

- I. THE CATALYTIC DECOMPOSITION OF n-BUTYL ALCOHOL.
THE EQUILIBRIUM BETWEEN THE THREE NORMAL BUTENES.
- II. THE USE OF CROTONALDEHYDE IN THE SYNTHESIS
OF LEPIDINE.

Thesis

by

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ABSTRACT

I

n-Butyl alcohol has been dehydrated at 350-450° with various catalysts. Soda lime, sodium aluminate and sodium hydroxide are without effect. Kaolin, tungsten oxide on asbestos and thorium oxide on asbestos, give good results. The compositions of the butene mixtures so obtained have been determined.

1-Butene and 2-butene respectively have been passed over pumice stone impregnated with phosphoric acid at 350, 400 and 500°. Equilibrium has been reached at 350 and 400°, and equilibrium constants and free energies have been calculated for the reactions:

- (1) 1-butene \rightleftharpoons trans 2-butene
- (2) 1-butene \rightleftharpoons cis 2-butene
- (3) trans 2-butene \rightleftharpoons cis 2-butene

II

The synthesis of lepidine has been attempted in three ways, using crotonaldehyde as a starting material:

- (1) By preparing an aldehyde-ammonia from B-phenyl butyral and ammonia, followed by ring closure with the use of $AlCl_3$.
- (2) By the condensation of aniline with B-chlor butyral.
- (3) By ring closure of B-phenyl butyric bromamide, with the use of $AlCl_3$.

A new compound, B-phenyl butyric bromamide has been prepared.

A new method for the preparation in good yield of B-phenyl butyric acid has been outlined.

INTRODUCTION

The present work on the decomposition of normal butyl alcohol was a continuation of similar work undertaken by Young and Lucas.

In 1881 Le Bel and Green¹ dropped 1-butanol upon hot zinc chloride and obtained butene. Sabatier and Reid² report the use of various catalyzts, including metal oxides, sulphuric and phosphoric acids and phosphoric anhydride for the decomposition of alcohols. Others³ have dehydrated butyl alcohol using different catalysts. The butene obtained is a mixture whose composition depends upon the nature of the catalyst used.

A few investigators have reported isobutene from the decomposition of normal butyl alcohol or secondary butyl alcohol, but the present work and that of Young and Lucas⁴ show no evidence for the formation of isobutene. It may be assumed, therefore, that any isobutene reported was due to isobutanol in the alcohol used.

There are various ways of preparing 1-butene:

- (a) By the action of zinc diethyl upon vinyl bromide⁵.
- (b) By the action of zinc dimethyl upon allyl iodide⁶.
- (c) By the catalytic dehydration of 1-butanol⁷.
- (d) By the action of alcoholic potash on 1-bromobutane⁸.
- (e) By the action of zinc upon 1,2-dibromobutane in alcohol.⁹
- (f) By the action of methyl magnesium iodide upon allyl bromide^{9,10}.
- (g) By pyrolysis of normal butyl chloride¹¹.

None of these methods is entirely satisfactory. It was hoped that in the course of the present work a proper catalyst could be found which would dehydrate 1-butanol giving pure 1-butene or

nearly so. The choice of catalysts was influenced by the observations of Young and Lucas that basic catalysts favor the production of 1-butene from 1-butanol. Accordingly, a number of dehydration experiments were carried out using as catalysts, soda lime, sodium aluminate, alone and on pumice, kaolin, sodium hydroxide pellets, thoria, alone, on pumice and on asbestos, and tungsten oxide on asbestos.

PROCEDURE

The decompositions were carried out in the following manner. The alcohol was forced into a heated tube filled with the catalyst and the products of the decomposition were passed through a condenser to remove water, unchanged alcohol and other liquid products. The gas was washed with 20% perchloric acid solution, dried in a calcium chloride drying tower and then led into an all-glass reaction vessel where the butenes were transformed into dibromides by addition of bromine. The crude dibromides were washed with sodium bisulfite solution, then with water, dried over calcium chloride and were then fractionally distilled at 50 mm., and analyzed by the method of Dillon, Young and Lucas.¹²

