[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Addition of Hydrogen Bromide to Pentene-2[1]

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Pentene-2 is the simplest unsymmetrical alkylene in which the carbon atoms at the double bond are equally hydrogenated, consequently its addition reactions with halogen acids have attracted the attention of a number of investigators. As early as 1875 Wagner and Saytzeff,[2] saw the need of a supplement to Markownikoff's rule which would include olefins of this type. As a result of a study of the addition of hydrogen iodide to pentene-2, these workers formulated the rule that the halogen attaches itself to the carbon atom bearing the shorter chain, for they concluded that the addition product was 2-iodopentane. Recently the addition of hydrogen bromide to this hydrocarbon in acetic acid was studied by Lucas and his co-workers,[3] in order to test the theory of electron displacement. According to this theory, pentene-2, with methyl and ethyl radicals situated on opposite sides of the double bond, should have the electrons of this bond closer to the methyl, since it exerts a stronger pull on the electrons than the ethyl radical; consequently, the halogen atom should attach itself mainly to the central carbon atom. Their prediction on the basis of this theory is in agreement with the decision they reached from their experimental study, namely, that the addition product consists of 78% 3-bromopentane and 22% 2-bromopentane.

Pentene-2, again, played an important role in the development of the theory of partial polarity of Kharasch. It was postulated that this unsaturated hydrocarbon exists in two electromeric forms: a stable electromer in which the extra pair of electrons is displaced toward the middle carbon atom and an unstable electromer in which the displacement is toward the other carbon atom of the double bond. Addition of hydrogen bromide perhaps constitutes the most striking evidence presented for this view, for it was concluded that the unstable electromer derived from 3-bromopentane adds hydrogen bromide in carbon tetrachloride to form 93–95% 3-bromopentane, whereas the stable isomer prepared from 2-bromopentane yields on addition without solvent 93–95% 2-bromopentane.[4]

Previous workers in this field have made use of the comparatively small difference in the refractive indices of 2-bromopentane (1.4412) and 3-bromopentane (1.4443) in order to arrive at the composition of the addition product. In view of the importance which the addition of hydrogen bromide to pentene-2 had assumed, it was considered advisable to reinvestigate the composition of the addition product by some method other than a refractive index determination, since by its use the presence of small amounts of unsuspected substances could easily lead to erroneous conclusions.

Accordingly, another method of analysis has been devised. It is based upon the facts that a mixture of 2- and 3-bromopentanes may be converted to a mixture of the anilides, $CH_3CH_2CH_2$-$CH(CH_3)CONHC_6H_5$ and $(CH_3CH_2)_2CHCONH$-C_6H_5, and that the composition of such a mixture of anilides may be determined satisfactorily using the method of thermal analysis of Rheinboldt and his co-workers.[5] As a result of the application of this method of analysis we have concluded that *hydrogen bromide adds to pentene-2 to yield nearly equivalent amounts of 2- and 3-bromopentanes.*[6] This does not conform with the Wagner–Saytzeff rule, a rule which was based on a study of the addition of hydrogen iodide to pentene-2. More significant however is the fact that our conclusions are not in agreement with those of more recent times. Thus, current views concerning electromeric displacement[6a] based on earlier studies of the composition of the addition product must be modified and the concept of electromerism receives no support from these findings.

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(1) The work here described constitutes part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Frank H. Stodola in partial fulfilment of the requirements for the degree of Doctor of Philosophy in June, 1933.

(2) Wagner and Saytzeff, *Ann.*, **179**, 313 (1875).

(3) Lucas and Jameson, THIS JOURNAL, **46**, 2475 (1924); Lucas and Moyse, *ibid.*, **47**, 1459 (1925).

(4) Kharasch and Darkis, *Chem. Rev.*, **5**, 571 (1928); Sherrill. Otto and Pickett, THIS JOURNAL, **51**, 3023 (1929); Sherrill, Baldwin and Haas, *ibid.*, **51**, 3034 (1929); Carr, *ibid.*, **51**, 3041 (1929); Clark and Hallonquist, *Trans. Roy. Soc. Can.*, [3] **24**, Sect. 3, 115–119 (1930); Seyer, THIS JOURNAL, **53**, 3588 (1931).

(5) Rheinboldt, *et al.*, *J. prakt. Chem.*, [2] **111**, 242 (1925); (2) **112**, 187 (1926); [2] **113**, 199 and 348 (1926).

