[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

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

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The transformation of 2-pentene prepared from 3-bromopentane by the action of ultraviolet light or by diffused light into an isomeric form differing slightly in physical properties and radically in the addition product formed by hydrogen bromide was indicative of electronic isomerism.[2] If these were electronic isomers then it ought to be possible to use as initial material 2-bromopentane in which the strongly electronegative bromine atom was attached to the second carbon atom (C-2) making it less electronegative than the adjacent carbon (C-3) and to obtain a 2-pentene in which the carbon atom (C-3) of the double bond adjacent to the ethyl group would be more electronegative than the carbon atom (C-2) adjacent to the methyl group. This 2-pentene should be the stable form and should be identical with the product obtained by the action of light on the 2-pentene obtained from 3-bromopentane. Lucas, Simpson and Carter[3] had prepared 2-pentene from 2-bromopentane but made no effort to separate it from the 1-pentene formed at the same time nor to compare it in physical properties with the 2-pentene from 3-bromopentane. The addition of hydrogen bromide to the mixture of 1-pentene and 2-pentene was carried out and the product obtained was fractionated but in view of the fact that the refractive indices of 1-bromopentane (n_D^{20} 1.4444, "I. C. T.") and of 3-bromopentane (n_D^{20} 1.44431) are so nearly identical and the boiling points of 2-bromopentane (117.5–118°) and of 3-bromopentane (118.2–118.5°) are so close together, the inferences made from the data are not conclusive.

The chief difficulty in the preparation of 2-pentene from 2-bromopentane or 2-pentanol lay in the fact that the removal of hydrogen bromide or the dehydration of 2-pentanol gave as products both 2-pentene and 1-pentene and a complete separation of these was necessary. Lucas, Simpson and Carter[3] estimated that from 2-bromopentane approximately 71% of 2-pentene and 29% of 1-pentene was obtained. Norris and Reuter[4] prepared 2-pentene by the dehydration of secondary amyl alcohol manufactured from petroleum and obtained a 90% yield of the hydrocarbon boiling between 36.5 and 40°. The amount of 1-pentene was not estimated. The data found in the literature with regard to 1-pentene are contradictory.

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

[2] Sherrill, Otto and Pickett, THIS JOURNAL, **51**, 3023 (1929).

[3] Lucas, Simpson and Carter, *ibid.*, **47**, 1462 (1925).

[4] Norris and Reuter, *ibid.*, **49**, 2630 (1927); *cf.* "Organic Syntheses," Wiley and Sons, New York, **1927**, Vol. VII.

Brochet[5] in the fractionation of boghead gas obtained a product, designated 1-pentene, with a boiling point 39–40°. Norris and Joubert[6] prepared 1-pentene from ethylmagnesium bromide and allyl bromide. The product obtained after rather rigorous treatment to remove the halide and the diethyl ether boiled at 39–41°. Some diallyl, boiling at 59–61°, was also obtained. Kirrmann[7] had prepared 1-pentene by a similar synthesis but the Grignard reagent was added to the allyl bromide to diminish polymerization and the solvent used was dipropyl ether, which being of much higher boiling point did not have to be removed by vigorous treatment with concentrated hydrochloric acid as in the Norris method. The boiling point of 1-pentene is given by Kirrmann as 30.5–31° at 767 mm. Bourguel[8] has prepared 1-pentene by the hydrogenation of a true acetylene pentine ($CH_3CH_2CH_2C{\equiv}CH$). The boiling point of 1-pentene as given by Bourguel is 32.5° at 760 mm. Bourguel found, in a series of hydrocarbons, that the hydrocarbon with the double bond between the first and second carbon atoms boiled lower than the one with the double bond between the second and third carbon atoms.

The results in the present work depended upon the separation of 1-pentene from 2-pentene and it was believed to be possible by the fractionation of an azeotropic alcohol mixture as used in the purification of the 2-pentene prepared from 3-bromopentane and 3-pentanol.[2] This method has been used with very satisfactory results. 2-Pentene, practically free from 1-pentene, has been obtained and its properties are different from those of the 2-pentene prepared from 3-bromopentane and 3-pentanol but are almost identical with those of the 2-pentene which had been transformed by light.