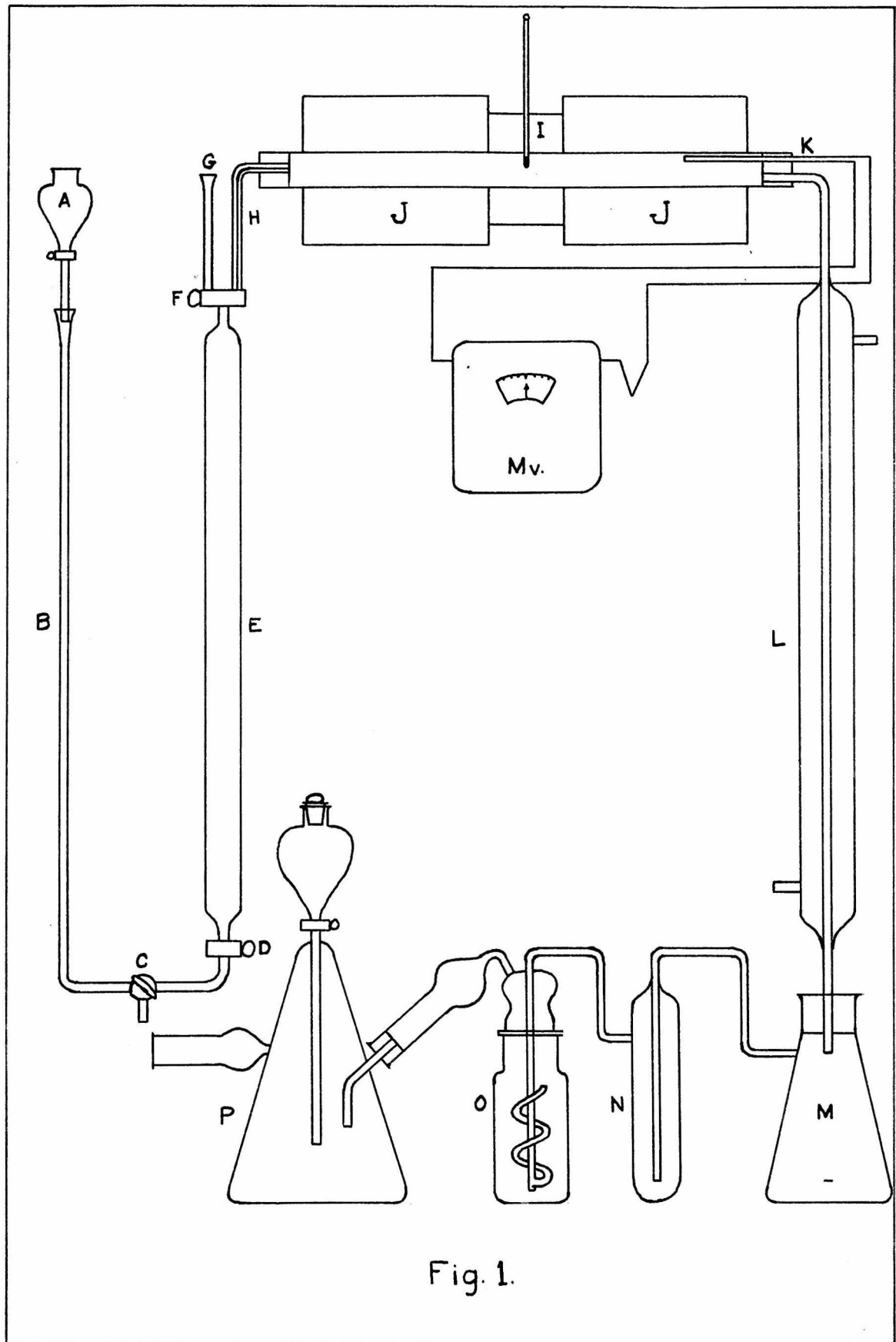


Fig. 1.

Figure 1 shows the apparatus used. Parts A to F include only the device used for admitting the alcohol at a constant rate. Mercury is dropped from the dropping funnel A into the glass tube B. The mercury flows into the gas burette E, which contains about 100 ml. of butyl alcohol, and forces the alcohol up and out the capillary tube H into the reaction tube. The other parts are used for filling and emptying the device. The rate of dropping of the mercury into *AB* is easily controlled by the stopcock which has the edges of the hole through the stopcock filed to a small V thus allowing a very small opening to be made. This device gives a very even flow of alcohol into the reaction tube.

The reaction tube was of Pyrex, 90 cm. long and 15 mm. outside diameter. The first half of the tube served as a preheater and a thermometer inserted in the gas stream through the side-arm at I measured the temperature of the alcohol vapor as it entered the second half of the tube, containing the catalyst. The two furnaces, J, were of the usual wire-wound resistance type, capable of heating to 600° and were manually controlled by means of external resistances. The catalyst was loosely packed into the tube and was held in place by plugs of glass wool.

An iron-constantan thermocouple protected by a small glass tube was inserted in the middle of the packed portion of the tube, to indicate the reaction temperature. The thermocouple voltage was read on a millivoltmeter which had been previously calibrated in conjunction with the thermocouple.

The vapors then passed through the condenser L and most of the liquids were retained at M. A trap N kept at 0° was also used

to take out any alcohol vapor that might be carried along. The butene was then washed with 20% HClO_4 in two spiral wash-bottles to further remove impurities. The gas was then dried in a drying tower containing soda lime and calcium chloride and was led into the brominating flask, kept at -20° with an ice-hydrochloric acid bath.

Bromine was added slowly in small quantities and the butene was kept in slight excess except at the end of the run, to avoid excess of bromine which might lead to the formation of tribromides or tetra-bromides.

The results of these experiments are shown in Table I.

