

lished by Partington and Coomber,²⁰ which does not affect its interpretation. The dioxane molecule, which has two possible forms, a Z-shape and a U-shape, has been shown by its moment^{21,22} to exist almost wholly in the Z-form. Similarly, the moment found for morpholine, which has two possible Z-forms and four possible U-forms, agrees well with the identical values calculated for the two Z-forms. Our reasoning has agreed with that of Partington and Coomber in leading to the conclusion that the morpholine molecule exists primarily in its Z-forms, although the presence of U-forms is not entirely excluded.

Summary

The dipole moments of tetranitromethane, nitroform and nitrogen pentoxide have been de-

(20) Partington and Coomber, *Nature*, **141**, 918 (1938).

(21) Hunter and Partington, *J. Chem. Soc.*, 87 (1933).

(22) Smyth and Walls, *THIS JOURNAL*, **53**, 2115 (1931).

termined in carbon tetrachloride solution and those of cyclohexylamine and morpholine have been measured in benzene solution. Tetranitromethane is concluded to have a large atomic polarization but zero dipole moment, which means that it is not trinitromethyl nitrite as sometimes suggested. The moment of nitroform is consistent with its tetrahedral structure, inductive effects in the molecule being smaller than those in chloroform, probably because of the lower polarizability of the atoms and of a staggering of the nitro groups in their rotation around their bonds to the central carbon atom. The moment of cyclohexylamine is of the same size as those of the primary alkyl amines, as it should be. The moment of morpholine shows that it exists primarily in the Z- or chair-shaped forms of the molecule.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. IX. The Isolation and Rearrangement of Primary and Secondary Pentenyl, Hexenyl and Heptenyl Bromides^{1,2}

BY WILLIAM G. YOUNG, LAWRENCE RICHARDS AND JULIAN AZORLOSA

In the first paper³ of this series it was recognized for the first time that the so-called crotyl bromide was actually a mixture of primary and secondary butenyl bromides which were far more mobile than previously suspected. Although they could be separated by low-temperature fractional distillation, they rearranged even at room temperature to an equilibrium mixture. Later papers⁴ have pointed out that studies involving the formation or reaction of these butenyl bromides must take into consideration the possibility of an allylic rearrangement during the reaction, and also a thermal rearrangement after the products are formed. Since other alkenyl bromides have been

prepared and used in the synthesis of many types of compounds without recognition by investigators of the need for carefully controlled conditions, there exists, therefore, a need for a careful and extended study of the alkenyl bromides, their equilibria and reactions.

It is the purpose of this paper to discuss the separation and thermal rearrangement of the primary and secondary pentenyl, hexenyl and heptenyl bromides. A separation of the hexenyl bromides^{5a} and the synthesis of several pure primary alkenyl bromides^{5b} have been reported, but it will be shown that sufficient precautions were not used in the isolation of the pure compounds.

(1) This work was accomplished with the aid of a grant from the Board of Research of the University of California.

(2) The terms primary alkenyl and secondary alkenyl bromides are used to designate the two allylic isomers, $R-CH=CHCH_2Br$ and $R-CHBrCH=CH_2$ respectively. Accordingly, the terms primary pentenyl, hexenyl and heptenyl bromides refer to 1-bromo-2-pentene, 1-bromo-2-hexene, and 1-bromo-2-heptene, respectively. Similarly, secondary pentenyl, hexenyl and heptenyl bromides refer to 3-bromo-1-pentene, 3-bromo-1-hexene, and 3-bromo-1-heptene, respectively.

(3) Winstein and Young, *THIS JOURNAL*, **58**, 104 (1936).

(4) (a) Young, Winstein and Prater, *ibid.*, **58**, 289 (1936); (b) Young and Winstein, *ibid.*, **58**, 441 (1936); (c) Young and Lane, *ibid.*, **59**, 2051 (1937); (d) **60**, 847 (1938); (e) Young, Lane, Loshokoff and Winstein, *ibid.*, **59**, 2441 (1937); (f) Young, Kaufman, Loshokoff and Pressman, *ibid.*, **60**, 900 (1938).

Experimental Part

Preparation of Materials

Alkylvinylcarbinols.—The ethyl, propyl and butylvinylcarbinols used as a source of the desired vinyl bromides were prepared in 60% yields by the action of the appropriate Grignard reagent on acrolein according to the method of Delaby⁶ as modified by Prévost.⁷

(5) (a) Van Risseghem and Gredy, *Compt. rend.*, **302**, 489 (1936);

(b) Delaby and Lecomte, *Bull. soc. chim.*, [5] **4**, 749 (1937).