Experimental

Preparation of 2-Pentanol (Methyl-*n*-propylcarbinol).—Secondary amyl alcohol was prepared according to the method of Wood and Scarf[9] by the action of *n*-propylmagnesium bromide on acetaldehyde.

Propyl Bromide.—Normal propyl bromide (Eastman Kodak Co.) was purified by washing with concentrated sulfuric acid (ice cold) and with sodium hydroxide (2 *M*) until neutral, was dried and distilled, the fraction boiling at 71–71.2° being used.

Grignard Synthesis.—The Grignard reagent was prepared in the usual way, 75 g. of magnesium (3.1 moles) and 394 g. (3 moles) of *n*-propyl bromide being used. The reaction mixture was stirred for two hours after all of the propyl bromide had been added. Then the required amount of acetaldehyde was passed into the reaction mixture, which was kept cold in an ice and salt mixture and was stirred continuously. The acetaldehyde was distilled from a flask provided with a reflux condenser; the water through the condenser was kept at 40°. From the condenser a tube led to a

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

[6] Norris and Joubert, THIS JOURNAL, **49**, 885 (1927).

[7] Kirrmann, *Bull. soc. chim.*, [4] **39**, 988 (1926).

[8] Bourguel, *ibid.*, [4] **41**, 1476 (1927).

[9] Wood and Scarf, *J. Soc. Chem. Ind.*, **42**, 13T (1923).

combustion tube containing calcium chloride and a tube from this led to the bottom of a side-arm test-tube. The test-tube was connected with a three-way stopcock, one arm of which was attached to a tube leading into the Grignard reaction flask. The aldehyde was heated on a water-bath (30–35°) and dried by passing over calcium chloride. In the beginning the test-tube was chilled so that enough aldehyde was condensed to a liquid, then the rate at which the gas bubbled through this served as a gage for the speed of addition of aldehyde to the reaction flask. After the addition of the aldehyde the reaction mixture was stirred for twelve hours. Then part of the excess ether and the excess aldehyde was distilled from the reaction mixture and the mixture decomposed with ice and ammonium chloride. The 2-pentanol was extracted with ether. The water layer was steam distilled and the distillate also extracted with ether. From the ether extracts 2-pentanol was obtained, boiling at 118.5–119.5° at 760 mm. and having a refractive index n_D^{20} 1.4060. The literature data for the methyl-*n*-propylcarbinol are as follows. Brunel[10] gives the boiling point as 119.275° at 754 mm. and index n_D^{25} 1.4043; Norris and Cortese[11] give the boiling point as 119.16–119.26° at 760 mm. and n_D^{25} 1.4048. "International Critical Tables" gives secondary amyl alcohol as b. p. 119.5°, 760 mm., and n_D^{20} 1.4072 and for *d*-secondary amyl, b. p. 118° and index n_D^{20} 1.4053. The yields of the carbinol were poor, due in part to the formation of hydrocarbons in the reaction and in part to acetal formation. Commercial 2-pentanol (Sharples Solvents Corporation) was fractionally distilled several times through Crismer columns and some very constant boiling fractions, b. p. 118–118.5°, $n_D^{20°}$ 1.4073, were obtained. This material was used in some comparison runs.

Preparation of 2-Bromopentane.—The 2-pentanol was hydrobrominated by the method given for the preparation of 3-bromopentane,[2] by the saturation of the 2-pentanol with hydrogen bromide at −10° and then by warming the mixture to 60° under atmospheric pressure. The product was purified as in the case of the 3-bromopentane, dried and distilled. The boiling point was 117–118° at 760 mm. and the refractive index was n_D^{20} 1.4412. Lucas, Simpson and Carter[3] give the refractive index as n_D^{20} 1.4416. In cases where the hydrobromination was carried out under increased