TABLE I

No.	Catalyst	Temperature °C	Time hours	Alcohol used ml.	Rate ml/hr	Contact time secs.	Dibromide gms.	yield %
1	Soda lime	400-450	6	82	13.6	20	4	1.9
2	NaAlO ₂ on pumice	350	No reaction					
3	NaAlO ₂	400-410	1	15	15	18	2	5.2
4	Clay balls	430-450	6	85	14	18.5	37	13.
5	"	430-440	4	25	6.2	42		
6	"	430-450	13	106	8.2	31.5	88	32.2
7	Thoria on pumice	400	No reaction					
8	Thoria	400	No reaction					
9	WO ₃ on asbestos	400-430	20	98	4.9	54	34	13.5
10	"	400	4	57	14.2	19	33	23.3
11	NaOH pellets	390	No reaction					
12	Thoria on asbestos	390	8	92	11.5	24	45	19
13	"	390	7	96	13.6	20.4	62	25

DISCUSSION OF RESULTS

Of the six catalysts used only three gave satisfactory results. These were thoria, tungsten oxide and kaolin, their effectiveness being in the order named, thoria being the best. The experiments with soda lime did not lead to success. As the table shows, a small amount of butene was formed but only at the outset of a run. After an hour the gas flow had practically stopped and the alcohol came through unchanged. The catalyst caused trouble by swelling and stopping the tube. This was due to formation of $\text{Ca}(\text{OH})_2$, which brought the catalytic activity to an end, since the $\text{Ca}(\text{OH})_2$ would not give up the water and therefore could no longer act as a dehydrating agent.

The NaAlO_2 was chosen for its similarity to $\text{Al}(\text{OH})_3$. This catalyst on pumice produced no butene at all and very little when used alone.

The most basic catalyst, NaOH pellets, used at 390° was entirely inactive.

It thus appears that an oxide is necessary. The possibility of finding a basic catalyst which would produce pure 1-butene seems remote.

The action of kaolin, thoria and tungsten oxide are of interest. The kaolin was used in the form of little balls. This catalyst gave good results and retained its activity for a considerable period of time. It could be reactivated by heating in a current of air to 400° for an hour or two.

The thoria, alone or mixed with pumice stone, gave very little butene, contrary to expectation. When precipitated on asbestos, however, it proved to be the most active of the catalysts employed.

Tungsten oxide on asbestos gave good results but was troublesome because it easily packed and caused stoppage of the tube.

The yield of butene was calculated from the amount of the purified dibromide and so does not represent the actual extent of the dehydration. The contact times were calculated from the extent of reaction, the mean of the volumes of entering and leaving gas, the volume of the catalyst-filled reaction tube (50 cc), and the perfect gas laws. The temperature as measured by the thermocouple was taken as the mean temperature of the gas in the reaction tube. The contact times calculated in this manner are evidently not the true values but give relative results.

PREPARATION OF THE CATALYSTS AND MATERIALS

Ordinary soda lime (1/4" lumps) was used. The NaAlO_2 on pumice was prepared by stirring pumice stone lumps, screened to one-quarter to one-quarter and one-eighth inch lumps, into a thin paste of NaAlO_2 and water, then heating in an iron crucible for two hours. The NaAlO_2 (practical) was obtained from the Mefford Chemical Co. in amorphous lumps and was not further purified.

The kaolin catalyst, was made by rolling little balls (1/4 inch) from a thick paste of kaolin and water, then drying over night in an oven at 150°. They were later heated in a porcelain dish for an hour with a strong flame. When dry they held their shape well and did not crumble to any great extent.

The thorium oxide was prepared in the following manner. Twenty grams of C.P. thorium nitrate (Eimer and Amend) were dissolved

in 100 ml. of warm water. This solution was slowly added with stirring to 15 cc. of 15 N NH_4OH in 200 cc. of water. The gelatinous precipitate of thorium hydroxide was washed, decanted, filtered and dried at $300-45^\circ$ for seven hours. It was then in small one-eighth inch pieces or less and was quite white and clean. The thorium oxide on asbestos was prepared by precipitating the hydroxide on the asbestos fibers, then washing and filtering, rolling into balls, and drying at 150° over night.

The tungsten oxide (yellow tungstic acid) was mixed dry with asbestos and put into the reaction tube. The first portions of the alcohol caused it to turn to the blue oxide.

The 1-butanol had been purified by fractional distillation after being dried.

Merck's bromine was shaken with a concentrated solution of potassium iodide and distilled from concentrated H_2SO_4 . Kahlbaum's purified bromine was also used.

Synthetic methanol (99.5%) was refluxed with iodine for 72 hours, then powdered zinc added and the alcohol distilled off. It was then diluted to 99%, $d_{20/4} = 0.7945$.

Baker's potassium iodide was finely ground, heated to 140° overnight and kept in a desiccator until used.

ANALYSIS OF THE DIBROMOBUTANES

The crude dibromides were shaken with NaHSO_3 solution to remove excess bromine, washed well with water and dried over CaCl_2 . They were then fractionated slowly at 50 mm. pressure, the mixtures usually distilling between 72° and 78° . The first small low-boiling fraction containing impurities was discarded, likewise any very high-boiling fractions.

The analysis was made according to the method developed by Dillon, Young and Lucas.¹² The density of the dibromides was measured with a 20-ml. pycnometer. The reaction rate of the dibromide mixtures with potassium iodide in 99% methanol solution was also measured at 75°C .

