has been found to be the most sensitive index of purity of these olefin hydrocarbons and the results with pentene-1 and heptene-1 indicated also that there was no change after the first distillation. The physical constants are given in Table I. These show excellent agreement with the most recent data.[13]

TABLE I

PHYSICAL CONSTANTS OF PENTENE-1 AND HEPTENE-1

	Pentene-1		Heptene-1	
Methods of preparation	I Allyl bromide and ethylmagnesium bromide	II 1-Bromo-2-ethoxypentane and zinc	I Allyl bromide and butylmagnesium bromide	II 1-Bromo-2-ethoxyheptane and zinc
Hydrocarbon	I	II	I	II
B. p., °C. (760 mm.) ±0.05	30.2	30.1	93.55	93.45
d^{20}_4	0.6420	0.6410	0.6972	0.6970
n^{20}_{D}	1.3711	1.3710	1.4000	1.3992
Mol. ref. Calcd.	24.73	24.73	34.06	34.06
Mol. ref. Found	24.76	24.78	34.12	34.07
Dielectric constant	1.91	1.92	2.06	2.05

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(8) Jean Rodgers, Master's Thesis, Mount Holyoke College, June, 1929.

(9) Kirrmann, *Bull. soc. chim. France*, **39**, 988 (1925).

(10) Swallen and Boord, THIS JOURNAL, **52**, 655 (1930); Dykstra, Lewis and Boord, *ibid.*, **52**, 3400 (1930).

(11) Crismer, *Bull. soc. chim. Belg.*, **29**, 257 (1920); **33**, 254 (1924).

(12) Norris and Reuter, THIS JOURNAL, **49**, 2624 (1927).

(13) Wilkinson, *J. Chem. Soc.*, 3057 (1931); Waterman and de Kok, *Rec. trav. chim.*, **52**, 298 (1933); Soday and Boord, THIS JOURNAL, **55**, 3300 (1933).

Addition of Hydrogen Bromide to Pentene-1 and Heptene-1.—The olefins freshly distilled from sodium were tested for the presence of peroxide just prior to treatment with hydrogen bromide. In the earlier work the test used was that of Hyman and Wagner.[14] In the later work a method suggested by Milas[15] was used. This method is said to be accurate to one part of peroxide per million of hydrocarbon. The hydrocarbon is added to a solution of sodium iodide in acetone containing glacial acetic acid and a few drops of 6 *N* sulfuric acid and left in the dark for a definite time (at least one hour). The iodine freed is titrated with 0.01 *N* thiosulfate solution and the volume used compared with blank tests. The hydrocarbons used in this work gave no test for peroxide.

I. Gaseous Hydrogen Bromide in Organic Solvents

The hydrogen bromide obtained by dropping 48% hydrobromic acid on phosphorus pentoxide was passed through a trap at −18 to −20°, then over phosphorus pentoxide, through an empty trap and conducted slowly into a solution of the olefin in an organic solvent. The reaction flask was equipped with a mechanical stirrer, a reflux condenser and a thermometer which registered the temperature of the reaction mixture. The temperature of the reaction mixture when carbon tetrachloride or hexane was the solvent was −10 to −12°, when glacial acetic acid was used the temperature was 0 to 5°. During the entire process the reactions were protected from the moisture of the air and from direct light. In some cases light was excluded entirely but no difference in result was obtained. Because of the volatility of the pentene its reaction mixtures were kept at a temperature of 0 to 5° until the reaction was complete. The heptene mixtures, however, were allowed to come to room temperature. All of these reactions took place at atmospheric pressure. In each case the solution was colorless. It was freed from excess acid, dried, and the solvent was removed by distillation. The colorless alkyl bromide was fractionally distilled through a short column and its physical constants were determined. The data obtained are given in Table II and for comparison the data on 1-bromo- and 2-bromopentane and 1-bromo- and 2-bromoheptane are given in Table III.