TABLE I

REPRESENTATIVE DATA

A. By saturation with gaseous hydrogen bromide at −10° and warming to 60°

			B. p. at 760 mm., °C.	n_D^{20}
(1)	Atmospheric pressure (repeated runs)		117–118	1.4412
(2)	Increased pressure	(a)	114.5–118	1.4416
		(b)	116.5–118	1.4416
	B. By the action of phosphorus tribromide			
(1)	Cold		116–117.5	1.44123[a]
(2)	Heated	(a)	116–117.5	1.4419
		(b)	116–118	1.4420
	C. By the action of 48% hydrobromic acid			
		(a)	116.5–118	1.4417
		(b)	117–119	1.4419

[a] The 2-bromopentane B (1) was obtained from R. E. Marker (prepared from synthetic 2-pentanol). It was refractionated in this Laboratory. The index was taken on a Zeiss dipping refractometer.

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[10] Brunel, THIS JOURNAL, **45**, 1337 (1923).

[11] Norris and Cortese, *ibid.*, **49**, 2644 (1927).

pressure the value obtained in this Laboratory was also n_D^{20} 1.4416. It should be noted that the 2-bromopentane is much more easily obtained as a rather pure compound than is the 3-bromopentane. Table I gives representative data.

Preparation of 2-Pentene

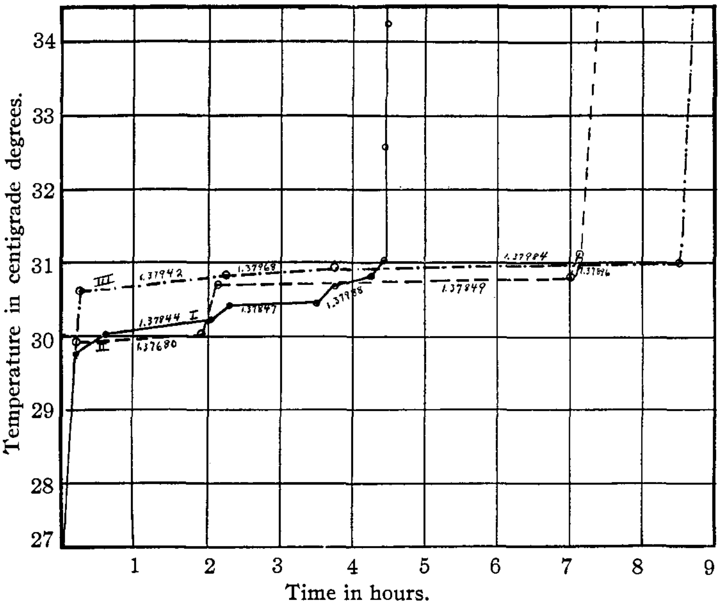
A. **From 2-Bromopentane by the Action of Alcoholic Potash.**—The 2-bromopentane (n_D^{20} 1.4412, 229 g.) was dropped slowly into a solution of potassium hydroxide (261 g.) in absolute methyl alcohol (500 cc.) heated on an oil-bath at 110–115°. The 2-pentene was collected in absolute methyl alcohol, cooled with ice and salt. The crude yield of hydrocarbon was 85–90%. In order to separate any 1-pentene which might be present with the 2-pentene a careful fractionation of the hydrocarbon as an azeotropic mixture was necessary. In view of the contradictory literature data with regard to the boiling point of 1-pentene, a preliminary fractionation in absolute ethyl alcohol through a Hempel column was first made. After two fractionations the hydrocarbon was washed free from alcohol, dried with calcium chloride and refractive indices were taken.

	B. p. of azeotropic mixture with ethyl alcohol at 760 mm., °C.	n_D^{20} of the hydrocarbon	% of total yield
I	32.8–33.1	1.3769	20
II	33.1–33.5	1.3773	21
III	33.5–33.8	1.3780	55
IV	33.8–34	1.3790	2