The percentage of 1-butene, cis-2-butene, and trans-2-butene can be calculated from the following equations:

$$X = \frac{-k_b(d_c - D) + k_c(d_b - D) - K_2(d_b - d_c)}{\Delta}$$

$$X = \frac{k_a(d_c - D) - k_c(d_a - D) + K_2(d_a - d_c)}{\Delta}$$

$$X = \frac{-k_a(d_b - D) + k_b(d_a - D) + K_2(d_a - d_b)}{\Delta}$$

where k_a , k_b , and k_c are the specific second order reaction rate constants for 1,2-dibromobutane, meso-2,3-dibromobutane and racemic 2,3-dibromobutane, and d_a , d_b , and d_c , are the corresponding densities in vacuo. K_2 and D are the reaction rate constant and density observed for a dibromide mixture. Δ is the determinant constant or discriminant,

$$\Delta = k_b(d_a - d_c) - k_c(d_a - d_b) - k_a(d_b - d_c)$$

The error of this method is presumed to be not more than 5%.

It is interesting to point out in connection with this method that the methyl alcohol used as a solvent influences the reaction rate by its purity. Different batches of alcohol from the same or different sources, subjected to the same purifications gave different results. The impurities reacted with the iodine liberated and apparently made the rate fall off. A correction can be made for this by running a blank of methanol and iodine of approximately the average concentration of iodine present during a rate experiment. It was observed by Dillon, Young and Lucas¹² that for three samples of methanol, corrections amounting to 0.00, 1.10, and 1.27 cc. of 0.02 N thiosulfate solution per 20 cc. of methanol solution were needed. These workers had carefully purified their methanol by refluxing with sirupy phosphoric acid, and with sodium hydroxide, to remove amines, aldehydes, etc., yet the corrections were still necessary.

During the present investigations the methanol was refluxed for 72 hours with iodine, about 2 grams per liter of alcohol. Powdered zinc was then added which removed the excess iodine and the alcohol was then slowly fractionated and diluted to 99%. Tests of different samples of methanol purified in this way show corrections of 0.11, 0.03 and 0.00 cc. of 0.02 N $\text{Na}_2\text{S}_2\text{O}_3$ solution, after having kept the methanol-iodine solution at 75° for 36 hours. Since the samples are analyzed up to periods of only 24 to 30 hours, these corrections are so small as not to affect the results. A large batch of methanol showing no correction was made up and used for the experiments.

TABLE II. Composition of Butene Mixtures.

No.	Catalyst	Temp.	K_2	$D_{25/4}$	% Composition		
					1-butene	trans	cis
4,5	Kaolin	430-450	.0516	1.7829	34	21	45
6	"	430-450	.0523	1.7832	36	18	46
	Average		.0520	1.7830	35	19.5	45.5
9	WO ₃ on asbestos	400-430	.0527	1.7826	34.7	24.5	40.8
10	"	400	.0537	1.7837	41.8	14.4	43.3
	Average		.0532	1.7832	38.8	19.2	42.
12	Thoria on asbestos	390	.0533	1.7843	44	9	47
13	"	390	.0532	1.7841	42.8	12.7	46.5
	Average		.0533	1.7842	43.4	10.9	46.7

The amount of 1-butene obtained is about the same for the thorium and tungsten oxides and is less for the kaolin. It is interesting to note that the amount of cis c-butene does not change very much; the change in composition occurs mainly between the 1-butene and the trans 2-butene. In all the experiments the amount of the cis isomer is much greater than the amount of the trans isomer. Young and Lucas⁴ found in their experiments, that the amount of the trans isomer predominated over the amount of the cis isomer, except in the case of the aluminum oxide decompositions.

The compositions of the mixtures obtained, show variation among themselves, that is, in runs made with the same catalyst. This variation is partly inherent in the method of analysis but Runs 9 and 10 indicate that contact time and temperature influence the composition of the butene mixtures produced.

EQUILIBRIUM OF THE BUTENES

It was thought that perhaps there exists an equilibrium among the three isomers and accordingly preliminary experiments were made in which 1-butene and 2-butene respectively were passed at 400° over pumice stone impregnated with phosphoric acid. The analysis of the dibromides from these showed a different composition from the original butene.

In the first experiment 2-butene made by decomposing 1-butanol with sulfuric acid, was the starting material. This has the composition, according to Young and Lucas⁴ of 68.5% trans and 31.5% cis. The analysis of the dibromides obtained after passing over the catalyst was 1-butene 24%, trans 2-butene 30%, and cis 2-butene 46%.

