diketones were obtained, resulting from the elimination of the methoxyl or aroxyl group through the action of the reducing agents. The loss of methoxyl or aroxyl occurs only in experiments in which the methoxy- or aroxyethanes, $ArCOCH_2CH(OCH_3)COAr$, are the starting materials or are the principal products in the reactions concerned. Apparently these substances do not decompose (splitting out alcohol or phenol) under the most drastic conditions involved during a reduction, namely, boiling in an acetic acid–anhydride mixture. The reaction, therefore, must involve direct reduction. In Table III are listed the methoxy- and aroxyethanes reduced in this manner.

Summary

1. A variety of reducing conditions are described under which six different substituted unsaturated 1,4-diketones are converted into the corresponding furans, and under which conditions the corresponding saturated 1,4-diketones are stable.
2. The bearing of these facts on the theory of 1,6-addition of hydrogen to unsaturated 1,4-dicarbonyl compounds is discussed and the conclusion is drawn that the dienol postulated by the theory is actually formed as the primary intermediate in reduction and accounts for the formation of the furans.
3. The diaryl-methoxy- and aroxy-substituted 1,4-diketones are easily dehydrated to the corresponding furans and decompose on heating into the corresponding dibenzoylethylene and alcohol or phenol.
4. The methoxyl groups in certain cases are eliminated by reduction from the methoxy-saturated 1,4-diketones.
5. New aroxy- and methoxydibenzoylethylenes are described.

UNIVERSITY, VIRGINIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

ISOMERS OF 2-PENTENE. I. PENTENE-2 FROM 3-BROMOPENTANE AND FROM 3-PENTANOL[1]

BY MARY L. SHERRILL, BELLE OTTO AND LUCY W. PICKETT

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The present study is one of a series involved in an investigation of the preparation and properties of the isomeric 2-pentenes.[2] Wurtz[3] was the first to report the preparation of 2-pentene and the reaction of this with

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[1] Presented in abstract before the Organic Division, at the Swampscott Meeting of the American Chemical Society, September, 1928.

[2] The work originated in the request of Professor Morris Kharasch (September, 1926) that Professor Carr make, in this Laboratory, absorption spectra measurements of a 2-pentene obtained from 3-bromopentane and of an isomeric form of this 2-pentene which Professor Kharasch had obtained by heating 2-pentene in xylene.

[3] Wurtz, *Ann.*, **125**, 114 (1863).

hydrogen bromide. Wagner and Saytzeff[4] prepared the 2-pentene from 3-iodopentane and reported an addition of hydrogen iodide to the pentene to form 2-iodopentane. Brochet[5] also reported the formation of 2-iodopentane by this addition reaction. Van Risseghem[6] prepared 2-pentene by the dehydration of 3-pentanol with *p*-toluenesulfonic acid. In the study of the reactions of the double bond Brunel[7] and Cuy[8] used the work of Wagner and Saytzeff to support their theories. Cuy interpreted the addition reactions in support of the theory of alternate polarity in carbon chains. Lucas and collaborators[9] in a series of investigations presented experimental evidence at variance with this theory and advanced in its place the theory of electronic displacement. According to the alternate polarity theory, addition of hydrogen bromide to 2-pentene should give largely 2-bromopentane, but according to the theory of electronic displacement as interpreted by Lucas, the chief product should be 3-bromopentane. In view of the fact that the accuracy of the older work seemed in doubt, Lucas and Moyse[9b] prepared 3-bromopentane and from this the 2-pentene was obtained by the action of alcoholic potash. The 2-pentene was distilled directly into xylene and from the dried xylene solution 2-pentene (boiling between 35 and 37°) was distilled into glacial acetic acid containing hydrogen bromide. The bromide obtained had a refractive index of n_D^{20} 1.4437 and was 78% 3-bromopentane and 22% 2-bromopentane. This percentage was determined entirely by the index of refraction, since Lucas had shown that the refractive index of a mixture of 3-bromopentane and of 2-bromopentane was a linear function of the composition. Lucas considered the electron displacement theory confirmed by these data. Kharasch[10] has determined the relative electronegativity of certain organic radicals and found that the methyl group is more electronegative than the ethyl group. This is in accord with Lucas' ideas but Kharasch disagrees with Lucas as to the resultant condition of the carbons at the double bonds. Lucas and Moyse[9b] state that "methyl exerts a stronger pull on electrons than ethyl does, as shown by the relative ionization constants of organic acids and bases, 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

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

[5] Brochet, *Bull. soc. chim.*, [3] **7**, 567 (1892).

