[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Investigation of the Preparation of Bromides from 1-, 2- and 3-Pentanol. Synthesis of Pure Bromopentanes

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The replacement of the hydroxy group in 1-, 2- and 3-pentanol by bromine was studied with special emphasis on the isomerization occurring during the reaction. Infrared spectral analysis was applied to determine the degree of isomerization. Pure 1-, 2- and 3-bromopentane for infrared standards were prepared by the action of sodium bromide on the tosylate esters of the corresponding alcohols. 3-Bromopentane undergoes isomerization to 2-bromopentane when treated with hydrogen bromide or with sulfuric acid.

The usual methods for the preparation of bromides from the corresponding alcohols involve the use of gaseous hydrogen bromide,[2] phosphorus tribromide,[3] or aqueous hydrogen bromide with sulfuric acid.[4] The conversion of a secondary alcohol to the bromide by the methods indicated in the literature is likely to proceed *via* a carbonium ion, and for that reason this reaction might be accompanied by rearrangement. The possibility of such a rearrangement was indicated by studies which involved isomerization during the alkylation of benzene with 1-, 2- and 3-pentanol in the presence of acid catalysts.[5,6]

The preparation of bromopentanes from 2- and 3-pentanol, in particular, has been studied in this connection.[7-10] The composition of the mixture of 2- and 3-bromopentane obtained from either of these alcohols with the reagents mentioned above has been determined by means of the index of refraction of the mixture.[7,8,11] However, the refractive indices of the two pure bromides are close together[12] and this method suffers from the further disadvantage that it does not reveal the presence of other components. This method of analysis has been superseded by use of the binary melting point diagram of the anilide derivatives of 2- and 3-bromopentane.[9] The melting point diagram has recently been corrected and applied by Cason and Mills.[10] This procedure, also, does not reveal the possible presence of any third component, without a rather careful and laborious examination.

The present study deals with the replacement of the hydroxy group in 1-, 2- and 3-pentanol by a bromine atom with special emphasis on the isomerization occurring during the reaction. Infrared spectral analysis was applied to determine the degree of isomerization. This method of analysis has the advantage of showing whether skeletal rearrangement has taken place during the conversion to the bromide.

Pure 1-, 2- and 3-bromopentane for infrared standards were prepared by the action of sodium bromide on the tosylate esters of the corresponding alcohols.[13] The replacement of the hydroxyl group of a secondary alcohol by the *p*-toluenesulfonyl group proceeds without rearrangement.[14] The infrared spectra of the 1-, 2- and 3-bromopentanes obtained by this method are given in Figs. 1, 2 and 3. The infrared spectrum of the pure 2-bromopentane was compared with that of 2-bromopentane prepared by Cason and Mills by the action of bromine on the silver salt of 2-methylpentanoic acid[10,15] and was found to be identical except that each of the bromides contained one minor band not present in the other.

Pure *s*-pentyl bromides can be prepared without rearrangement but the yields are not high enough for preparative purposes (Table III).

Results and Discussion

The compositions of the bromopentanes obtained from 2- and 3-pentanol by the usual methods of

TABLE I

s-AMYL BROMIDES FROM 2- AND 3-PENTANOL

-Pentanol	Reagents	Procedure[a]	Composition of product, % 2-Bromopentane	3-Bromopentane
2-	Gaseous HBr	A	86	14
3-	Gaseous HBr	A	20	80
2-	Aq. HBr–H_2SO_4	B	72	28
3-	Aq. HBr–H_2SO_4	B	40	60
2-	PBr_3	C	81	19
2-	PBr_3	D	90	10
3-	PBr_3	C	27	73
3-	PBr_3	D	12	88[b]

[a] See Experimental part. [b] Average of five runs giving products containing from 87 to 94% 3-bromopentane. One sample of 3-bromopentane, which was not adequately freed of acid during its separation, gave off hydrogen bromide on distillation. The distillate in this case contained 81% 3-bromopentane and 19% 2-bromopentane. Evidence to be presented below establishes that this discrepancy is probably due to the isomerizing action of hydrogen bromide on the secondary halide.

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(2) E. E. Reid, J. R. Ruhoff and R. E. Burnett, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 246.