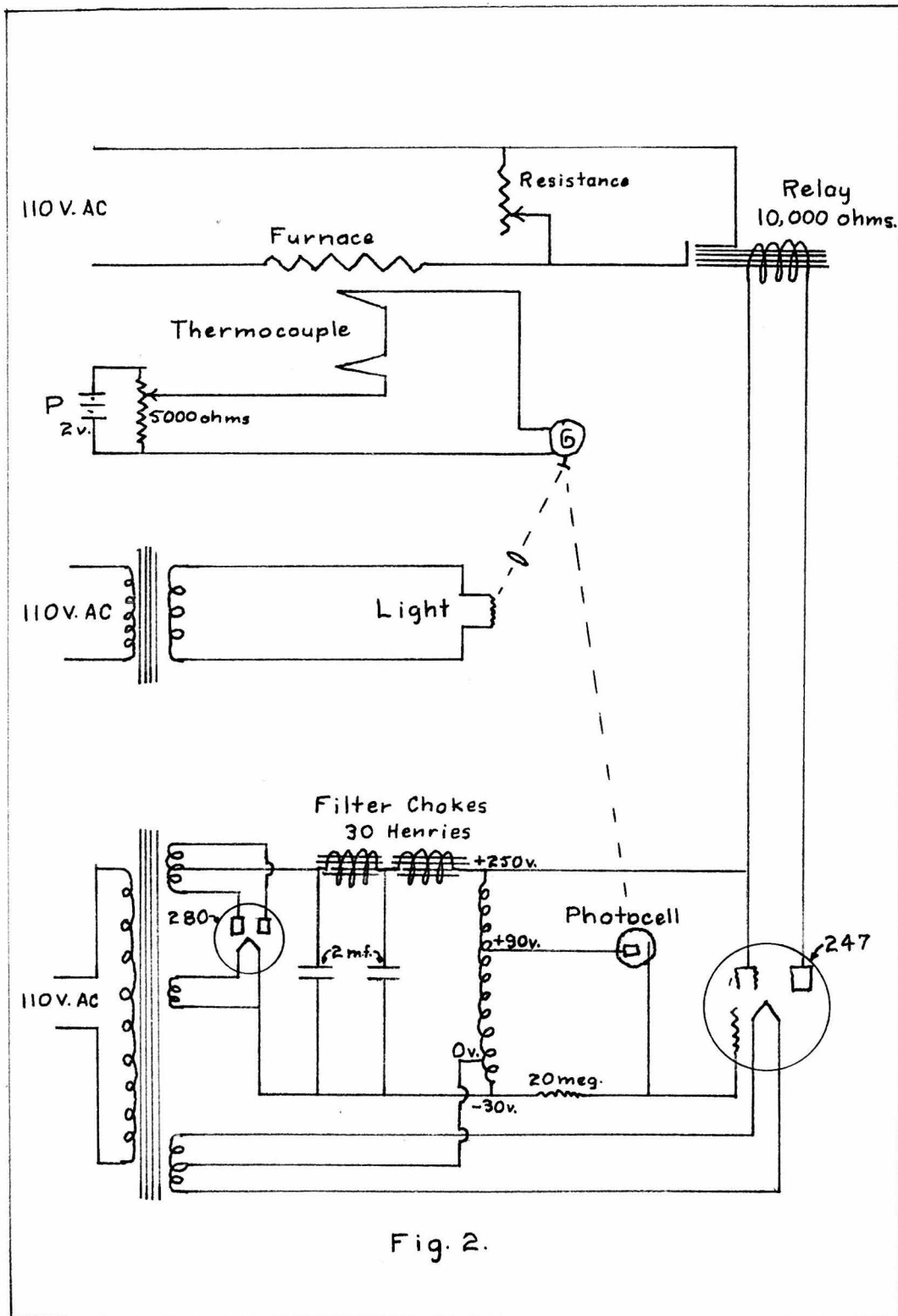
In the second experiment, 1-butene made by the pyrolysis of n-butyl chloride, according to the method of Weston and Haas¹¹ was used. Due to the fact that 1-butene prepared in this manner gives a dibromide whose density is greater than that of any of the dibromobutanes, because of some impurity, the analysis of the dibromides after conversion with the phosphoric acid catalyst is not accurate. By assuming that the ratio of cis to trans was 2 to 1, an approximate analysis is: 1-butene 58%, trans 14%, cis 28%.

These experiments show conclusively that the butenes undergo conversion from one form to another under the influence of a catalyst at elevated temperatures.

A series of experiments were next undertaken to determine the effect of temperature on the conversion and to determine the existence of equilibria between the isomeric forms. In these experiments, the same catalyst was used throughout, namely, pumice stone impregnated with phosphoric acid. In order to avoid errors arising from fluctuating temperature, an automatic temperature control was designed, details of which will be given later. The equilibria were approached from each side; conversions were made using 2-butene and also with butene obtained from the catalytic decomposition of 1-butanol with aluminum oxide. This last has a composition of about 73% 1-butene.⁴

DESCRIPTION OF APPARATUS

The catalyst was contained in a pyrex reaction tube 45 mm. in diameter and 60 cm. long. It was heated in a specially constructed furnace having a core of extra heavy copper pipe $1\frac{1}{2}$ inches inside diameter, and wound with 35 feet of No. 18 chromel wire. The purpose of the core was to have large heat capacity to insure even heating and to avoid rapid temperature fluctuations. The temperature of the furnace was adjusted to somewhat under the desired temperature by means of an external manually operated resistance. The exact temperature control was effected by a photoelectric relay device actuated by a thermocouple placed in the furnace between the core and the reaction tube. The essential features of the furnace control are shown in the accompanying sketches (Figure 2).



The control is set for any desired temperature by opposing the electromotive force of the thermocouple with an equal E M F obtained from the potentiometer circuit P.

The apparatus is arranged so that at the desired temperature the light beam from the galvanometer falls on the photoelectric cell, which is connected by the amplifier circuit to the relay. A slight fall in temperature of the furnace decreases the E M F of the thermocouple and the opposing E M F then swings the galvanometer light beam off the photoelectric cell, causing the relay to close, thus putting the full line current into the furnace. As the furnace heats up to temperature, the light beam moves onto the photoelectric cell again and the relay opens the furnace circuit.