[6] Van Risseghem, *Bull. soc. chim. Belg.*, **28**, 53, 187, 288 (1914).

[7] Brunel and Probeck, *Am. Chem. J.*, **44**, 431 (1910).

[8] Cuy, THIS JOURNAL, **42**, 503 (1920).

[9] (a) Lucas and Jameson, *ibid.*, **46**, 2475 (1924); (b) Lucas and Moyse, *ibid.*, **47**, 1459 (1925); (c) Lucas, Simpson and Carter, *ibid.*, **47**, 1462 (1925).

[10] Kharasch and Reinmuth, *J. Chem. Ed.*, **5**, 404 (1928); Kharasch and Marker, THIS JOURNAL, **48**, 3130 (1926).

middle carbon atom." According to the Kharasch theory the substitution of an electronegative atom or radical for a hydrogen in the methyl group decreases the electronegativity of the group, and since the methyl group is more electronegative than the ethyl group, the carbon atom in the ethylenic linkage which carries the methyl group will be *less* electronegative than that which has the ethyl group. As a consequence the pair of electrons should be displaced toward the carbon atom to which the ethyl group is attached and when hydrogen bromide is added to 2-pentene the product should be 2-bromopentane and not 3-bromopentane as would follow from the hypothesis of Lucas.

As a corollary of this theory of the partial polarity of the ethylene bond, Kharasch[11] predicted the existence of electronic isomers in cases where the radicals attached to the two carbon atoms of the double bond differ very slightly in electronegativity, as is the case in 2-pentene. In one isomer the second pair of electrons would be displaced toward the carbon atom to which the ethyl group is attached and in the other isomer toward the carbon atom carrying the methyl group, but the latter isomer should be the less stable. In the preparation of 2-pentene from *3-bromopentane* it was reasonable to expect the formation of the less stable isomer since the carbon atom to which the bromine is attached would have its electronegativity decreased and the electrons would be displaced in such a way that with the splitting off of hydrobromic acid in the formation of the pentene the second pair of electrons of the double bond would be displaced toward the methyl group. This form of 2-pentene should add hydrogen bromide to give 3-bromopentane. Kharasch further postulated the possibility of transforming this form of 2-pentene into the more stable form which should add hydrogen bromide to form 2-bromopentane.

In order to confirm this theory, Kharasch repeated the work of Lucas and, under similar conditions, obtained results identical with those of Lucas. Kharasch found, however, that whereas this 2-pentene, made from 3-bromopentane, in glacial acetic acid added hydrogen bromide to form 78% of 3-bromopentane and 22% of 2-bromopentane, in a nonpolar solvent such as carbon tetrachloride or petroleum ether or by direct addition of hydrogen bromide without a solvent, the 2-pentene gave 97–100% of 3-bromopentane. Kharasch then heated a solution of 2-pentene in xylene in a sealed glass tube at 90–100° for varying lengths of time and found that the 2-pentene was gradually transformed into an isomeric form of 2-pentene which gave addition products with hydrogen bromide varying from 63% of 3-bromo- and 37% of 2-bromopentane to 16% of 3-bromo- and 84% of 2-bromopentane depending on the length of time

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[11] Private communication, September, 1926; paper presented at Organic Symposium, Columbus, Ohio, December, 1927. Since the preparation of this article a full discussion of Kharasch's theory has been published in *Chemical Reviews*, **5**, 571 (1928).

it had been heated. The percentage composition was determined by the index of refraction of the bromide obtained. This work of Kharasch gave evidence of the two electromers which he had believed theoretically possible. To obtain additional data Professor Kharasch asked Professor Carr to make absorption spectra measurements of these compounds. The preparation, the purification of the 2-pentene and its transformation into the isomeric form were undertaken in this Laboratory, the products to be used for absorption measurements. The addition products and the physical properties of the 2-pentene have been studied. The work of Kharasch has been duplicated and additional data have been obtained.