This fractionation differed markedly from that of the 2-pentene obtained from 3-bromopentane.[2] The ethyl alcohol mixture in that case boiled constantly at 34.7 ± 0.05° and the refractive index of the 2-pentene obtained was n_D^{20} 1.3796. The results of this fractionation indicate the presence of at least two hydrocarbons, one (I) lower boiling occurring in the smaller amount. The main fraction (III) is higher boiling, and II is probably a mixture of I and III. The fact that nothing was obtained higher than 34° would indicate that the 2-pentene (III) is not identical with the 2-pentene obtained from 3-bromopentane. In the continuation of the work the purification of the 2-pentene was made by the repeated fractionation of methyl alcohol mixtures through Crismer columns (50 cm. and 1.5 m. in length). After the third fractionation the separation of 2-pentene from 1-pentene seemed practically complete. Curves I and II in Fig. 1 are typical of various runs and show the difference in the results of a first and third fractionation and also the relative rates of distillation. Practically all of the 1-pentene distilled off in the azeotropic mixture boiling below 30°. It is of interest to compare the values of the hydrocarbons obtained by methyl alcohol fractionation with those given above for ethyl alcohol fractionation.

	B. p. of azeotropic mixture with methyl alcohol at 760 mm., °C.	n_D^{20} of the hydrocarbon	% of the total yield
I	29.9 –30.1	1.37680	15
II	30.75–30.95	1.37849	80
III	30.95–31.2	1.37896	5

B. **From 2-Pentanol by the Action of 60% Sulfuric Acid.**—The method of Norris and Reuter[4] was employed. The yield from 200 g. of 2-pentanol, fraction boiling at 118–118.5°, n_D^{20} 1.4073 (obtained from material from the Sharples Solvents Corporation), was 146 g. or 92% of the theoretical amount. The crude 2-pentene, washed with sodium hydroxide and dried, was fractionated in methyl alcohol (Curve III, Fig. 1) and the physical constants of the pentene were measured. All of the values, boiling points of azeotropic mixture and of the pure hydrocarbon, the density and the refractive indices were higher than those of the 2-pentene from 2-bromopentane. This was believed to be due to some polymeric material, as found in the case of the preparation of the 2-pentene from 3-pentanol by this method. From the residual alcoholic solution, after fractionation, a rather large amount of material of high index was obtained.



——, I, 2-Pentene from 2-bromopentane, n_D^{20} 1.4416 (753 mm.); - - -, II, 3d fractionation of 2-pentene from 2-bromopentane, n_D^{20} 1.44123 (755 mm.); — - —, III, 2-pentene from 2-pentanol, n_D^{20} 1.4073 (750 mm.).

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

Properties of 2-Pentene.—The azeotropic mixture with ethyl alcohol boiled at 33.7 ± 0.2° at 760 mm. The methyl alcohol mixture boiled at 30.85 ± 0.05° at 760 mm. The physical properties of the best 2-pentene prepared from 2-bromopentane considered practically free from 1-pentene are given below with those for the 2-pentene prepared from 3-bromopentane and the 2-pentene formed by the action of light on the latter.

	B. p. (760 mm.), °C.	d_4^{20}	n_D^{20}
2-Pentene from 2-bromopentane	35.85 ± 0.05	0.6481	1.37849
2-Pentene from 3-bromopentane	36.40 ± 0.05	.6503	1.37965
Same 2-pentene after action of light	36.4 ± 0.2	.6500	1.3793

The properties of the 2-pentene prepared from 2-pentanol by sulfuric acid are as follows, with the data given by Norris and Reuter[4] for comparison. This Laboratory data: b. p. 36.15 ± 0.2° at 760 mm.; d_4^{20} 0.6506; n_D^{20} 1.37968; Norris and Reuter data, b. p. 36.39 ± 0.04° at 760 mm.; d_4^{20} 0.65054; n_D^{20} 1.3808. It is also of interest to compare the boiling points of the azeotropic mixtures with methyl alcohol and the refractive indices of other samples of 2-pentene which were not so completely freed from the low-boiling 1-pentene.

	1	2	3
B. p. of azeotropic mixt. (760 mm.)	30.85 ± 0.05°	30.5 ± 0.2°	30.3 ± 0.05°
n^{20}_{D} of the 2-pentene	1.37849	1.37826	1.37803

Addition Reactions of 2-Pentene.—The possible products of the 2-pentene prepared from 2-bromopentane with hydrogen bromide are 3-bromopentane (n^{20}_{D} 1.4443) and 2-bromopentane (n^{20}_{D} 1.4416). In addition, if 1-pentene is present there is also the possibility of 1-bromopentane (n^{20}_{D} 1.4444). The 2-bromopentane has a lower refractive index, as well as a lower boiling point, than either of the other two. In the case of the addition compounds formed by bromine and 2-pentene there should be only one, the 2,3-dibromopentane; if there is 1-pentene present, however, it would be possible to have some 1,2-dibromopentane. The addition compounds and their boiling points and indices are listed below.