(6) This work was completed before attention was directed to the possible peroxide oxide effect [see Kharasch, *et al.*, THIS JOURNAL, **55**, 2468, 2521, 2531 (1933)].

(6a) Robinson, "Outline of an Electronic Theory of the Course of Organic Reactions," The Institute of Chemistry of Great Britain and Ireland, 30, Russell Square, London, W. C. 1, 1932, p. 17.

A. Preparation of Pentene-2.—The pentene-2 was obtained from two different sources: (1) 3-bromopentane, which allowed a duplication of the addition carried out by Sherrill, Otto and Pickett, and (2) the stable form of $CH_3CH{=}C(C_2H_5)COOH$, which yielded a pentene-2, prepared in a manner different from that used for the electromeric pentenes, and which permitted a demonstration of the fact that the mode of preparation had no effect upon the composition of the addition product. The pentene-2 from this second source is one of the geometrical isomers and its physical properties agreed with those of the pentene prepared from 3-bromopentane. It is presumably the stable geometrical isomer since its physical properties are also in agreement with those of the pentene-2 of van Risseghem[7] which resisted all attempts at isomerization.

1. Pentene-2 from 3-Bromopentane

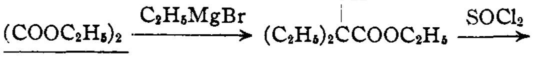
3-Bromopentane.—The pentanol-3 from which this bromide was prepared was obtained by Grignard synthesis according to the procedure of Lucas and Moyse.[3] The physical constants compared with those of previous workers are as follows: b. p. 113.2–114.7° at 740 mm., n_{D}^{20} 1.4130 (Lauer and Stodola); b. p. 114.8–115.2°, n_{D}^{20} 1.4078 (Sherrill, Otto and Pickett[4]); b. p. 114–15°, n_{D}^{20} 1.4100 (Clark and Hallonquist[4]). The 3,5-dinitrobenzoate melted at 98.5–99.5°. Conant and Blatt[8] give 101° as the melting point, while Boese, Jones and Major[9] report 97°.

For the conversion of the alcohol into the bromide the convenient method of Clark and Hallonquist[4] was found to give a product of high purity. The 3-bromopentane, obtained in 82% yield (550 g.), had the following properties: b. p. 117.4–118.4° (corr.) at 734 mm.; n_{D}^{20} 1.4443. These values compare favorably with those of Sherrill, Otto and Pickett (b. p. 118.2–118.6° at 760 mm.; n_{D}^{20} 1.4443) and Clark and Hallonquist (b. p. 117.8–118.5°; n_{D}^{20} 1.44429). This sample of 3-bromopentane was used for the preparation of pentene-2 and for the development of the method of analysis.

Pentene-2.—The excellent procedure of Sherrill, Otto and Pickett gave pure pentene-2 in good yields. Its physical constants are listed below with the data of some other workers: Lauer and Stodola, b. p. 35.7–35.9° at 743 mm., n_{D}^{20} 1.3797; Lauer and Stodola, b. p. 35.9–36.0° at 744 mm., n_{D}^{20} 1.3796; van Risseghem, b. p. 36.4°; Sherrill, Otto and Pickett, n_{D}^{20} 1.37965; Clark and Hallonquist, b. p. 36.5°, n_{D}^{20} 1.37960.

2. Pentene-2 from α-Ethylcrotonic Acid

The following synthesis was developed for the preparation of pentene-2



$$(COOC_2H_5)_2 \xrightarrow{C_2H_5MgBr} (C_2H_5)_2\overset{OH}{\overset{|}{C}}COOC_2H_5 \xrightarrow{SOCl_2}$$

$$CH_3CH{=}C(C_2H_5)COOC_2H_5 \xrightarrow{\text{alc. KOH}}$$

$$CH_3CH{=}C(C_2H_5)COOH \xrightarrow{HBr}$$

$$CH_3CHBrCH(C_2H_5)COOH \xrightarrow[Na_2CO_3]{\text{Aqueous}}$$

$$CH_3CH{=}CHCH_2CH_3$$

It is similar to one carried out by Lucas, Dillon and Young[10] for the preparation of the *cis* and *trans* forms of butene-2.

$(C_2H_5)_2C(OH)COOC_2H_5$.—The Grignard synthesis of Hepworth[11] using ethyl oxalate and ethylmagnesium bromide gave a 39% yield of ester boiling at 172.5–175.0° (743 mm.); the value given by Hepworth is 175–177°.