In view of the fact that for absorption measurements it is highly important to have materials of a high degree of purity, it seemed essential to have the measurements made on each of the pure isomers rather than on possible mixtures. This involved the consideration of methods of separation. In addition to the electronic isomers considered by Kharasch, there is also the possibility, in 2-pentene, of *cis-trans* isomerism. In the present work this possibility has been kept constantly in mind. Van Risseghem[6] attempted the separation of the *cis-trans* isomers of 2-pentene. She prepared the 2-pentene by the dehydrating action of *p*-toluenesulfonic acid on diethylcarbinol at 135–140°. Repeated fractionation through a Young column gave no evidence of separation and since attempts to isomerize also failed she concluded that only one form was stable or that there was an equilibrium mixture of the two. In spite of these results it was considered advisable to use the method so successfully used by Van de Walle[12] in the separation of *cis-trans* isomers of the halogen ethylenes, that is, the fractionation of azeotropic mixtures of the pentenes with absolute alcohol. In the separation of *cis-trans* isomers the alcohol has seemed to have a stabilizing effect and by its use isomers have been separated which had not been separated by any other method. The method has proved highly satisfactory for the purification of the pentenes.

Experimental

Preparation of 3-Pentanol (Diethylcarbinol).—3-Pentanol was prepared by a Grignard synthesis from ethylmagnesium bromide and ethyl formate. A detailed description of the method is given by Lucas and Moyse[9b] and their work was repeated in this Laboratory. The ethyl formate, prepared from ethyl alcohol (6 moles), concentrated sulfuric acid (6.8 moles) and sodium formate (6 moles) was obtained in 90% yield (b. p. 54.2 ± 0.1°). The final distillation of the 3-pentanol gave a product (70% yield) which boiled at 114.8–115.2° and had a refractive index, n^{20}_{D} 1.4078. Lucas and Moyse[9b] give the boiling point as 117–119° (corr.) at 745 mm. The values given by other investigators[13] correspond more closely to that obtained in this Laboratory.

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[12] Van de Walle, *Bull. soc. chim. Belg.*, **27**, 209 (1913); *Mémoires de l'Acad. roy. Belg. Classe des Sciences*, 2e serie, **7**, 49 (1923); *Bull. soc. chim. Belg.*, **34**, 10, 339 (1925); **35**, 29 (1926).

[13] Timmermans, *ibid.*, **27**, 334 (1913), gives 115.35 ± 0.10° at 760 mm.; Willcox

In addition to the 3-pentanol prepared in this Laboratory, pentanol-3 (synthetic) was obtained from R. E. Marker. This material (b. p. 114–116.8° corr., and n_D^{20} 1.4078) was used in some comparison runs. Commercial 3-pentanol (Sharples Solvents Corporation) was fractionated several times through a 50-cm. Crismer column and gave fractions 114–115.8°, n_D^{20} 1.4078, and 115.8–116.2°, n_D^{20} 1.4079. This material was used only in trying some variations of method and not for any of the conclusive experiments.

Preparation of 3-Bromopentane.—This compound was formed by treating the carbinol according to the method given by Kharasch.[14] The carbinol was placed in a round-bottomed flask and cooled to −10°. It was then saturated with hydrogen bromide which was obtained by the action of bromine on red phosphorus and water, passed through U-tubes containing moist red phosphorus and one tube containing anhydrous sodium sulfate. After saturation the flask containing the carbinol was closed with a stopper to which a toy rubber balloon was attached and was heated in a water-bath up to 60° and kept at that temperature until the collapse of the balloon indicated complete absorption of the hydrogen bromide. This saturation process was repeated several times until no more gas was absorbed. The product was separated from the hydrobromic acid–water layer, washed four times with ice water, twice with ice-cold concentrated sulfuric acid, once with ice water, twice with a cold saturated solution of sodium carbonate and once with ice water. It was then dried over potassium carbonate and distilled from a flask with fractionating neck. The 3-bromopentane was obtained in 84–85% yields and had the following properties: boiling point, 118.2–118.5° at 760 mm.; n_D^{20} 1.4443 (Abbé), 1.44431 (Zeiss dipping); d_4^{20} 1.2170. Repetition of the above procedure in many runs gave identical results. The process was slow and in an effort to hasten the process variations in the above procedure were tried which brought out the interesting fact that unless great care was taken in the preparation of the bromopentane the product was not pure 3-bromopentane but a mixture of 3-bromopentane and 2-bromopentane (b. p. 117.5–118.5° at 745 mm., n_D^{20} 1.4415).[9c,3] The variations in treatment of the carbinol were the use of gaseous hydrogen bromide under pressure,[9b] the action of phosphorus tribromide in the cold and gently warmed