(6) Delaby, *Compt. rend.*, **175**, 967 (1922).

(7) Prévost, *Ann. chim.*, [10] **10**, 113, 147 (1928).

Alkenyl Bromide Mixtures.—The pentenyl, hexenyl and heptenyl bromide mixtures used in this work were prepared by the action of a mixture of 240 ml. of 48% hydrobromic acid and 24 ml. of 95% sulfuric acid on one mole of the appropriate alkyvinyl carbinol for two days at room temperature. The bromides were all washed with dilute bicarbonate solution, then with water and dried over calcium chloride before distillation. The yields varied from 75–90% for different runs.

Fractional Distillations of the Bromide Mixtures.—All distillations were conducted at pressures of 1–5 mm. The 80-cm. fractionating columns were packed with glass helices and were surrounded with an appropriate thermostated liquid, when the distillation temperature was appreciably below room temperature. All materials were stored in a refrigerator at -15 to -20° between distillations, and the various fractions were collected in receivers maintained at -78° during the distillations to avoid the thermal rearrangements which were known to occur even at room temperatures with the butenyl bromides.³ Since the bromide mixtures, as prepared, contained 80–90% of the primary alkenyl bromides, these isomers were readily isolated by low temperature fractionations. The criteria of purity of the isolated compounds were the constancy of the refractive indices upon repeated distillation and the agreement of the Carius analyses with the theoretical values.

The isolations of the secondary alkenyl bromides involved what may be described as a three-stage process. In the first stage, the secondary forms, present as 10–20% of the original bromide mixtures, were removed by fractionation and stored until sufficient amounts had been collected for the third stage. In the second stage, the mixtures almost completely freed of their secondary bromides were heated until equilibrium had been established. These rearranged mixtures were then treated as in the first stage. In the case of the pentenyl bromides, the first and second stages were combined by slowly fractionating at a distillation head temperature of 70 – 80° . The process in this case was continuous since the secondary isomer was re-formed by rearrangement in the boiler as rapidly as it was removed at the top of the column. In the third stage, the accumulated mixtures rich in the secondary forms were fractionated as practised in the isolation of the primary alkenyl bromides. The physical properties of the bromides prepared by the method described above are listed in Table I. See the discussion

of results for explanation of difficulty encountered during the isolation of the secondary heptenyl bromide.

Determination of Physical Properties.—Refractive indices were determined with the aid of a Zeiss-Abbe refractometer with water-jacketed prisms and the D sodium line as a light source. The alkenyl bromides have been found to attack optical glass and slowly deposit a hard white film upon the surface of the prism of the refractometer. Consequently, small glass cells containing the alkenyl bromides were fastened to the prism face with α -bromonaphthalene while the measurements were taken.

Densities were determined with a 10-ml. cone-shaped pycnometer having a thermometer ground in the neck. All density measurements were made at 25.00° , and the values were corrected to vacuum. As a precautionary measure the samples were checked with a refractometer before and after the densities were taken.

Boiling points were determined by rapidly distilling small amounts of the pure bromides at reduced pressures through a small Vigreux type column. The refractive indices were determined before and after the distillations in order to show that no rearrangements had occurred during the distillations.

The pure compounds were analyzed for bromine by the method of Carius.

Composition of the Equilibrium Mixtures at 100° .—Small samples of each pure bromide were sealed in dry test-tubes and heated at 100° in a steam-bath until no changes were observed in the refractive indices. The primary and secondary alkenyl bromides rearranged to the same refractive indices, showing that equilibria were established. This required from one to eight hours depending on the alkenyl bromide and the particular sample being rearranged. Except in the case of the heptenyl bromides (see below) the composition of each equilibrium mixture (Table III) was determined from the refractive index of the mixture and the refractive index of each pure isomer. The assumption was made that the refractive indices are additive for each of the isomeric pairs and the validity of this assumption which had been tested in the case of the butenyl bromides³ was also demonstrated for mixtures of the two pentenyl bromides (see Table II).