(3) C. R. Noller and R. Dinsmore, *ibid.*, Vol. II, p. 358.

(4) O. Kamm and C. S. Marvel, *ibid.*, Vol. I, p. 30.

(5) V. N. Ipatieff, H. Pines and L. Schmerling, *J. Org. Chem.*, **5**, 253 (1940).

(6) H. Pines, W. D. Huntsman and V. N. Ipatieff, THIS JOURNAL, , 4483 (1951).

(1) M. L. Sherrill, B. Otto and L. W. Pickett, *ibid.*, **51**, 3023 (1929).

(7) M. L. Sherrill, C. Baldwin and D. Haas, *ibid.*, **51**, 3034 (1929).

(8) W. M. Lauer and F. H. Stodola, *ibid.*, **56**, 1215 (1934).

(90) J. Cason and R. H. Mills, *ibid.*, **73**, 1354 (1951).

(11) H. J. Lucas, T. P. Simpson and J. M. Carter, *ibid.*, **47**, 1462 (1925).

(12) J. Cason and R. H. Mills (ref. 10) report n^{20}_{D} 1.4452 for 3-bromopentane and n^{20}_{D} 1.4389 for 2-bromopentane. Present work: $n^{19.5}_{\mathrm{D}}$ 1.4449 and $n^{19.8}_{\mathrm{D}}$ 1.4401, respectively.

(13) Replacement of the tosyloxy group by halogen has been carried out in the aliphatic series by A. J. H. Houssa, J. Kenyon and H. Phillips (*J. Chem. Soc.*, 1700 (1929)).

(14) H. Phillips, *ibid.*, **127**, 2552 (1925).

(15) The authors are grateful to Professor Cason for this sample of 2-bromopentane.

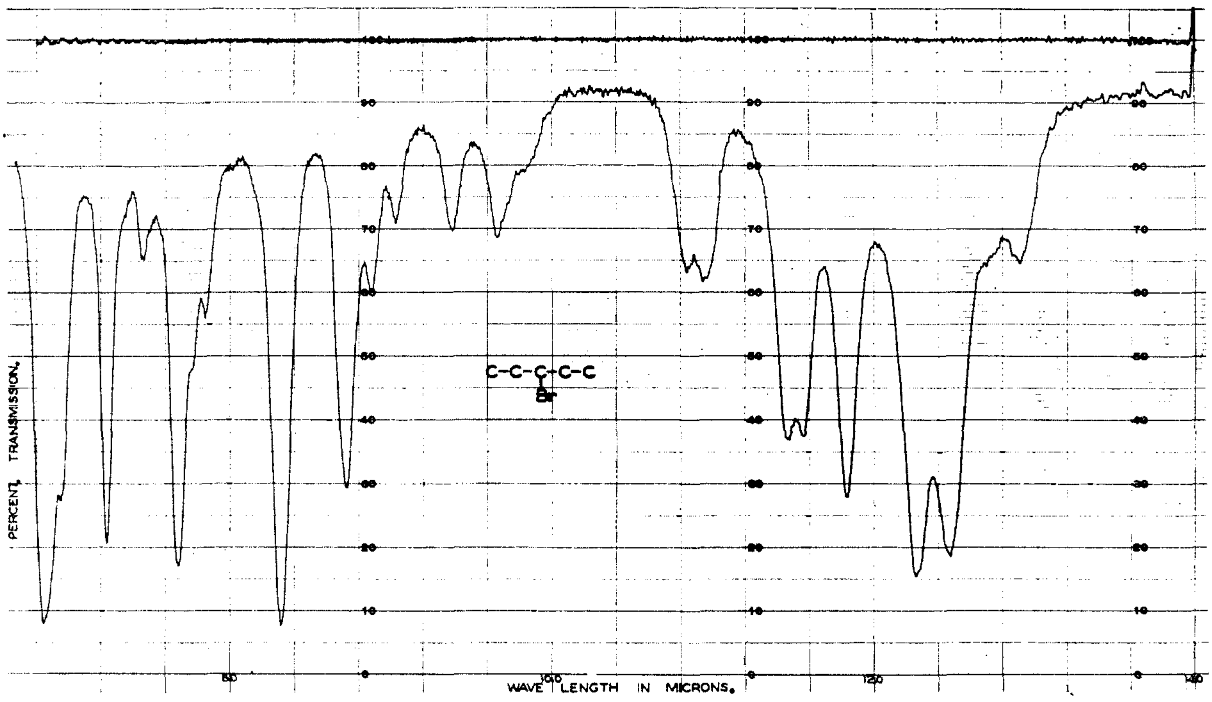

Fig. 1.