TABLE I

RESULTS OF EXPERIMENTS

		B. p. at 760 mm., °C.	n_D^{20}
A. By saturation with gaseous hydrogen bromide at −10° and warming to 60°			
(1) Atmospheric pressure	(repeated runs)	118.2–118.5	1.44431
(2) Increased pressure	(a)	118 –118.5	1.4443
	(b)	117.5–118.3	1.4432
	(c)	117.6–119.1	1.4427
	(d)	36 at 43 mm.	1.4422
B. By action of phosphorus tribromide			
	(a)	116.5–118.5	1.4424
	(b)	115 –118.5	1.4404
C. By action of 48% hydrobromic acid			
	(a)	115–118	1.4419
	(b)	115–118	1.4422

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and Brunel, THIS JOURNAL, **38**, 1838 (1916), give 114.8–115.2° at 760 mm.; Brunel, *ibid.*, **45**, 1337 (1923), gives 115.4° at 754 mm., n_D^{25} 1.4077; Norris and Cortese, *ibid.*, **49**, 2644 (1927), give 115.8–116° and n_D^{25} 1.4079.

[14] Kharasch, private communication, 1926.

to 60° and the action of 48% hydrobromic acid refluxed for several hours. Table I shows the variations in the product obtained.

Not only does the variation in boiling point and refractive index give evidence of the presence of 2-bromopentane in these products, but the absorption spectra of 2-pentene obtained from these give more conclusive evidence of this.[15] The results obtained in C indicated the probable course of the transformation. In that case a considerable amount of 2-pentene distilled over. The hydrocarbon is therefore evidently formed by the more vigorous method and after being formed under these conditions of higher temperature or pressure adds to form 2-bromopentane in varying amounts. This may be considered as some evidence in favor of the fact that this 2-pentene is the more stable form of 2-pentene.

Preparation of 2-Pentene

A. From 3-Bromopentane by the Action of Alcoholic Potash.—Bromopentane-3 (n_D^{20} 1.4443, 229 g.) was dropped slowly into a solution of potassium hydroxide (261 g.) in absolute methyl alcohol (500 cc.) heated on an oil-bath kept at 110–115°. The vapors were passed through a reflux condenser kept at 40°, then through a cold downward condenser and the distillate was collected in absolute methyl alcohol protected from the moisture of the air and kept cold with ice and salt. When ethyl alcohol was used as the collecting solvent it was then used for the alcoholic potash and the temperature of the bath was 125–127°. The distillate was fractionated through a Crismer column (50 cm. or 1.5 m. in various runs) surrounded by an air jacket and the azeotropic mixture which was distilled was collected in a flask surrounded by ice and salt. The 2-pentene was separated from the alcoholic solution by repeated washings with ice water; then it was dried over calcium chloride. The yield of 2-pentene was 89–92%. Whenever pure 3-bromopentane (n_D^{20} 1.4443) was used the distillation of the azeotropic mixture was practically constant throughout, and the 2-pentene isolated was pure. When, however, the 3-bromopentane used contained some 2-bromopentane, the distillation was not constant, and the hydrocarbon isolated had different physical properties. This variation is shown in Table II.

TABLE II

RESULTS OF EXPERIMENTS

				2-Pentene	
		n_D^{20}		B. p. at 760 mm., °C.	n_D^{20}
1	3-Bromopentane	1.44431		36.30 ± 0.05	1.37963
2	3-Bromopentane	1.4437	after 2d fractionation		1.37935
			after 3d fractionation		1.37945
3	3-Bromopentane	1.4432			1.37930
4	3-Bromopentane	1.4427			1.37923
5	3-Bromopentane	1.4417			1.3791

The rate of fractionation of azeotropic mixtures of the pure 2-pentene and of a mixture done simultaneously is shown in Fig. 1, Curve I, representing the fractionation of 2-pentene from (1) above, and II representing the fractionation of 2-pentene from (4) above.