Estimation of the Composition of the Heptenyl Bromide Equilibrium Mixture.—Although only the primary heptenyl bromide has been isolated in a pure state and hence data are not available to

TABLE I
THE PHYSICAL PROPERTIES OF THE PRIMARY AND SECONDARY ALKENYL BROMIDES³

Alkenyl bromide	B. p., $^{\circ}$ C	Press., mm.	n_D^{20}	d_4^{25}	% bromine		
					Obsd.	Calcd.	
Butenyl	Primary ³	49	93	1.4795	1.3335	59.13	59.2
	Secondary ³	31	93	1.4602	1.2998	59.25	59.2
Pentenyl	Primary	43.5	30	1.4777	1.2606	53.56	53.63
	Secondary	30.5	30	1.4626	1.2417	54.06	53.63
Hexenyl	Primary	28	9	1.4761	1.2049	49.18	49.01
	Secondary	22	9	1.4627	1.1849	48.97	49.01
Heptenyl	Primary	32	3	1.4745	...	45.35	45.14
	Secondary	23–25	3	1.4560–1.4590	...	38.46 ^b	45.14

^a Due to an oversight this material was used before density measurements were taken. ^b This fraction was shown to contain heptadiene by bromine absorption.

TABLE II
EVIDENCE FOR THE VALIDITY OF THE ADDITIVE
RELATIONSHIP OF REFRACTIVE INDICES IN ANALYZING
ALKENYL BROMIDE MIXTURES

Mixture	% primary pentenyl bromide	n_D^{25} obsd.	n_D^{25} calcd.
(1)	51.7	1.4704	1.4704
(2)	36.4	1.4681	1.4682

TABLE III
COMPOSITION OF THE ALKENYL BROMIDE EQUILIBRIUM
MIXTURES AT 100°

Alkenyl bromides	n_D^{25} at equilibrium	% primary bromide
Butenyl ²	1.4767	85.5
Pentenyl	1.4747	80.1
Hexenyl	1.4742	85.8
Heptenyl	1.4737	Estimated 89.0

calculate the composition of the heptenyl bromide equilibrium mixture, nevertheless it has been possible to *estimate* the composition by two independent methods. It had been noticed that the conversion of methyl,^{4c} ethyl³ and propyl⁸ vinylcarbinols into bromide mixtures using standard method VI^{4c} (phosphorus tribromide + pyridine at -75°) gave approximately 47% primary bromide. Hence, the assumption could be made that 47% primary heptenyl bromide would be produced using the same standard method on butylvinylcarbinol. The bromide mixture, thus prepared, possessed refractive indices n_D^{25} 1.4691 and 1.4690 for two different preparations. After rearrangement at 100° these preparations came to equilibrium at n_D^{25} 1.4736 and 1.4738, respectively. Consequently we know that these preparations which contained 47% primary bromide increased on an average of 0.00465 refractive index unit in rearranging to equilibrium. The change in composition which will cause a change of 0.00465 refractive index unit was determined by recording the observed difference between the refractive indices of the primary and secondary butenyl, pentenyl and hexenyl bromides shown in Table I, and extrapolating to get the difference for the heptenyl system. Knowing that this difference of 0.0110 unit equals 100% change in composition, we find that the change of 0.00465 unit during rearrangement of the bromide mixture represented an increase of 42% in primary bromide content. Since the mixture started with 47% primary bromide, the equilibrium mixture must have approximately 89% primary bromide. In view of the fact that a similar calculation based on data obtained upon conversion of the primary

(8) Young, Richards and Azorlosa, unpublished work.

heptenol into bromide mixtures by standard method VI gave the same value for the composition of the heptenyl bromide equilibrium mixture, we feel justified in using this estimate until it has been possible to isolate the pure secondary heptenyl bromide and thus get a more direct evaluation of the composition of the equilibrium mixture.

Mobility of the Alkenyl Bromides.—The absolute mobilities or rates of rearrangement of the alkenyl bromides have not been determined. The rearrangements are very sensitive to minute traces of catalytic substances and it has been impossible to obtain reproducible results. Qualitative observations have indicated that at 100° the order of decreasing mobility is: butenyl, hexenyl, pentenyl, and heptenyl, respectively.

Discussion of Results

Separation of the Alkenyl Bromides.—Careful and repeated fractional distillation at low temperatures has resulted in the isolation of the pure primary and secondary forms of the pentenyl bromides (1-bromo-2-pentene and 3-bromo-1-pentene), and the hexenyl bromides (1-bromo-2-hexene and 3-bromo-1-hexene). In the case of the heptenyl bromides, the pure primary form (1-bromo-2-heptene) was obtained, but the pure secondary form (3-bromo-1-heptene) has not yet been isolated. This is due to the fact that the primary heptenyl bromide could readily be isolated in quantity by low temperature fractional distillation of a bromide mixture. However, in an attempt to produce the secondary isomer continuously by high temperature fractionation (above 100°) of a mixture rich in the primary form as had been done with the butenyl and pentenyl bromides, the mixture lost hydrogen bromide, forming some heptadiene, although this fact was not apparent at the time. Consequently, the fraction which was thought to be mainly secondary bromide was later found to be low in bromine content and to contain some heptadiene (see Table I). Likewise the refractive index of this fraction was lower than anticipated for the secondary isomer, n_D^{25} 1.4560 to 1.4600. From our knowledge of the other secondary alkenyl bromides the 3-bromo-1-heptene would be expected to have a value of n_D^{25} 1.4637. A new supply of material must be synthesized before another attempt can be made to purify this bromide.