II. Aqueous Hydrobromic Acid

The hydrocarbon (0.4 mole) was added to a well cooled 48% solution of hydrobromic acid (equivalent to 2 moles of hydrogen bromide) in a pressure bottle. The bottle was closed, wrapped to exclude light and put on a shaking machine. At intervals of several days the hydrocarbon was separated from the acid layer and found to be practically unchanged olefin, so additional acid was added and the mixture was allowed to react for almost two months at room temperature. At the end of this period both the water layer and the oil layer were colorless. Due to the fact that an emulsion, which could not be satisfactorily separated into layers, was obtained, the organic product was extracted with ether. The solution was freed from acid, dried, the ether removed and the bromide was fractionated. The properties of the products obtained are given in Table IIA, 1–5 and B, 1–6.

For comparison the data for the four bromo derivatives previously obtained in this Laboratory are listed in Table III;[16] they compare favorably with the most recent literature data.[17]

Discussion of Results

From a comparison of the data in Table IIA and B with that in Table III, it is evident that when pentene-1 and heptene-1 are treated with gaseous hydrogen bromide in organic solvents the product in each case is the 1-bromo derivative. In the experiments of IIA, 1–4, it is to be noted that although the boiling point of 2-bromopentane is 118–119°, only a minimum amount of distillate is in this range and traces of solvent were present in this distillate. Even if the assumption is made that the fractions up to 127° are mixtures of 2-bromopentane and 1-bromopentane, then on the basis of the refractive index, a straight line function of the composition, 1-bromopentane is 94% of the total distillate. It seems evident that except for traces of solvent the entire product formed from heptene-1 (IIB, 1–5) is 1-bromoheptane. In addition to the usual physical data, boiling point, index, density which check those of the 1-bromo- rather than those of 2-bromoheptane, the dielectric constant of the addition product is 5.36, which corresponds to that of 1-bromoheptane, 5.38, rather than to the much higher one of 2-bromoheptane, 6.46.

Therefore under the conditions of these experiments, that is, the saturation of the primary olefin in certain organic solvents with dry hydrogen bromide at −10°, and allowing the addition reaction to take place at zero degrees or at room temperature under atmospheric pressure, it has been found that contrary to the Markownikoff rule the bromine atom adds to form 1-bromo derivatives rather than the expected 2-bromo compounds.

The difference between these products and those obtained by other investigators from 1-butene and propylene may be due to the presence of a solvent and to the fact that the reactions were carried out at atmospheric pressure. It is believed that the difference is not due to the presence of peroxide as suggested by Kharasch,[7] for it has been found in this Laboratory, in confirmation of the work of Hyman and Wagner,[14] that 1-olefins do not readily form peroxides whereas those olefins with the double bond in the two or three

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(14) Hyman and Wagner, THIS JOURNAL, **52**, 4345 (1930).

(15) Dr. N. A. Milas, Massachusetts Institute of Technology, private communication.

(16) Sherrill, Baldwin and Haas, THIS JOURNAL, **51**, 3034 (1929); Sherrill, *ibid.*, **52**, 1982 (1930).

(17) Ellis and Reid, *ibid.*, **54**, 1674 (1932).

TABLE II

A. ADDITION OF HYDROGEN BROMIDE TO PENTENE-1

Hydrocarbon, g. (mole)	Solvent, conditions	Yield. %	Fractionation, °C. at 760 mm.	Product, g.	n^{2}_{D}	d^{20}_{4}
(1) 7	Eq. vol. Gl.HAc, ice-bath, HBr, 1.5 hours	60	....	Crude	1.4442	
(0.1)		(approx.)	(a) up to 125	Trace	1.4437	
			(b) 125–128	8	1.4440	
(2) 35	Gl.HAc, 3 two-hour periods, ice-bath	66	(a) 94–120	2	1.4365	
(0.5)			(b) 120–126	5	1.4433	
			(c) 126–127	7	1.4438	
			(d) 127–128	30	1.4440	1.2179
			(e) 128–130.6	4	1.4442	
			Residue	Trace		
(3) 7	Eq. vol. hexane −10°	65	74–127	Sm. amt.	1.4228	
(0.1)		(approx.)	127–128.2	9	1.4439	
(4) 35	Eq. vol. hexane, HBr, 3 two-hr. periods, −10 to −12°	75	(a) 111–123	1	1.4300	
(0.5)			(b) 123–127	4	1.4420	
			(c) 127–128	2	1.4438	
			(d) 128–129	40	1.4440	
			(e) 129–130.6	10	1.4440	
(5) 25	Water, 540 g. 48% HBr, 55 days. 337 hrs. of shaking	63	(a) 117.6–118.4	3	1.4385	
(0.35)			(b) 118.4–118.5	25	1.4411	1.2044
			(c) 118.5	3	1.4411	