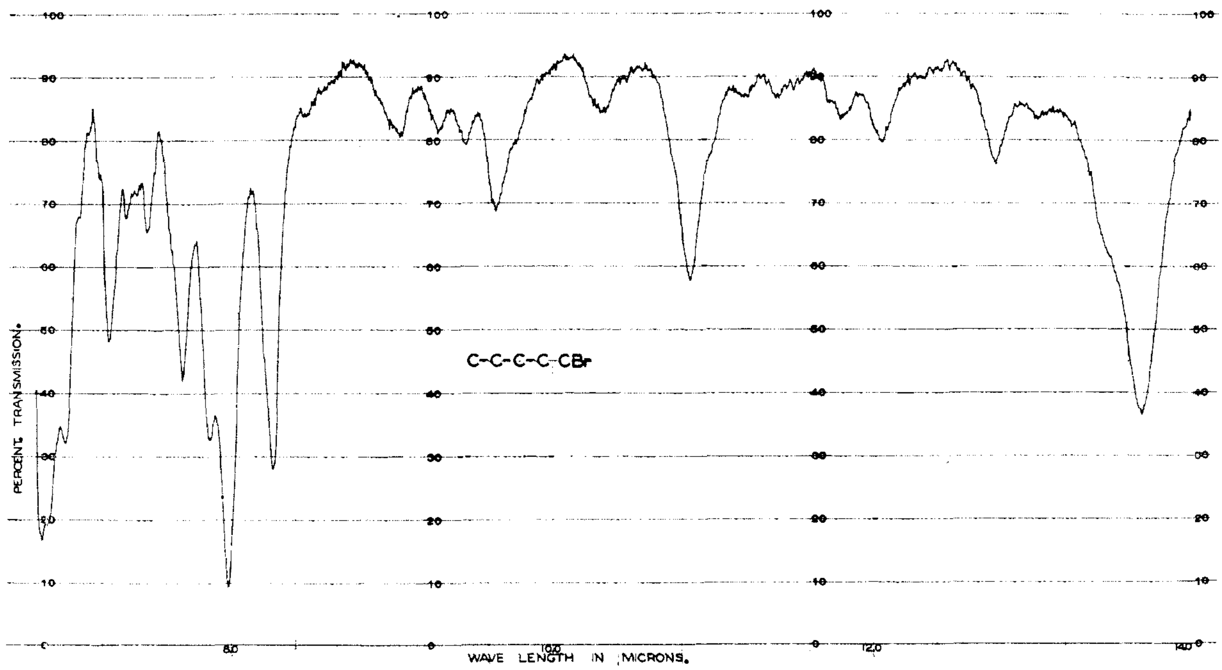

Fig. 2.

replacement of the hydroxy group by a bromine atom are summarized in Table I. In contrast to the isomerization accompanying the reaction observed with the secondary alcohols, 1-pentanol gave pure 1-bromopentane, when treated with these reagents[16] except that the infrared spectrum of the 1-bromopentane prepared from the alcohol with hydrobromic acid and sulfuric acid (method B in the Experimental section) showed the presence of about 1% of an impurity. There was no indication of the presence of either 2-bromopentane or 3-bromopentane in this case.

In order to determine whether the bromopentanes once formed might undergo isomerization during the reaction, a mixture of the two secondary bromopentanes of known composition was subjected to the same conditions as were used in their preparation. The experimental results are summarized in

[16] The infrared spectrum of the 1-bromopentane obtained by the action of hydrogen bromide gas (method A) on 1-pentanol was identical with that prepared through the *p*-toluenesulfonyl ester. The infrared spectrum of the material from the interaction of 1-pentanol and phosphorus tribromide (method D) showed the presence of about 10% of unreacted alcohol. Otherwise the spectrum was identical with those of the two bromides mentioned above.