B. From 3-Pentanol by the Action of 60% Sulfuric Acid.—The method is that reported by Norris,[16] in which commercial 2-pentanol was treated with sulfuric acid.

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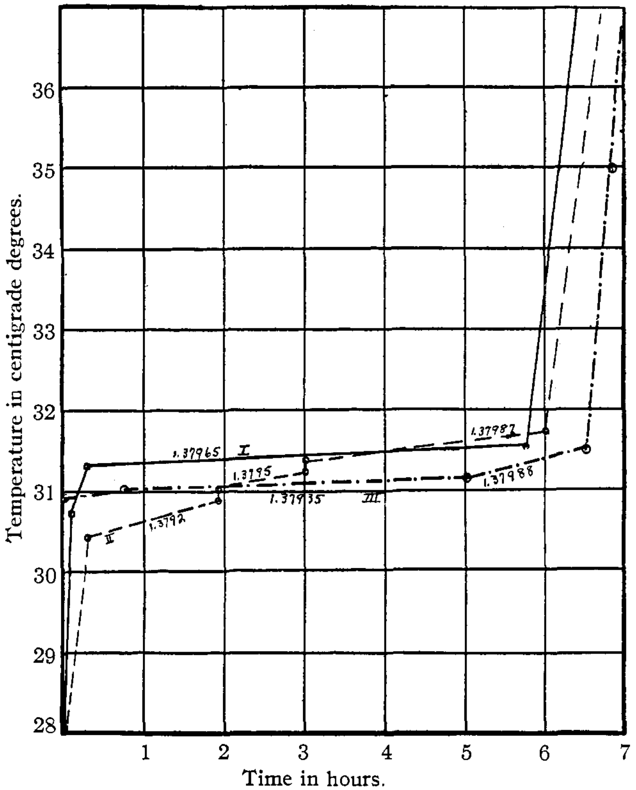
[15] Carr, THIS JOURNAL, **51**, 3041 (1929).

[16] (a) Norris and Reuter, *ibid.*, **49**, 2630 (1927); (b) Norris and Joubert, *ibid.*, **49**, 885 (1927), had dehydrated 3-pentanol with phosphorus pentoxide.

A 60% solution of sulfuric acid (containing 105 g. of concentrated acid) was placed in a flask provided with a drop funnel and connected with a long condenser, and 3-pentanol (43 g.) was slowly added from the funnel. The flask was cooled in ice and shaken gently during the addition of the alcohol. The mixture was then heated slowly on a water-bath and finally on a boiling water-bath as long as the hydrocarbon distilled. The distillate was collected in a bottle surrounded by ice and salt. It was washed with 5% sodium hydroxide and dried over calcium chloride; yields, 73–90%. The crude pentene had a refractive index of 1.3820–1.3823 at 20°. Refractionated as an azeotropic mixture with methyl alcohol the following fractions were obtained.



——, I, 2-Pentene from 3-bromopentane, n_D^{20} 1.44431 (762 mm.); – –, II, 2-pentene from 3-bromopentane, n_D^{20} 1.4427 (762 mm.); — - —, III, 2-pentene from 3-pentanol, n_D^{20} 1.4078 (755 mm.).

Fig. 1.—Fractionation of azeotropic mixtures of 2-pentane in methyl alcohol.

	B. p. at 760 mm., °C.	Time	Wt. of 2-pentene, g.	n_D^{20}
I	31.1–31.2	45 min.	6.7	1.3793
II	31.2–31.3	4 hours	11.7	1.3794
III	31.3–31.7	1.5 hours	12.9	1.37988

Fractions I and II, from absorption spectra measurements, were identical and when mixed gave a refractive index of 1.37935 at 20°. The lower index and lower boiling azeotropic mixture would indicate a small amount of the isomeric 2-pentene. Fraction III contained a large amount of more absorptive material, the higher index being due to this. This may be polymeric material and it is present in much greater quantities in 2-pentene made by this method than in that from the alcoholic potash method. The alcoholic solution after fractionation was washed with water and gave a large amount of a residue of high index, much larger than any ever obtained by the other method.