Previous Preparations of the Alkenyl Bromides.—The pentenyl, hexenyl and heptenyl

TABLE IV
CALCULATION OF COMPOSITION OF ALKENYL BROMIDES PREVIOUSLY DESCRIBED BY OTHER INVESTIGATORS

Bromide	Investigator	Refractive index, n_D	Calcd. composition		Notes
			% prim.	% sec.	
Butenyl	Delaby and Lecomte ^{5b}	1.4815 (16°)	87.0	13.0	Although reported as pure primary bromide, this is the equilibrium mixture
Pentenyl	Hurd and McNamee ^{10b}	1.4757 (21°)	73.5	26.5	
Pentenyl	Hurd and Pollock ^{10c}	1.4654 (20°)	2.0	98.0	Frac. 1
		1.4769 (20°)	78.2	21.8	Frac. 2. Ozonization gave 18.5% secondary and 81.5% primary
Hexenyl	Delaby and Lecomte ^{5b}	1.4731 (20°)	53.0	47.0	Reported as the pure primary isomer
	Van Risseghem and Gredy ^{5a}	1.4657 (20°)	3.7	96.3	Reported to be pure secondary bromide
		1.4777 (20°)	93.3	6.7	Reported to be pure primary bromide
		1.4744 (21°)	72.4	27.6	Reported to be equil. mxt. from 30 dist. of <i>s</i> -bromide (see Table III)
		1.4750 (21°)	76.8	23.2	Reported to be equil. mxt. from 22 dist. of prim. bromide (see Table III)
	Hurd and Parrish ^{10a}	1.4715 (26°)	69.4	30.6	
Heptenyl	Delaby and Lecomte ^{5b}	1.4778 (16°)	79.0	20.9	Reported as the pure primary isomer
	Hurd and Parrish ^{10a}	1.4693 (24°)	51.0	49.0	
	Delaby and Lecomte ^{5b}	1.4760 (17°)	59.0	41.0	Reported as the pure primary isomer

bromides have been synthesized many times for one purpose or another but in most cases the investigator was unaware of their mobility and hence thought that only one product, the primary isomer, $R-\overset{H}{C}=\overset{H}{C}-CBr$ reported by Bouis,⁹ was

present. Fortunately, in a few cases sufficient data have been given so that we can use our refractive index data and calculate the composition of the materials reported. Table IV contains this information. Van Risseghem and Gredy^{5a} have reported the separation of the primary and secondary hexenyl bromides (1-bromo-2-hexene and 3-bromo-1-hexene). If they had not underestimated the mobility of the bromides and as a result used too high a distillation temperature (50–60°) they would have made a successful separation. Actually their primary bromide contained 6.7% of the secondary isomer and the secondary bromide contained 3.7% of the primary form. Their attempt to attain equilibrium by repeated distillation at 100° in a sealed tube could not possibly give an equilibrium mixture. Judging from our experience the bromides are mobile enough so that the secondary form would be continually formed in the boiling liquid to replace the secondary form which is removed in excess in the vapor. Hence the final distillate would of necessity contain more secondary bromide than that present at equilibrium, regardless of the number of distillations performed. Moreover, the composition probably would depend upon the

conditions maintained during the last distillation rather than on the previous distillations. Their secondary hexenyl bromide after thirty distillations ($n_D^{21} 1.4744$) was actually 72.4% primary bromide instead of the 85.8% called for by our equilibrium measurements and the 90–95% which they report. Likewise, their primary bromide after twenty-two distillations ($n_D^{21} 1.4750$) contained 76.8% primary bromide in place of the 90–95% which they reported. It should be noted that these two products contained far more secondary bromide than these authors report by Raman measurements and that they differ in composition by 5%, although they were reported to be identical in composition.