A metal stop was put on the galvanometer to prevent the beam from moving off the photocell on the wrong side due to the slight lag in the furnace-thermocouple set-up.

The photocell was a Radiotron RCA 868; one of the gas-filled caesium type. It operated on a potential of 90 volts maximum with a current carrying capacity of 20 microamperes. The plate circuit of the amplifier carried about 10 milliamperes, which was sufficient to operate the sensitive high-resistance relay. The light source was a Mazda photocell excitor, straight filament, type T-8, 8.5 volt, 4 ampere bulb. This light was focused on the galvanometer mirror and gave a tall narrow beam reflected on the photocell.

With this apparatus the furnace could be kept to within two or three degrees either side of the desired temperature. This control allowed gas to be passed through the furnace for long periods of time, and took care of fluctuations which might have been caused by uneven flow of gas.

Experimental Procedure

The butene was slowly distilled from one receiver through the reaction tube into a trap and through two spiral wash-bottles containing 20% HClO_4 to remove polymers and other possible decomposition products; the purified butene was then dried in a drying tower containing CaCl_2 and soda lime and was then condensed in a second receiver cooled in an ice-hydrochloric acid bath to -20° . When the butene was all distilled the receiver was changed and the butene passed through the apparatus again; this was repeated the desired number of times. Finally the butene was led into the brominating flask and converted to the dibromides, which were subsequently washed, dried and fractionally distilled at 50 mm.

So much handling brought about a considerable loss of butene from the beginning to the end of a run, but this seemed unavoidable in view of the comparatively long time necessary for the conversion.

The dibromides were distilled in a semi-micro fractionating column, fashioned after directions given by Weston and Haas. The densities of the dibromides were measured at 20°C with a 10-ml. pycnometer. Considerable difficulty in density determinations was noted because of the large temperature coefficient of expansion and volatility of the dibromides. By working quickly however and making many determinations these variations were minimized.

The reaction rates and subsequent calculation of composition were carried out as described previously.

PREPARATION OF CATALYST AND MATERIALS

The phosphoric acid catalyst was prepared by thoroughly mixing pumice stone, screened to 1/4 inch lumps, with sirupy phosphoric acid and heating with a bunsen flame for eight hours to evaporate the water.

2-Butene was prepared by heating 1 mol H_2SO_4 (60% by volume) with 1 mol of 1-butanol and washing the gas with dilute sulfuric acid and 20% potassium hydroxide; the butene was condensed, redistilled and passed through a wash-bottle containing 20% perchloric acid, recondensed and kept in sealed ampoules till used.

1-Butene (73%) was prepared by decomposing 1-butanol with aluminium oxide (Al_2O_3).¹³

n-Butyl chloride, used in the preliminary experiments was prepared by the action of hydrochloric acid on n-butyl alcohol.¹⁴

1-Butene was also prepared by the action of alcoholic potassium hydroxide on 1-bromobutane.

TABLE III

No.	Temp.	Original butene Kind	Am't.	Contact time, min.	Dibromide obtained gms.	K ₂	D _{20/4}
1	400 ^a	II	100	28	37	.0512	1.7916
2	400 ^a	I	70	36	42	.0536	1.7928
3	400 ^a	I	80	24	75	.0574	1.7933
4	400 ^a	II	80	40.5	96	.0493	1.7896
5	400	II	80	37.5	79	.0540	1.7915
6	400	I	50	102	24	.0546	1.7922
7	500	II	60	58	-	-	-
8	500	II	45	8.8	48	.0537	1.7880
9	500	I	40	14.7	20	.0566	1.7914
10	500	II	40	51.5	-	-	-
11	350	I	80	54.8	77	.0555	1.7899
12	350	II	70	137	10	.0558	1.7899
13	350	II	80	38	36	.0541	1.7900

Run No.	Temp.	Percentage Composition		
		1-butene	Trans 2-	Cis 2-
1	400 ^a	37	15	47
2	400 ^a	48	6	46
3	400 ^a	57	4	39
4	400 ^a	25	33	42
5	400	42	18	40
6	400	47	12	41
8	500	24	51	25
9	500	46	21	33
11	350	37	34	29
12	350	37	35	28
13	350	35	32	33

a Temperatures not exact. Probably varying up to 420°
 I represents butene from aluminum oxide decompositions.
 II represents 2-butene from sulphuric acid decomposition.

DISCUSSION OF RESULTS

The results of these conversion experiments clearly indicate the existence of equilibria and the effect of changing conditions such as temperature, condition of catalyst, and contact time upon the composition of the butene mixture.

The temperature in Runs 1-4 inclusive cannot be considered to be actually 400°. Due to an error in the measurement of thermocouple voltages the temperature of these runs is uncertain. A possible value is 420°. Runs No. 1 and 2 show the effect of insufficient contact time. Equilibrium has not been established. Runs No. 3 and 4 show this effect and that of decreased catalytic activity. The same batch of catalyst was used in the first four runs, an attempt being made to reactivate it between runs by heating it to 400° and passing steam, air, and oxygen through it separately. This treatment was not sufficient, however, and the catalyst became badly blackened with carbon after a single run, so for the remainder of the experiments, a fresh amount of catalyst was used for each experiment.