B. ADDITION OF HYDROGEN BROMIDE TO HEPTENE-1

Hydrocarbon, g. (mole)	Solvent conditions	Yield, %	Fractionation °C.	mm.	Product, g.	n^{20}_{D}	d^{20}_{4}	Dielectric const.
(1) 33	Eq. vol. Gl.HAc, HBr, 3 hrs. (ice-bath)		(a) 64.8	16.5	8	1.4503		
(0.33)		65	(b) 63.1 ± 0.1	15	26	1.4502	1.1374	
(2) 28	Same conditions	60	(a) 62.7–63.0	15	16	1.4501		
(0.3)			(b) 63.6–63.8	16	12	1.4500	1.1376	
(3) 33	Eq. vol. hexane, satd. HBr, −10 to −12°	80	(a) 62.6–62.8	15.5	5	1.4494		
(0.33)			(b) 63.2–63.4	16	36	1.4497	1.1376	
			(c) 64.6–64.4	17	10	1.4497		
(4)	Duplicate of 3	80	(a) 78.2–78.6	29	5±	1.4485		
(0.3)			(b) 75.4–75.6	25	25±	1.4495	1.1381	
			(c) 76.0	25	20±	1.4495		
	(b) fr. from (1), (2), (3), (4), refract. over P_2O_5		(a) 71.8–72.2	21	5±			
			(b) 70.4–70.6	19	78	1.4509	1.1378	5.34
(5) 49	Two vols. CCl_4 stirred 2.5 hrs., soln. −10 to −15°	90	(a) 70.6–71.2	20	1.5	1.4500		
(0.5)			(b) 71.2–71.4	20	54	1.4503		
			(c) 73.0–73.4	22	14	1.4503		
			Residue		10			
	(b), (c) and residue from (5) refractionated		(a) 71.7–72.0	21	6	1.4500		
			(b) 72.0–72.2	21	56	1.4503	1.1378	5.36
			(c) 72.8–73.0	22	7.5	1.4503		
			Residue		5	1.4504		
(6) 40	Water, 825 g. 48% HBr, 53 days shaken 300 hrs.	70	(a) 63.0–63.8	20	3	1.4464		
(0.4)			(b) 63.8–64.0	20	20	1.4474		
			(c) 64.6–64.8	21	25	1.4477	1.1277	6.50

TABLE III

Compound	B. p., °C.	Pressure in mm.	d^{20}_{4}	n^{20}_{D}	Molecular refraction Found	Molecular refraction Calcd.
1-Bromopentane	129.6–129.8	760	1.2175	1.4440	32.94	33.06
2-Bromopentane	118.4–118.6	760	1.2039	1.4411	33.13	
1-Bromoheptane	71.3 ± 0.05	20	1.1384	1.4503	42.31	42.29
2-Bromoheptane	63.8 ± 0.05	20	1.1277	1.4476	42.46	

position form peroxides easily. The hydrocarbons were free from peroxide before the addition of hydrogen bromide. Moreover, the reaction mixtures were never colored as they were in cases where peroxide was known to be present.

The reaction of pentene-1 and heptene-1 (IIA 5, B 6) with aqueous hydrobromic acid gave in each case exclusively 2-bromopentane and 2-bromoheptane. If peroxide were present in any of the reactions, it would be in these for the reactants were well mixed with air in the shaking process. The fact that no color developed in the solution, however, indicates that there was no peroxide formed in these reactions.