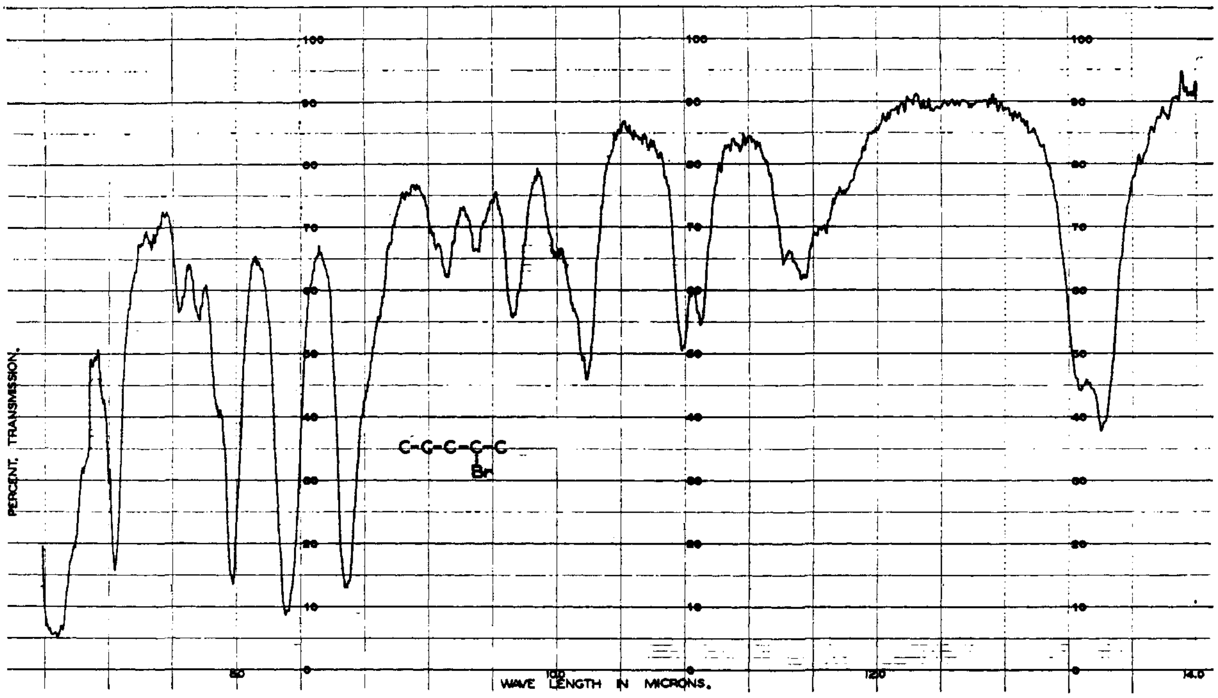

Fig. 3.

Table II. The production of the isomeric bromide is obviously not accomplished solely by rearrangement of the reaction complex formed from the alcohol, since the secondary bromopentanes are sensitive to acids.

The above data illustrate the striking dependence of the product composition on the acidic strength of the medium; sulfuric acid causes the most isomerization. Merely treating the secondary bromide with sulfuric acid leads to rearrangement to the isomeric bromopentane.

As a further evidence that sulfuric acid treatment seems to affect the degree of isomerization, it was found that bromides prepared with phosphorus tribromide by method C which were washed with sulfuric acid are less pure than those made by method D in which the material was not exposed to this acid. The presence of water seems to decrease the extent of isomerization by hydrogen bromide on 3-bromopentane (Table II).

TABLE II

ISOMERIZATION OF BROMOPENTANES

Composition of starting material, % 2- Bromopentane	3- Bromopentane	Reagents	Procedure[a]	Composition of product, % 2- Bromopentane	3- Bromopentane
6	94	HBr (gas.)	Ea	21	79
6	94	HBr (gas.)	Eb	12	88
12	88	HBr (gas.) + H_2O	F	15	85
12	88	PBr_3	G	17	83
12	88	HBr (aq.) + H_2SO_4	H	*ca.* 14	*ca.* 77[b]
13	87	H_2SO_4 (concd.)	I	28	72

[a] See Experimental section. [b] The other component in this case was probably a branched chain isomer of the normal bromides. Elementary analysis showed C, 40.66; H, 7.30; calcd. for $C_5H_{11}Br$: C, 39.75; H, 7.34.