Considering the accuracy of the analysis and the slowness of conversion, an average of the values of Runs 5 and 6 may be accepted as equilibrium values. Likewise in Runs No. 11 and 12.

The conversions at 500° did not attain equilibrium values. In Runs No. 7 and 10 decomposition took place to such an extent that there was insufficient dibromide obtained to fractionate and analyze.

Runs No. 8 and 9 were made with two and three passes respectively of the butene through the furnace. This reduced contact time, lessened the decomposition but gave insufficient time for attaining equilibrium.

Run No. 13 was likewise passed through the furnace only three times.

In all the experiments decomposition and polymerization was noticed. A small amount of liquid was carried over by the gas stream through the wash-bottles, into the receiver. On distilling out the butene the liquid remained. This amounted to about 0.5 to 1 cc. for 50 cc. liquid butene. A micro boiling point determination on this residue from Run 7, B.Pt 120° , indicated that it might be octene, a dimer of butene.

A relatively large quantity, about 2 cc. was collected in Run No. 11 and was distilled in a special column. The residue boiled between 106° and 115° , half of it distilling at the higher temperature.

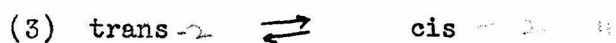
A solution of 0.2 gms. of the residue in 100 ml. CCl_4 solution was used for a bromine titration. This gave a molecular weight of 110.7, which is in good agreement with the molecular weight of octene, 112.

The perchloric acid wash bottle solution in several cases was neutralized with sodium carbonate, extracted with ether and distilled. The results in all cases were a tarry residue after the ether had been driven off, so further investigation was not attempted.

Unpublished work of W.F.Eberz in this laboratory has shown that iso-butene is readily hydrated to tertiary butyl alcohol in strong acid solution. The presence of tertiary butyl alcohol in the wash-bottles would indicate the formation of isobutene in the reaction tube. In no case was any tertiary butyl alcohol detected. This is in agreement with Young and Lucas.⁴

EQUILIBRIUM CONSTANTS AND FREE ENERGIES

There are three reactions possible for the conversion of the three isomers, one into the other.



$$\text{where } k_1 = \frac{P_{\text{trans}}}{P_1}, \quad k_2 = \frac{P_{\text{cis}}}{P_1}, \quad k_3 = \frac{P_{\text{trans}}}{P_{\text{cis}}}$$

Since in the gas phase, pressure fraction equals mol fraction, the pressures may be replaced by percentage composition.

The average equilibrium composition values and the equilibrium constants calculated therefor are shown in Table IV.

TABLE IV

Temp.	1-butene	trans	cis	k_1	k_2	k_3
400°	44.5	15	40	.337	.91	2.7
350°	37	34.5	28.5	.932	.77	.826

From these values free energies may be calculated by means of the relation $-\Delta F = RT \ln K$.

TABLE V

		ΔF 673°	ΔF 623°
(1)	1-Butene \rightarrow trans	1448	820
(2)	1-Butene \rightarrow cis	128	327
(3)	trans \rightarrow cis	-1330	238

This shows that at the temperatures indicated both the trans and the cis forms are unstable with respect to 1-butene. Also that at 400°C (673°K) the trans form tends to shift to the cis, but at 350° (623°K) and presumably at lower temperatures the trans is the more stable of the two. This is in agreement with the observations that at room temperature the trans forms of similar compounds are more stable; for example, it has been found that crotonaldehyde $\text{CH}_3\text{-CH=CH-CHO}$, is completely converted at room temperature to the trans form by the action of sunlight¹⁵ and that ordinary commercial crotonaldehyde is mostly the trans form.

Summary

n-Butyl alcohol has been dehydrated by passing the vapors at 350-450° over kaolin, tungsten oxide on asbestos and thorium oxide on asbestos. Soda lime, sodium aluminate and sodium hydroxide are without action. The butene mixtures produced have been converted to the dibromides and these have been analyzed by measuring the densities at 20° and second order reaction rate constants of the reaction with potassium iodide in 99% methanol solution at 75°.

Experiments have been made in which 1-butene and 2-butene respectively have been passed over pumice stone impregnated with phosphoric acid, at temperatures of 350°, 400° and 500°. The compositions of the resulting butene mixtures have been determined.

Equilibrium has been attained at 350° and 400°, and equilibrium constants and free energies have been calculated for the three reactions:

- (1) 1-butene \rightleftharpoons trans 2-butene
- (2) 1-butene \rightleftharpoons cis 2-butene
- (3) trans 2-butene \rightleftharpoons cis 2-butene

Apparatus for the dehydration and conversion experiments has been described.

A description is also given of an automatic device for controlling furnace temperatures, involving the use of a photoelectric cell, amplifier and relay.

ACKNOWLEDGMENTS

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II

The Use of Crotonaldehyde in the Synthesis of Lepidine

In recent years the preparation of lepidine has become of considerable interest both from a practical and from a purely scientific standpoint. Lepidine, or 4-methyl-quinoline, is used as a dye sensitizer in the manufacture of motion picture film in color photography. As prepared at the present it is quite expensive.