-Bromopentane	3-	2-	1-	2,3-Di-	1,2-Di-
n^{20}_{D}	1.44431	1.4416	1.4444	1.5074	1.5088 (21°)
B. p., °C.	118.5	117.5	127.9	178	184

Reaction of 2-Pentene with Hydrogen Bromide.—The 2-pentene (prepared from 2-bromopentane), either pure or in a solvent, was placed in a flask surrounded by an ice and salt mixture and saturated with hydrogen bromide. The bromide was washed once with ice water, twice with ice-cold concentrated sulfuric acid, once with ice water, twice with sodium carbonate solution, once with water, dried with calcium chloride and distilled. Typical results are given in Table II. The main product formed by the hydrobromination of 2-pentene is 2-bromopentane nearly 100% pure. In glacial acetic acid the product is about 80–85% 2-bromopentane, but the presence of some 3-bromopentane is indicated by the higher refractive index of the higher-boiling fractions. In the cases where there was the possibility of some 1-pentene being present, the higher boiling point and higher index of the product may be due to the presence of some 1-bromopentane. In some of the addition reactions of hydrogen bromide to this 2-pentene the temperature was not maintained as low as advisable and the results therefore are not as reliable as those made with the isomeric-2-pentene. It is of interest here to note that Norris[4] found that the chief product formed by the addition of hydrogen chloride to 2-pentene was 2-chloropentane.

TABLE II

ADDITION PRODUCTS OF 2-PENTENE

A. 2-Pentene from 2-bromopentane

	2-Pentene, n^{20}_{D}	Addn. prod. with HBr B. p. at 760 mm., °C.	Addn. prod. with HBr n^{20}_{D}	Addn. prod. with bromine B. p. 760 mm., °C.	Addn. prod. with bromine n^{20}_{D}
(1)	1.37849	117–118	1.4416 50%	178	1.5074
		118–120	1.4418 50%		
(2)	1.37862	118–120	1.4422 75%	178–179	1.5072 86%
		120–123	1.4432 25%	179–184	1.5088 14%
(3)	1.37803	118–119	1.4424 (in hexane)		
		119–120	1.4431 (in hexane)		
		118–119	1.4430 (in glacial	178	1.5078
		119–120	1.4430 acetic acid)		

B. 2-Pentene from 2-pentanol

	2-Pentene, n^{20}_{D}	Addn. prod. with HBr B. p. at 760 mm., °C.	Addn. prod. with HBr n^{20}_{D}	Addn. prod. with bromine B. p. 760 mm., °C.	Addn. prod. with bromine n^{20}_{D}
(1a)	1.37968	117–118	1.4418		
(1b)	1.37942	117–118	1.4425 62%	178–180	1.5079 70%
		118–120	1.4429 38%	180–182	1.5098 30%

Reaction of 2-Pentene with Bromine.—The 2-pentene (prepared from 2-bromopentane) dissolved in either carbon tetrachloride or in glacial acetic acid was cooled in an ice and salt mixture and treated with a solution of bromine in the corresponding solvent as long as the bromine was absorbed. The dibromopentane was washed as in the case of the monobromopentane, dried and distilled. Typical results are given in Table II. In the case of the 2-pentene which from its index of refraction was free from 1-pentene, the dibromopentane seemed to be pure 2,3-dibromopentane; in samples which were believed to contain some 1-pentene there was more or less of a product with a higher boiling point and higher index than the 2,3-dibromopentane, indicating some 1,2-dibromopentane.