In addition to the method given for the preparation of 2-pentene, the dehydration of the 3-pentanol by *p*-toluenesulfonic acid was tried. The product obtained, however, contained an impurity which was very absorptive in the ultraviolet and therefore made the method of no value for the purposes of this problem.

Properties of 2-Pentene.—The azeotropic mixture with methyl alcohol boiled at 31.40 ± 0.05° at 760 mm. Fifty grams of the mixture gave 47 g. of the 2-pentene (87%). The azeotropic mixture with ethyl alcohol boiled at 34.7 ± 0.05°. The physical properties of the 2-pentene were obtained as follows and comparative literature data are also given. Boiling point, 36.40 ± 0.05°, 760 mm.; d_4^{20} 0.6503; n_D^{20} 1.37965 (Zeiss dipping); Van Risseghem,[6] b. p. 36.40°, 760 mm.; d_4^{11} 0.6595; n_D^{11} 1.3857; $d_4^{17.2}$ 0.6535; $n_D^{17.2}$ 1.3817. Auwers,[17] b. p. 36–37°; d_4^{20} 0.653; n_D^{20} 1.3812. Lucas and Moyse,[9b] b. p. 35–36°. Norris and Joubert,[16b] from synthetic 3-pentanol, b. p. 36–37.5°. Norris and Reuter,[16a] from 2-pentanol (commercial), b. p. 36.39 ± 0.04°, 760 mm.; d_4^{20} 0.65054; n_D^{20} 1.38081.

Addition Reactions of 2-Pentene.—Since Lucas and Moyse[9b] used the addition reaction of hydrogen bromide to 2-pentene as conclusive proof of their theory and since the directive addition of an unsymmetrical substance as hydrogen bromide should in the case of electronic isomers give different products, it was necessary to study the addition under varying conditions. The possible addition products formed by the action of hydrogen bromide on 2-pentene are 3-bromopentane (b. p. 118.2–118.5°, n_D^{20} 1.4443) and 2-bromopentane (b. p. 117.5–118.5°, n_D^{20} 1.4416). Lucas and co-workers[9c] have shown that the refractive index of mixtures of the two bromides is a linear function of the composition. The addition of bromine to 2-pentene should give 2,3-dibromopentane. The dibromide formed had b. p. 178–179°, n_D^{33} 1.5010, n_D^{20} 1.5074, n_D^{15} 1.5102. Wagner and Saytzeff[4] gave the boiling point as 178° uncorrected. Van Risseghem[6] gives the boiling point as 60.5–61° at 14 mm.; n_D^{17} 1.50926; n_D^{11} 1.5119. Norris and Reuter[16a] prepared the dibromide by addition of bromine to 2-pentene (36.3–36.4°) made from 2-pentanol and obtained a dibromide which boiled with slight decomposition at 180.2–180.8° at 754 mm. and had a refractive index, n_D^{20} 1.5098; n_D^{10} 1.5149. These values are higher than other recorded values ("International Critical Tables," b. p. 175°, n_D^{15} 1.5094) and higher than those obtained in this Laboratory (given previously). The fact that the 2-pentene used by Norris and Reuter may have had some 1-pentene in it may account for the higher values. The 1,2-dibromide boils at 184° corr. at 760 mm. and 68° at 12 mm. and the refractive index is n_D^{21} 1.5088 according to Kirrmann.[18]

Reaction of 2-Pentene with Hydrogen Bromide.—The 2-pentene, either pure or in a solvent, was placed in a flask surrounded by ice and salt mixture and saturated with gaseous hydrogen bromide. The hydrogen bromide was prepared as given above, in the preparation of 3-bromopentane, but an additional tube containing naphthalene (to remove traces of bromine) was added to the drying train. The saturation was repeated two or three times, then the bromopentane was washed in the usual way with

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[17] Auwers, *Ann.*, **415**, 142 (1916).