The results of this investigation lead to the conclusion, which is in agreement with previous observations reported in the literature,[9-11] that pure secondary alkyl bromides cannot be prepared from the corresponding secondary alcohols by direct replacement of the hydroxy group by a bromine atom by the methods described in the literature, if isomeric secondary bromides can be formed.

Various investigators have attempted to correlate the mechanism of the replacement of a secondary alcoholic hydroxyl group by halogen with the optical rotation of the product obtained; 2-octanol, in particular, has been investigated.[17] The present results indicate that the decrease in rotation of the halide might be in part due to the shifting of the halogen within the chain.

Experimental Part[18]

Materials. 1. **Alcohols. a. 1-Pentanol.**—Diethyl *n*-propylmalonate was prepared from diethyl malonate and *n*-propyl bromide[19] and then saponified and decarboxylated[20] to valeric acid. This acid was converted to 1-pentanol by reduction with lithium aluminum hydride.[21] The 1-pentanol (50% yield based on *n*-propyl bromide) boiled at 135.5° with $n^{21}D$ 1.4091. Its infrared spectrum contained one band of minor intensity not found in the API reference spectrum.[22] This alcohol was at least 98% pure.

b. 2-Pentanol.—This alcohol was prepared by the method of Wood and Scarf.[23] During one preparation a 16% yield was obtained of a material which was identified by its boiling point, refractive index and semicarbazone as 2-pentanone.[24] Hydrogenation under the same conditions

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[17] For leading references see: W. A. Cowdrey, E. P. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *J. Chem. Soc.*, 1252 (1937); W. Gerrard, *ibid.*, 741 (1946).

[18] All boiling points are uncorrected except as noted in Table IV.

[19] R. Adams and O. Kamm, "Organic Syntheses," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 250.

[20] E. B. Vliet, C. S. Marvel and C. M. Hsueh, *ibid.*, Vol. II, p. 416.

[21] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 2548 (1947).

[22] American Petroleum Institute Research Project 44, Serial No. 433 in Index of March 31, 1950.

[23] C. E. Wood and F. Scarf, *J. Soc. Chem. Ind.*, **42**, 13T (1923).

[24] The formation of the ketone corresponding to the secondary alcohol resulting from the normal addition of a Grignard reagent to an aldehyde was first reported by J. Marshall, *J. Chem. Soc.*, **105**, 527 (1914). For leading reference as to subsequent work see R. V. Shankland and M. Gomberg, THIS JOURNAL, **52**, 4973 (1930).

TABLE III

PREPARATION OF PURE AMYL BROMIDES

Tosylate ester from -Pentanol	Tosylate ester from Mole	NaBr, mole	Diethylene glycol, g.	Reaction conditions Temp., °C.	Reaction conditions Duration, hr.	Yield, %[a]	Product 2-Bromopentane, %	Product 3-Bromopentane, %	Product 1 Bromopentane, %
1-	0.208	0.48	70	Room	160	11	...	...	100
3-	.124	.52	60	Room	110	36	0	100	...
3-	.141	.195	77	60-70	2.5	37	10	90	...
3-	.125	.58	85	Room	168		0	100	...
2-	.198	.45	155	Room	120	32	100	0	...
3-	.07	.10	38	[b]	168	0			

[a] Yield is based on the alcohol. [b] The solution of tosyl ester in diethylene glycol was stirred at 60–70° for 2.5 hours before the sodium bromide was added and the procedure was continued as for the other preparations.