$CH_3CH{=}C(C_2H_5)COOC_2H_5$.—For the dehydration of the hydroxy ester $SOCl_2$ was found to be superior to phosphorus trichloride which was used by Fittig and Howe.[12] The product consisted of a mixture of the esters of the unstable and stable α-ethylcrotonic acids and had a boiling range of 159.5–165.3°. For the ester of the unstable acid v. Auwers[13] gives a boiling point of 158–159° and for the other 167°.

Stable Form of $CH_3CH{=}C(C_2H_5)COOH$.—Saponification of the unsaturated esters with alcoholic potash gave a mixture of the stable and unstable α-ethylcrotonic acids. They were separated by distillation and crystallization from petroleum ether. The stable isomer of melting point 41–42° was obtained in 33% yield [Fittig and Howe 41.5°, and Blaise and Bagard[14] 45° (misprint ?)]. The yield can be increased materially by the conversion of the unstable acid into the stable form by the use of the phosphorus trichloride method of Blaise and Bagard.

$CH_3CHBrCH(C_2H_5)COOH$.—The bromo acid of melting point 29–31° was obtained in 30% yield from the stable form of the unsaturated acid (m. p. 41–42°) and concentrated hydrobromic acid using the method of Fittig and Howe. The melting point reported by Fittig and Howe, and later by Hagman and Johannson[15] was 25°; repeated crystallization from low boiling petroleum ether gave us a melting point of 31–32°.

Pentene-2.—Treatment of 85 g. of $CH_3CHBrCH(C_2H_5)COOH$ (m. p. 29–31°) with 36.2 g. of sodium carbonate in water according to the procedure of Fittig and Howe gave 15 g. of pentene-2 which after drying distilled between 35.65–35.70° at 737 mm. (yield 12.5 g.). The refractive index of this pentene-2 at 20° was 1.3795.

B. The Addition of Hydrogen Bromide.—The mode of addition was studied in the presence of a polar solvent (acetic acid) and without solvent. Three different samples of pentene-2 were used; the addition was carried out eight times and each addition product was analyzed in triplicate. The results are given in Table I.

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(7) Van Risseghem, *Bull. soc. chim. Belg.*, **28**, 187–98 (1914).

(8) Conant and Blatt, THIS JOURNAL, **51**, 1234 (1929).

(9) Boese, Jones and Major, *ibid.*, **53**, 3536 (1931).

(10) Lucas, Dillon and Young, *ibid.*, **51**, 2528 (1929). See also Wislicenus, Talbot, Henze and Schmidt, *Ann.*, **313**, 207-250 (1909).

(11) Hepworth, *J. Chem. Soc.*, **115**, 1207 (1919).

(12) Fittig and Howe, *Ann.*, **200**, 21 (1880).

(13) V. Auwers, *ibid.*, **432**, 46 (1923).

(14) Blaise and Bagard, *Ann. chim.*, [8] **11**, 128 (1907).

(15) Hagman and Johannson, *Ber.*, **55**, 647 (1922).

Table I

Analysis of the Addition Products of Hydrogen Bromide to Pentene-2

Source of pentene-2	Solvent	n^{20}_D	M. p. of anilide mixture, °C.	3-Bromopentane, %
3-Bromopentane (1st preparation)	None	1.4437	95.5	52
			98.3	56
			96.0	53
	None		96.5	54
			94.7	51
			97.7	55
	Acetic acid	1.4432	93.3	49
			93.0	49
			91.5	47
3-Bromopentane (2nd preparation)	None	1.4438	95.9	53
			96.0	53
			92.8	49
	None	1.4438	97.0	54
			96.9	54
			96.3	53
	None	1.4432	93.5	50
			93.7	50
			92.8	49
	Acetic acid	1.4436	92.1	47
			90.0	44
			90.8	46
$CH_3CH{=}C(C_2H_5)$-COOH (Stable form)	None		94.0	50
			96.3	53
			95.2	52

In order to duplicate exactly the work of Sherrill, Otto and Pickett, their method of preparation and purification of hydrogen bromide was used for several of the additions. In this case the final drying agent was anhydrous sodium sulfate. For the remaining additions, hydrogen bromide was obtained by the action of pure bromine on tetrahydronaphthalene. To ensure complete drying of the gas, phosphorus pentoxide was used, being preceded by fused calcium bromide and naphthalene. In case the addition was conducted in the absence of solvent, the hydrogen bromide was bubbled through the pentene-2 contained in an all-glass (Pyrex) absorber cooled in an ice and salt bath (−10°). The unused gas was passed through a drying train. Complete addition required from twenty-six to thirty hours.