[18] Kirrmann, *Bull. soc. chim.*, [4] **39**, 989 (1926).

ice water, ice-cold sulfuric acid, with water, sodium carbonate and water. The dried products were distilled in fractionating flasks and the refractive indices taken. When the addition reaction was carried out in a non-polar solvent such as carbon tetrachloride or with the 2-pentene without a solvent, the product was almost pure 3-bromopentane. When the solvent was a polar one, as glacial acetic acid, the product was 78% 3-bromopentane and 22% 2-bromopentane, as found by Lucas and Moyse.[9b] When the 2-pentene was prepared from a mixture of 2- and 3-bromopentanes the quantity of 2-bromopentane obtained by addition of hydrogen bromide was considerably greater. It was found also that if the addition of hydrogen bromide was not made very carefully at low temperatures (−10°), a larger proportion of 2-bromopentane was formed. The 2-pentene made from mixtures of 3-bromopentane and 2-bromopentane might also contain some 1-pentene and the resultant bromopentane might then contain some 1-bromopentane (n^{20}_D 1.4444, I. C. T.). Representative data are given in Table III.

Reaction of 2-Pentene with Bromine.—The 2-pentene, dissolved either in glacial acetic acid or carbon tetrachloride, was cooled in ice and salt and a solution of bromine in the corresponding solvent was added drop by drop until a permanent yellow color remained. The amount absorbed was in every case practically the theoretical quantity. The dibromide was washed and dried in the same way as the monobromide. Whenever pure 2-pentene was used, there was only one product, the 2,3-dibromide, formed as indicated by the distillation temperature and the refractive index. In some cases where the 2-pentene used had been made from a mixture of 3-bromopentane and 2-bromopentane and therefore might possibly have had a small amount of 1-pentene present, there was a small amount of higher-boiling dibromide, probably the 1,2-dibromide. Some representative data are given in Table III.

TABLE III

REPRESENTATIVE DATA

Bromopentane from which 2-pentene was prepared, n^{20}_D	Pentene, n^{20}_D	Addn. prod. with HBr		Addn. prod. with Br_2	
		B. p. (760 mm.), °C.	n^{20}_D	B. p. (760 mm.), °C.	n^{20}_D
(1) 1.44431	1.37965	118–118.5	1.4442 (in CCl_4) (98% 3-bromo)	178–179	1.5074 (100% 2, 3-dibromo)
		118–118.5	1.4437 (in glacial acetic acid) (78% 3-bromo, 22% 2-bromo)		
(2) 1.4437	1.37935 (2d fractionation)	Without solvent	1.4422 12%[a]	178–179	1.5074 85%[a]
			1.4430 75%[a]	179–182	1.5090 15%[a]
			1.4441 12%[a]		
	3d fractionation		1.4429		
			1.4434		
(3) 1.4432	1.37930		1.4426		
(4) 1.4427	1.37923		1.4430		
(5) 1.4417	1.3791	117–118	1.4429		
		118–121	1.4434		
Pentanol from which 2-pentene was prepared					
1.4079	1.37935		1.4434 (in glacial acetic acid) (66% 3-bromo, 34% 2-bromo)		

[a] The percentages in (2) above are based on the weights of the fractions obtained.

Transformation of 2-Pentene into an Isomeric Form.—Kharasch[14] had found that the 2-pentene prepared from 3-bromopentane when heated in xylene gave an isomeric form. In the work in this Laboratory it was found that heat alone did not produce this change but that light was necessary. Since, too, the presence of even a minute trace of xylene was detrimental to absorption spectra measurements, the use of this solvent was avoided and the 2-pentene, without any solvent, was exposed to sunlight and ultraviolet light.

(1) Some of the 2-pentene (n_D^{20} 1.37965) was sealed in a glass tube and heated in a water jacket at 70–80° at intervals for a total of sixty-five hours and was then left in the laboratory under a skylight for thirteen weeks, thus exposed to the available sunlight. At the end of this time, the tube was opened and the material investigated. The refractive index was taken, the absorption spectra were measured and addition compounds with hydrogen bromide and with bromine were prepared. The data are given in Table IV.

(2) Some 2-pentene (n_D^{20} 1.37945) from the third fractionation of 2-pentene from bromopentane (n_D^{20} 1.4437) was placed in a small quartz flask fitted with a reflux condenser; the flask and condenser were kept cold with solid carbon dioxide and the flask was placed about 10–12 cm. away from an Hanovia quartz mercury vapor lamp. The material was exposed to the ultraviolet light for a total of four hours and thirty minutes. Absorption spectra measurements were made after one hour and fifty minutes, after three hours and forty minutes and after four hours and thirty minutes. The physical properties were determined and the addition reactions of this transformed 2-pentene were studied. The data are given in Table IV.