TABLE IV

PHYSICAL PROPERTIES OF THE PURE BROMIDES

Compound, -pentane	B.p.,[a] °C. This work	B.p.,[a] °C. Lit.	Refractive index This work	Refractive index Lit.	M.p. of anilide,[c] °C. This work	M.p. of anilide,[c] °C. Lit.
1-Bromo-	129.7 (751.6 mm.)	129.6-129.8[b]	$n^{20}D$ 1.4440	$n^{20}D$ 1.4440[b]		
2-Bromo-	117.2 (753.0 mm.)	117.0-117.8[d]	$n^{19.8}D$ 1.4401	$n^{24}D$ 1.4389[d]	95.5–96.0	95.9–96.2[d]
3-Bromo-	119.2 (741.2 mm.)	118.1–118.9[d]	$n^{19.5}D$ 1.4449	$n^{20}D$ 1.4452[d]	126.2	127.2–127.7[d]

[a] The boiling points of the pure bromides were determined by the micro method described by R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 27. [b] M. L. Sherrill, K. E. Mayer and G. F. Walter, THIS JOURNAL, **56**, 926 (1934). [c] Anilides were prepared by the method by W. M. Lauer and F. H. Stodola, ref. 9. [d] J. Cason and R. H. Mills, ref. 10.

as were used in the preparation of 3-pentanol, described below, gave 2-pentanol. The 2-pentanol boiled at 117.0–117.5° with $n^{20}D$ 1.4060. Its infrared spectrum was identical with that of the API 2-pentanol.[25]

c. **3-Pentanol.**—This material was prepared by the hydrogenation of diethyl ketone (b.p. 100.5–101.5°, $n^{20}D$ 1.3910) under 100 atmospheres of hydrogen pressure and in the presence of 10% by weight of nickel-on-Kieselguhr catalyst.[26] The alcohol, obtained in 85% yield, boiled at 114.0° with $n^{18}D$ 1.4100. Comparison of its infrared spectrum with that of the API standard[27] showed it to be pure 3-pentanol.

2. **Pure 1-, 2- and 3-Bromopentane.**—1-, 2- and 3-pentanol were converted to the corresponding *p*-toluenesulfonate esters by the method of Tipson[28] except that ether, rather than chloroform, was used as the extraction solvent for the liquid esters (from 1-pentanol and 2-pentanol). The solvent was removed at room temperature under reduced pressure, and the residue was used directly. The tosyl ester of 3-pentanol, which was the only solid of the three, melted at 43–43.5°. The tosylate was dissolved in the diethylene glycol suspension of sodium bromide, and the bottle containing the reaction mixture was agitated on a mechanical shaker for the stated length of time (Table III). Reactions at higher temperatures were carried out by stirring the reaction mixture in a flask heated by an electric heater. On completion of the reaction, a large volume of water was added, and the lower layer of bromide was separated, dried with potassium carbonate, and distilled through a short Vigreux column. The reaction conditions and compositions of the products are summarized in Table III.

3. **Conversion of Pentanols to Pentyl Bromides.**[29]—The following procedures were used for the replacement of the hydroxyl group by bromine.[1]

A.—Hydrogen bromide gas was passed through the alcohol at 80–90° according to the procedure cited.[2] Potassium carbonate was used as the drying agent. The 3-bromopentane obtained boiled at 117° with $n^{20}D$ 1.4445, the 2-bromopentane boiled at 114–115° with $n^{18}D$ 1.4418, and the 1-bromopentane had a boiling point of 128.5–130° and $n^{19.5}D$ 1.4442.

B.—The alcohol was refluxed for five hours at 123° flask temperature with 48% aqueous hydrobromic acid and concentrated sulfuric acid.[4] The isolation of the bromides from the two secondary alcohols differed from the procedure cited in that the reaction mixture was first extracted with ether, the ether was boiled off, and the residue was steam distilled. The lower layer of the distillate was washed with concd. sulfuric acid, water, and dilute aqueous sodium carbonate and then dried with potassium carbonate and distilled. The physical constants of the products are as follows: 3-bromopentane, b.p. 114–117°, $n^{18.5}D$ 1.4442; 2-bromopentane, b.p. 115–117°, $n^{19.7}D$ 1.4443.

C.—Phosphorus tribromide was added dropwise to the cooled alcohol according to the procedure of Noller and Dinsmore.[3] The 3-bromopentane prepared in this manner boiled at 116°, with $n^{20}D$ 1.4436, while the 2-bromopentane had b.p. 117–118.5° and $n^{18}D$ 1.4422.