Since this work was reported,[18] a similar addition of gaseous hydrogen bromide to form exclusively the primary bromide has been reported in the case of 4,4-dimethylpentene-1 by Whitmore and Homeyer.[19] Kharasch and co-workers[20] consider the 1-bromo-4,4-dimethylpentane obtained by Whitmore as the "abnormal" product and formed because of peroxide content. The 2-bromo-4,4-dimethylpentane is considered the "normal" product of the reaction and was obtained by Kharasch through the addition of hydrogen bromide in the absence of solvents and in the presence of antioxidants.

Linstead and Rydon[21] in an article appearing since this present material was reported give data which support the conclusions reached in this paper, namely, that the formation in organic solvents of the 1-bromo derivatives is not due to the effect of peroxide but rather to the type of solvent used. Hydrogen bromide added to allylacetic acid in hexane gave only the primary bromide, while in the absence of solvent the secondary bromide was obtained. These results are analogous to those obtained by Walker and Lumsden,[22] when undecylenic acid was treated with hydrogen bromide.

Summary

1. The primary olefins pentene-1 and heptene-1 have been prepared in a high degree of purity by two different methods and the physical constants of each measured.

2. The addition compound formed by saturating the olefin in an organic solvent with dry hydrogen bromide and allowing the reaction to take place under atmospheric pressure is exclusively the 1-bromo derivative.

3. The addition compound formed by the reaction of the olefin with aqueous hydrobromic acid is exclusively the 2-bromo derivative.

4. The difference in the products formed by the two methods is believed to be due primarily to the difference in the solvents and not to the presence of any peroxide in the olefin.

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[18] Organic Division, American Chemical Society, Chicago, September, 1933.

[19] Whitmore and Homeyer, THIS JOURNAL, 55, 4555 (1933).

[20] Kharasch, Hannum and Gladstone, *ibid.*, 56, 244 (1934).

[21] Linstead and Rydon, *Nature*, 132, 643 (1933).

[22] Walker and Lumsden, *J. Chem. Soc.*, 29, 1193 (1901).

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[CONTRIBUTION FROM THE LABORATORY OF BIOLOGICAL CHEMISTRY, WASHINGTON UNIVERSITY MEDICAL SCHOOL]

Methylated Sugars. I. The Preparation of Tetramethylglucose[1]

BY EDWARD S. WEST AND RAYMOND F. HOLDEN

The preparation of tetramethylglucose by Haworth's procedure[2] requires much time, the yields are relatively small and the product is difficult to purify. The writers have introduced modifications by which it is now possible to obtain good yields of crystalline tetramethylglucose in eight to ten hours. This has been accomplished by changing radically both the methylation procedure and the method of hydrolyzing the tetramethylmethylglucoside.

Concentrated glucose or methylglucoside solution is methylated completely and quickly by treatment with a carbon tetrachloride solution of methyl sulfate and 60% sodium hydroxide solution. The tetramethylmethylglucoside either before or after isolation is hydrolyzed in 2 N hydrochloric acid by steam distillation.

The specific rotation of our rigorously purified tetramethylglucose was found to be $[\alpha]_D^{20}$ +81.3° in water, which is two degrees lower than the generally accepted value (83.3°) found in the literature.[3] Our value is believed to be the correct one. The rotation of the product of first crystallization from petroleum ether was not changed by four succeeding crystallizations from petroleum ether or followed by crystallization from either water or alcohol. Preparations of

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[1] Supported by a grant from the Rockefeller Foundation to Washington University for research in science. The material of this paper was presented in part at the meeting of the American Chemical Society, Denver, Colorado, August, 1932.

[2] Haworth, *J. Chem. Soc.*, 107, 8 (1915); 113, 188 (1918).

[3] Purdie and Irvine, *J. Chem. Soc.*, 85, 1049 (1904); Haworth and Hirst, *ibid.*, 119, 193 (1921); Gustus and Lewis, THIS JOURNAL, 49, 1515 (1927).