(3) Some 2-pentene (n_D^{20} 1.37930) which had been prepared from 3-bromopentane (n_D^{20} 1.4432) containing a little 2-bromopentane as an impurity, was placed in a quartz flask with a reflux condenser, cooled with solid carbon dioxide and exposed to ultraviolet light for eight hours and thirty minutes. The data obtained from the transformed material are given in Table IV. Some of the transformed material was fractionated with methyl alcohol and three fractions were obtained. The boiling point of each of these mixtures was lower than the boiling point of the azeotropic mixture of the original untransformed material, indicative of a transformation to the lower-boiling form.

	Azeotropic mixture, b. p. at 760 mm., °C.	Refractive index of the pentene, n_D^{20}
Original material	31.3 –31.4	1.37930
Material after transformation	(1) 30.5 –30.9	1.3793
	(2) 30.95–31.15	1.3792
	(3) 31.15–31.25	1.3795

The bromide formed from the third fraction had a somewhat higher index and higher boiling point than the bromide made from the unfractionated sample of the transformed material, showing that the two isomers were partially separated.

The following points are worthy of note: (1) the azeotropic mixture of the transformed material has a lower boiling point and a wider range than the original; this seems indicative of a mixture. (2) The transformed pentene boils over a wider range than the untransformed. (3) The refractive indices of the transformed material are lower than those of the original except in the case of long exposure to ultraviolet light, and

TABLE IV

DATA OF TRANSFORMED MATERIAL

		Untransformed 2-pentene	Transformation product (1) Sunlight	(2) Ultraviolet 4.5 hrs.	(3) Ultraviolet 8.5 hrs.
1	B. p. of azeotropic mixt. with MeOH	31.35 ± 0.05°	.....	.....	30.50–31.25°
2	B. p. of 2-pentene	36.30 ± 0.05°	.....	.....	36.4 ± 0.20°
3	n_D^{20}	1.37965	1.37934	1.37937	1.37956
4	d_4^{20}	0.6503	......	0.6500	.....
5	n_D^{20} of monobromide	1.4437 (78% 3-bromo, 22% 2-bromo)	1.4420 (15% 3-bromo, 85% 2-bromo)	1.4423	1.4421 (av.)
6	n_D^{20} of dibromide	1.5074	1.5074	.....	.....

the increase here may be due to the formation of polymeric material or decomposition products. There is evidence of this in the absorption measurements. (4) The monobromide from the transformed material is largely 2-bromopentane rather than 3-bromopentane, as in the case of the untransformed 2-pentene. (5) The dibromide formed from the light-transformed pentene is identical with that from the original pentene, indicating that there has been no shift in the double bond. There was a possibility of a racemic mixture or a *meso* form if isomers were *cis-trans*, but no evidence of two kinds has been obtained.

Summary

1. Pentene-2 has been prepared from 3-bromopentane and from 3-pentanol. This has been purified by fractionation of constant-boiling mixtures with methyl and with ethyl alcohol. The physical properties of this 2-pentene have been determined. This pentene adds hydrogen bromide in a non-polar solvent such as carbon tetrachloride to give 98–99% of 3-bromopentane. In glacial acetic acid it adds hydrogen bromide to give 78% of 3-bromopentane and 22% of 2-bromopentane. Addition of bromine to this 2-pentene gives 2,3-dibromopentane.

2. Sunlight and ultraviolet light transform this 2-pentene into an isomeric form which has slightly different physical properties. The transformed 2-pentene adds hydrogen bromide to form 15% of 3-bromopentane and 85% of 2-bromopentane. With bromine it forms the same dibromopentane, 2,3-dibromo-, as the original 2-pentene.

3. The 3-bromopentane can be prepared pure only by great care in the hydrobromination of the 3-pentanol. Strong reagents like phosphorus tribromide or higher temperatures and pressures give mixtures of 3-bromopentane and 2-bromopentane.

SOUTH HADLEY, MASSACHUSETTS