The results by Hurd and co-workers¹⁰ are of particular interest because they offer a comparison of refractometry and ozonolysis methods of analysis. The approximate agreement observed in the case of the pentenyl bromides is gratifying, especially since there seems to be complete disagreement between our results and those obtained from Raman and infrared absorption measurements. For example, Delaby and Lecomte^{5b} have synthesized bromides from the alkylvinylcarbinols and claim to obtain only pure primary bromides. However, analysis of their results using refractive index data shows that in every case their product was a mixture of both the primary and secondary bromides. In order to justify our confidence in the refractive index method of analysis,

(10) (a) Hurd and Parrish, *THIS JOURNAL*, **57**, 1732 (1935); (b) Hurd and McNamee, *ibid.*, **59**, 104 (1937); (c) Hurd and Pollock, *J. Org. Chem.*, **3**, 565 (1939).

(9) Bouis, *Bull. soc. chim.*, [4] **41**, 1160 (1927).

it should be recalled that a mixture of butenyl bromides comparable to that reported by Delaby and Lecomte was actually fractionated³ at low temperatures into fractions comparable in size to those expected from refractive index analysis.

Further confirmation of the above conclusions has been obtained in this Laboratory⁸ from experiments on the *controlled* conversion of alkylvinylcarbinols into bromides with phosphorus tribromide. In each case approximately 47% secondary bromides was present.

Summary

Several pure primary and secondary alkenyl

bromides of the type $R-\overset{\text{H}}{\text{C}}=\overset{\text{H}}{\text{C}}-\text{CBr}$ and $R-\overset{\text{H}}{\text{C}}-\overset{\text{H}}{\text{C}}=\overset{\text{H}}{\text{C}}\text{H}$ ($R = \text{Et to Bu}$) have been isolated for the first time.

The isomeric bromides have been rearranged at 100° to equilibrium mixtures the compositions of which have been determined.

The refractive index method of analysis of alkenyl bromide mixtures has been tested further with pentenyl bromide mixtures.

Conflicting reports in the literature concerning the composition of bromides made from alkylvinylcarbinols have been discussed and corrected values calculated.

LOS ANGELES, CALIF.

RECEIVED JULY 17, 1939

[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND]

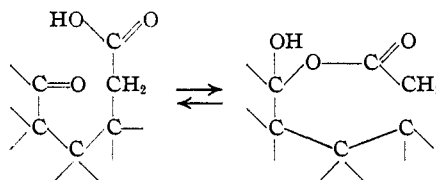
Cerin and Friedelin. V. A Study of Friedonic Acid¹

BY NATHAN L. DRAKE AND JOHN K. WOLFE²

Friedonic acid, a monobasic keto acid, is produced from friedelin by vigorous oxidation.³ The acid is esterified readily, but neither free acid nor ester yields the ordinary derivatives of a carbonyl compound. However, the fact that the acid can be reduced both by sodium and alcohol and by hydrogen in the presence of a catalyst to an hydroxy acid which spontaneously undergoes inner esterification to yield a lactone, make it clear that friedonic acid is a keto acid and not an hydroxy acid. It is the purpose of this paper to present additional evidence of the presence of a carbonyl group in friedonic acid, and to show the relation of carbonyl to carboxyl.

From the reaction products of one of many routine oxidations of friedelin was isolated a substance, isomeric with friedonic acid, which melted at 126–127°. The same compound had been isolated earlier by Campbell,⁴ but never in quantity sufficient to warrant further investigation. We have found that this product, which is unaffected by dilute sodium hydroxide in the cold, can be converted into a methyl ester identical with the methyl ester of friedonic acid, and that friedonic acid, when allowed to stand at room temperature for

some time in alcoholic solution containing sodium ethoxide, is converted in part into this same compound (m. p. 126–127°). We shall call this substance "isomer A." The possibility that this substance is an hydroxylactone formed by interaction of the carboxyl and carbonyl of friedonic acid has been considered



Such a formulation would account for the fact that both isomer A and friedonic acid yield the same methyl ester, and that isomer A cannot be titrated with alkali in the cold, but does give normal values of saponification equivalent. The failure of "isomer A" to take up alkali in the cold makes it very unlikely that stereoisomerism only is involved in the difference between friedonic acid and this isomer. However, our ignorance of a suitable method of preparing the substance has rendered further work upon it impossible. Our supply of this material has been limited to several grams obtained for some unknown reason during a routine preparation of friedonic acid, and a very small amount formed by the action of sodium alkoxide on friedonic acid as mentioned above.

(1) Presented before the Division of Organic Chemistry at the Baltimore meeting of the American Chemical Society, April, 1939.

(2) From the Ph.D. dissertation of John K. Wolfe.

(3) Drake and Campbell, *THIS JOURNAL*, **58**, 1681 (1936).

(4) Campbell, Thesis, U. of Md., 1936.