In the case of the addition in the presence of acetic acid, dry hydrogen bromide was passed into acetic acid (m. p. 16.7°) until a 20% solution was obtained. One-tenth of a mole of pentene-2 was then dissolved in sufficient hydrogen bromide–acetic acid mixture to provide two-tenths of a mole of hydrogen bromide. The addition was conducted at room temperature in a glass-stoppered bottle out of contact with moist air. Addition was complete in less than five days.

The bromides were purified according to the method of Sherrill, Otto and Pickett. In all cases the distillation was carried out carefully so that only a very small first fraction and residue had to be rejected, thereby causing little change in the relative amounts of the bromides. The mixture of bromides obtained after distillation was analyzed by the method described in the following section.

C. The Method of Analysis and the Analysis of the Addition Product.—A carefully standardized procedure was developed for the conversion of the bromides to their anilides and a large number of bromide mixtures of known composition were subjected to this procedure. The curve (heavy line in Fig. 1) which was used for all of the determinations herein reported, was based on the melting points of the mixed anilides obtained from known mixtures of the bromides by means of this standardized procedure. Thus the value 93.6° is an average of seven different determinations, starting in each case with *equal amounts* of 2-bromopentane and 3-bromopentane (the lowest and the highest melting points of the group, 91.6 and 95.5°, would then correspond to 47 and 53% 3-bromopentane, respectively). The average melting point of the mixture of anilides which was obtained from the mixture of bromides resulting from the addition of hydrogen bromide to pentene-2 was 95.5°. This corresponds to the presence of 53% 3-bromopentane in the addition product. The extreme values in this group of eighteen separate determinations correspond to 49 and 56% 3-bromopentane. (The values for the addition products in case acetic acid was used as solvent are not included. They were somewhat lower than those obtained in the absence of a solvent.)

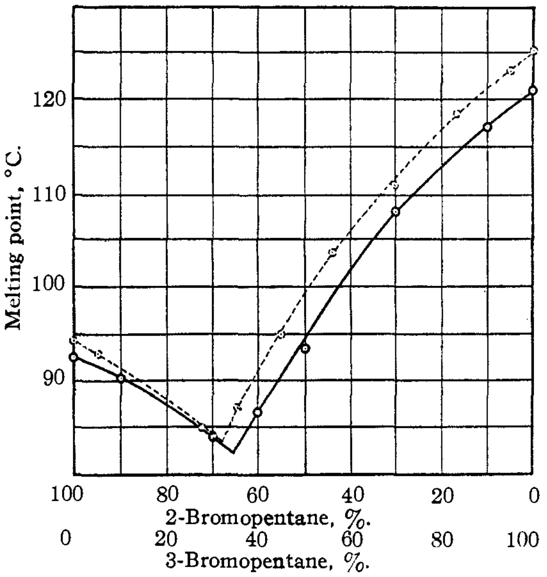

Fig. 1.

In order to make certain that the melting points of the anilides obtained from the addition product actually correspond to this composition, a weighed amount of the anilide, $(CH_3CH_2)_2CHCONHC_6H_5$, was added to each of seven different samples after their melting points had been taken. The compositions of these new mixtures as indicated by their new melting points agreed with the values calculated.

Furthermore, the anilide mixture obtained from a one to one mixture of bromides, when added in equal amount to the anilide mixture obtained from the addition product, caused no significant change in melting point.

Finally, systematically varied mixtures of carefully purified anilides were prepared and their melting points were taken (dotted line in Fig. 1). The mixture of pure anilides of composition 46% $(CH_3CH_2)_2CHCONHC_6H_5$ and 54% $CH_3CH_2CH_2CH(CH_3)CONHC_6H_5$ melts at 95.5°, the average temperature at which the mixture of anilides obtained from the addition product melts.

For the development of the method very pure samples of 2-bromopentane and 3-bromopentane were used.