D.—The bromides were made from the alcohols with phosphorus tribromide by the method of Bartleson, Burk and Lankelma.[30] A study was made of the effect of reaction conditions on the compositions of the product. It was found that varying the temperature of the reaction mixture from −26 to +2° during the addition of phosphorus tribromide to the alcohol did not affect the composition of the product to any significant extent. Variations of the mole ratio of phosphorus tribromide to alcohol from 0.38 to 0.53 resulted in no discernible trend. Preparations which were allowed to stand at room temperature in the reaction vessel from two to four days before the bromide was isolated had almost the same composition. In all but three of the runs Eastman Kodak Co. phosphorus tribromide was used directly from the bottle, without further purification. Phosphorus tribromide which had been distilled through a short Vigreux column (middle cut, b.p. 171.8° uncor.) gave a product with the same composition as that obtained by using the undistilled reagent from the same original bottle. The physical constants of the products were as follows: 3-bromopentane, b.p. 118–120°, $n^{22}D$ 1.4432; 2-bromopentane, b.p. 116°, $n^{19}D$ 1.4418; 1-bromopentane, b.p. 129°, $n^{19}D$ 1.4406.

4. **Isomerizations of Bromopentanes.**—A known mixture of 2- and 3-bromopentane was subjected to the same conditions as prevailed in the reaction mixture during the preparation of the bromides from the alcohols by procedures A–D in the preceding section.

Ea.—Hydrogen bromide gas was passed through a calcium chloride drying tube and then bubbled through the bromopentane at 75–95°. After 2.5 hours the hydrogen bromide flow was stopped and water was added to the reaction mixture. Part of the lower layer was subjected to the same procedure as was used in the isolation of the bromide prepared by method A. That is, the bromide was washed with sulfuric acid, washed with water, neutralized with

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(25) Reference 22, Serial No. 436.

(26) V. N. Ipatieff and B. B. Corson, *Ind. Eng. Chem.*, **30**, 1039 (1938).

(27) Reference 23, Serial No. 753.

(28) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(29) All distillations of bromides were made through a short Vigreux column. The distilling flask contained a small amount of potassium carbonate.

(30) J. D. Bartleson, R. E. Burk and H. P. Lankelma, THIS JOURNAL, **68**, 2513 (1946).

ammonia and then dried with sodium carbonate and distilled.

Eb.—The remainder of the lower layer from Ea was dried with sodium carbonate and distilled.

F.—The procedure was the same as Eb except that an equimolar amount of water was added dropwise to the bromopentane during the hydrogen bromide addition.

G.—Moist air was blown through phosphorus tribromide for eight hours at room temperature. The residue was warmed for 20 minutes on the steam-bath. The bromopentane was added to this cooled material and the stoppered flask was kept in a Dry Ice–acetone-bath for two days and at room temperature for four days. The reaction mixture was worked up as in method D for the preparation of the halides with phosphorus tribromide.

H.—The bromopentane was refluxed for five hours at 123° flask temperature with the charge of 48% aqueous hydrobromic acid and concd. sulfuric acid that would have been used with an equimolar amount of alcohol in procedure B. The reaction mixture was diluted with water and extracted with ether. The black material formed during the refluxing period was filtered off and the ether solution was then dried with potassium carbonate and distilled.

I.—Seven grams of the bromopentane was shaken with 2.5 ml. of concd. sulfuric acid for 2.5 hours at room temperature. The mixture was diluted with water and the two layers were separated. The aqueous layer was made alkaline with solid sodium carbonate and then extracted twice with ether. The bromopentane layer was treated with solid sodium carbonate and added to the ether layers. The combined material was dried with sodium carbonate and distilled, 65% recovery of material boiling from 117.5–120° (uncor.).