Effect of Ultraviolet Light.—Some 2-pentane (from 2-pentanol) was irradiated by ultraviolet light for eight and one-half hours under identical conditions with those used for the 2-pentene prepared from 3-bromopentane.[2] There was a slight increase in the refractive index of the pentene, due in part, perhaps, to polymerization. The monobromopentane formed from the pentene before and after exposure seemed the same, that is, about 93% of 2-bromopentane.

	Exposure to light	
	Before	After
n_D^{20} of 2-pentene	1.37968	1.37989
n_D^{20} of addn. prod. with HBr	1.4418	1.4418

Summary

1. Pentene-2 has been prepared from 2-bromopentane and from 2-pentanol. The pentene has been obtained practically free from 1-pentene by the fractionation of constant-boiling mixtures with methyl alcohol. The 1-pentene is separated in the lower-boiling fractions. The 2-pentene obtained from 2-pentanol by the action of sulfuric acid contains some higher-boiling product which can probably be removed by repeated fractionation of alcoholic mixtures, for a large amount of it remains in the alcoholic residue.

2. The physical properties of the 2-pentene obtained from 2-bromopentane have been determined and have been found to differ slightly from those of the 2-pentene prepared from 3-bromopentane, the former having a slightly lower boiling point, refraction index and density.

3. This 2-pentene (without solvent) adds hydrogen bromide to form 93–95% 2-bromopentane. In a polar solvent such as glacial acetic acid the 2-pentene adds hydrogen bromide to form 85% of 2-bromopentane. It adds bromine to form 2,3-dibromopentane.

4. The action of ultraviolet light on the 2-pentene obtained from 3-bromopentane tends to alter its properties in the direction of those of the isomeric 2-pentene obtained from 2-bromopentane, while the latter isomer remains practically unchanged by ultraviolet light.

5. The differences in physical properties between the two 2-pentenes are such as might be expected in the case of *cis-trans* isomers. The fact,

however, that each isomer has been prepared in a directed manner from a compound of definite and different polarity and that each adds a polar compound in a directed manner corresponding to the method of preparation for each seems to indicate that the two isomers are electronic rather than geometrical. Moreover, the fact that the 2-pentene prepared from 3-bromopentane is transformed into a more stable form is in accord with this theory.

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[Contribution from the Chemical Laboratory of Mount Holyoke College]

ISOMERS OF 2-PENTANE. III. THE ULTRAVIOLET ABSORPTION SPECTRA OF THE ISOMERIC 2-PENTENES[1]

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A study of the ultraviolet absorption spectra of the isomeric 2-pentenes prepared by M. L. Sherrill and co-workers of this Laboratory[2] has been of particular interest in its relation to the electro-isomerism of these compounds and has given further experimental evidence in support of Kharasch's theory of the partial polarity of the ethylene bond.[3] The effect of unsaturation on all of the optical properties of a compound is well known but this effect is particularly marked in the ultraviolet absorption spectra. For example, a 3-cm. length of optically pure hexane transmits to λ = 2000 Å. or even further, while the limit of transmission for the same length of pentene is in the region of λ = 2600–2800 Å. A quantitative study of the influence of the ethylene group on the infra-red and ultraviolet absorption has been made by Henri,[4] and he shows that, in general, the simple ethylenic compounds have two bands in the ultraviolet, one of very small intensity in the region 2600–2300 Å. and another very intense band in the extreme ultraviolet, λ = 2000–1800 Å. These conclusions were based on the investigation of several olefin acids and of allyl alcohol, the *exact* position of the bands due to the double bond being dependent upon the other groups in the molecules. The results of recent spectrographic study of substances in liquid, solution or vapor phase point to the conclusion that ultraviolet absorption is closely related to *electronic* motion within the molecule and on this basis one would expect that slight differences in the electronic condition of the molecule might be detected by light absorption methods.

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

[2] (a) Sherrill, Otto and Pickett, This Journal, **51**, 3023 (1929); (b) Sherrill, Baldwin and Haas, *ibid.*, **51**, 3034 (1929).

[3] M. S. Kharasch and F. R. Darkis, *Chem. Reviews*, **5**, 571 (1928).

[4] V. Henri, "Études de Photochemie," Gauthier-Villars, Paris, **1919**, p. 98.