2-Bromopentane.—For the preparation of pentanol-2, the method of Sherrill, Baldwin and Haas was used. The alcohol boiled at 117.4–118.9° at 734 mm. (n^{20}_{D} 1.4067). The values reported by Sherrill and co-workers were b. p. 118.5–119.5 (760 mm.), n^{20}_{D} 1.4060; Clark and Hallonquist give 118.2–119.6°; n^{20}_{D} 1.40602. The 3,5-dinitrobenzoate melted at 61.5–62.0°. Reid and Malone[16] found 62.1°. The 2-bromopentane was obtained in 84% yield by the method of Clark and Hallonquist; b. p. 116.4–117.4° at 737 mm.; n^{20}_{D} 1.4414. The constants of Sherrill and co-workers are b. p. 117–118° (760 mm.), n^{20}_{D} 1.4412 and of Clark and Hallonquist, b. p. 117–118° (755 mm.). n^{20}_{D} 1.44125.

3-Bromopentane.—Already described in the section dealing with the preparation of pentene-2.

The Method of Analysis

To 0.4 g. of magnesium and a *trace* of iodine in a loosely-corked 20-cm. test-tube, sufficient pure freshly distilled ether to cover the metal was added. One-half cc. of the bromide mixture to be analyzed was then added; after the initial reaction had subsided, the addition of two 0.25 cc. portions of the bromide mixture was made. (Ether was added from time to time in order to keep the tube about one-fourth full.) The ether solution was next transferred to a 50-cc. Erlenmeyer flask and 0.25 cc. of pure phenyl isocyanate in 7 cc. of ether was added dropwise. The reaction product was then decomposed with 1 cc. of concd. hydrochloric acid in 10 cc. of water. The ether layer was separated and the aqueous layer extracted once with ether. The combined ether extracts were placed in a small beaker and the solvent removed by means of a stream of air. The solid anilide mixture after standing for several hours at room temperature and for several hours in an ice box, was then pressed out on a porous plate. Two-tenths of a gram of this material was boiled for ten minutes with a small amount of methyl alcohol and norite. After filtration, the methyl alcohol was removed in part on a steam-bath. When only 3 cc. of solution remained, water was added to the point of incipient crystallization and the solution placed in an ice–salt bath. Seventeen cc. of water was then added portionwise after crystallization had begun. The solid obtained was then separated by filtration and allowed to air dry.

For the thermal analysis a small amount of this solid was packed into a melting point tube (approx. 3 mm. in diameter). This tube into which a glass stirring rod was inserted, was then placed in a melting point apparatus, which permitted stirring of the contents of the melting point tube. The point at which the last crystal disappeared was designated as the melting point of the mixture.

A number of mixtures of 2-bromopentane and 3-bromopentane were then subjected to this method of analysis, the results being given in Table II.

TABLE II

MELTING POINTS OF THE ANILIDE MIXTURES OBTAINED FROM BROMIDE MIXTURES OF KNOWN COMPOSITION

2-Bromopentane, %	100	90	70	60	50	30	10	0
3-Bromopentane, %	0	10	30	40	50	70	90	100
	92.8	90.3	84.7	85.3	91.7	107.7	117.0	121.7
	93.2	90.0	83.0	87.7	92.7	107.6	117.1	120.5
	93.2	90.3	85.0	84.7	91.6	109.0	117.2	120.2
	91.6	90.2	83.5	88.0	94.7	107.6	116.5	121.2
	92.4	90.0	83.2	88.5	95.2	107.8	116.6	120.5
	92.7	90.0	84.2	86.8	93.7	108.0	116.9	121.7
	92.1	90.3	83.8	85.5	95.5	108.5	118.1	121.0
Av.	92.6	90.2	83.9[a]	86.6[a]	93.6	108.0	117.1	121.0

[a] The eutectic point lies in this region. In order to prove that there was no overlapping a weighed amount of one of the pure anilides was added in each of the determinations and the melting point was again determined.

The addition products which were obtained by the action of hydrogen bromide on three specimens of pentene-2 yielded the results in Table I.

Summary

1. A study of the addition of hydrogen bromide to pentene-2 has led to the conclusion that nearly equivalent amounts of 2-bromopentane and 3-bromopentane result.

2. The rule of Wagner and Saytzeff does not hold; current views concerning electromeric displacement in pentene-2 must be modified and the theory of partial polarity is invalidated in so far as it derives support from previous studies of the behavior of pentene-2 upon the addition of hydrogen bromide.

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[16] Reid and Malone, THIS JOURNAL, **51**, 3426 (1929).