5. Analytical.—The infrared spectra were taken at 30° against rock salt as standard with the bromopentane in a 0.03 mm. rock salt cell. A sing-beam memory-recording Beckman IR2T infrared spectrophotometer was used The analytical bands for 3-bromopentane were at wave lengths of 12.24 μ and 12.44 μ, while the characteristic peaks of 2-bromopentane were at wave lengths of 10.18, 13.23 and 13.39 μ. Mixtures of the bromides were analyzed in the usual manner by the application of the Beer–Lambert law at these five wave lengths. These two bromides were the only components present in the mixture with the one exception cited in Table II. The sensitivity of this method of analysis was checked by mixing accurately weighed amounts of bromide mixtures of known composition.

1-Bromopentane has a peak at 13.70 μ.

Acknowledgment.—The authors are grateful to Mr. E. Baclawski of Universal Oil Products Company for some of the infrared spectral analyses.

EVANSTON, ILL.

[A CONTRIBUTION FROM COLUMBIA UNIVERSITY AND UNIVERSITY OF RHODE ISLAND]

Ultraviolet Absorption Spectra of Derivatives of Usnic Acid

BY SCOTT MACKENZIE

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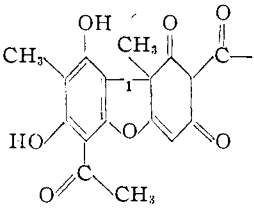
Ultraviolet absorption spectra for usnetic acid, ethyl acetylusnetate, deacetyldecarbousnic acid, decarbousnic acid and the diacetates of the latter two substances, when compared with spectra for usnetol and its diacetate, confirm the accepted relationships among these derivatives. Spectra for dihydrousnic acid and its diacetate are analyzed in terms of previously proposed structures.

Structure I has been proposed for the lichen acid usnic acid, by Curd and Robertson.[1] Both they and Schöpf and Ross[2] have discussed those reactions[3] of usnic acid which can not be, as yet, reconciled with formula I.



I

Other reactions have been interpreted as demanding acceptance of I. The ozonolysis of diacetylusnic acid, giving a lactone (assigned structure II) and ethoxalylacetone,[2,4] has been thus construed, the assumption being made tacitly that substances similar to III could not exist. This assumption has been well supported for usnetol[5] and diacetyldecarbousnic acid[2] which have been ozonized.

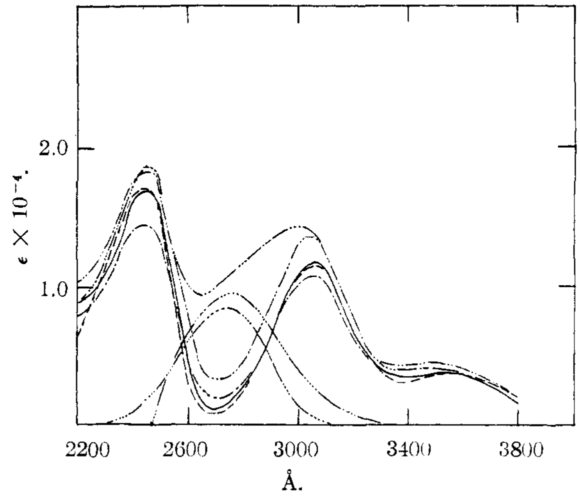


Fig. 1.— ——, usnetic acid; — — —, usnetol; —-—·—, deacetyldecarbousnic acid; —--——-—, ethyl acetylusnetate; —·---——--, decarbousnic acid; ——----——----, acetylacetone; —·-----———---- values for decarbousnic acid less values for usnetol.

Were substances similar to III possible, an admissible structure for usnic acid could be written which would provide a ready explanation for both the acidity of usnic acid and its facile racemization. On the other hand, if this assumption regarding bond placement is, in general, valid for this type of substance, the ozonolysis information severely limits the number of formulas possible for this acid.

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[1] F. H. Curd and A. Robertson, *J. Chem. Soc.*, 894 (1937).

[2] C. Schöpf and F. Ross, *Ann.*, **546**, 1 (1941).

[3] Usnic acid is monobasic; further, racemic usnic acid is obtained when xylene solutions of active forms are refluxed.

[4] Confirmed by Y. Asahina and K. Okazaki, *J. Pharm. Soc. Japan.*, **63**, 618 (1943); *C. A.*, **45**, 5146 (1951).

[5] C. Schöpf, K. Heuck and A. Kraus, *Ann.*, **459**, 233 (1927).