It has been prepared by Mikeska¹ by the condensation of acetone and formaldehyde with aniline with about 14% yield. The condensation of aniline and aldol in the presence of hydrochloric acid gives quinaldine in good yield.² Crotonaldehyde acts like aldol, and in the Skraups Synthesis also gives 2-methyl-quinoline.³ It was considered desirable to investigate the possibility of preparing lepidine cheaply from crotonaldehyde.

In order to get a methyl group in the 4 position of the quinoline nucleus, the benzene ring must be joined to the proper end of the aliphatic chain, with subsequent ring closure. Accordingly two plans suggested themselves. In the first, the benzene ring was to be joined to the crotonaldehyde chain at the B position, after which the nitrogen was to be introduced into the compound and the ring closed. In the second method, aniline was to be coupled to the crotonaldehyde or a derivative, then the ring closed by heating with $AlCl_3$, in a manner similar to that used in the preparation of hydrocarbostyryl.

The first method involved the following steps:

- (1) Preparation of a B-chlor butyracetal from crotonaldehyde.⁴
- (2) Friedel and Crafts reaction with B-chlor butyracetal and benzene.
- (3) Reaction with liquid ammonia to give substituted aldehyde-ammonia.
- (4) Elimination of alcohol to give an imine.

- (5) Ring closure by means of AlCl_3 .
- (6) Oxidation to lepidine.

The second method involved the following steps:

- (1) Preparation of substituted aldehyde-ammonia from aniline and B-chlor butyral.
- (2) Ring closure by means of AlCl_3 .
- (3) Oxidation to lepidine.

Both of these methods were tried. In the first method the Friedel and Crafts reaction gave poor results. The reaction was carried out with conditions varying widely (1) as to solvent, (2) temperature, (3) duration of reaction, (4) amount of AlCl_3 catalyst used, and (5) the method of admixture. In nearly all cases the reaction appeared to go smoothly. After decomposing the reaction product and working it up, it was vacuum distilled.

One run gave a 25% yield of the oily liquid distilling at 80-83 degrees C at 2 mm pressure, while another run carried out under the same conditions gave a 15% yield of an oil which distilled at 100 to 105° at 2 mm. A third run yielded a small amount of a viscous strong smelling liquid boiling over the range of 100 to 170° at 2 mm.

Fractionation of the material was not a successful means of obtaining a pure product. A considerable portion of each distillation decomposed leaving a tarry residue. While distillation was taking place, the boiling point gradually rose. This would seem to indicate that polymerization was taking place. This seems reasonable in view of the fact that aldehydes and acetals are fairly unstable and show tendencies to polymerize.

The reaction of aniline with B-chlor butyraldehyde and also with B-chlor butyraldehyde was quite rapid and vigorous. It was not found possible to control the reaction however, the result was a tarry mass, which became badly polymerized on distillation.

The small amount of material boiling at 80-83° obtained in the second step of the first method was allowed to remain in contact with liquid ammonia for several days in a sealed tube. Upon opening and boiling off the ammonia the rest was fractionated at 2 mm yielding a small amount of light oil distilling at 70 and 71°. A considerable residue of high boiling material and tar in the distilling flask was discarded. A qualitative test by means of a sodium fusion gave positive results for halogen but negative for nitrogen. A molecular weight determination by the camphor method⁵ gave a molecular weight of 170. Because of the small amount of material it was not possible to make further analyses. Several attempts to repeat the last steps were fruitless. Polymerization occurred despite low pressure distillation and care to keep out acids or bases which might act as catalysts. The result was always an unworkable tar.

In order to stabilize the compounds the acid group rather than the acetal or aldehyde was used. This plan of attack made necessary the following steps:

- (1) Preparation of B-chlorbutyric acid from crotonaldehyde by method similar to that used for making B-chlor propionic acid.⁶
- (2) Preparation of B-phenyl butyric acid from B-chlor butyric acid by Friedel and Crafts reaction.
- (3) Preparation of B-phenyl butyral chloride from B-phenyl butyric acid by action of SOCl_2 .
- (4) Preparation of B-phenylbutyramide from B-phenyl butyryl-chloride and ammonia.

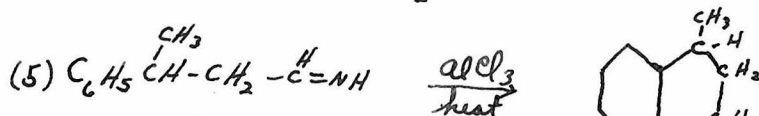
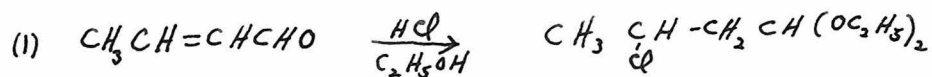
- (5) Preparation of B-phenylbutyric-bromamide by action of Br_2 on B-phenyl butyramide in the presence of KOH.
- (6) Ring closure by heating with AlCl_3 .
- (7) Oxidation to lepidine.

B-phenyl butyric acid has been prepared by the action of AlCl_3 on benzene and crotonic acid,⁷ over a period of a month. It has also been made by reducing methyl cinnamic acid.⁸ The method outlined above using crotonaldehyde etc, gave very good results. The overall yield of the butyramide was 57%.

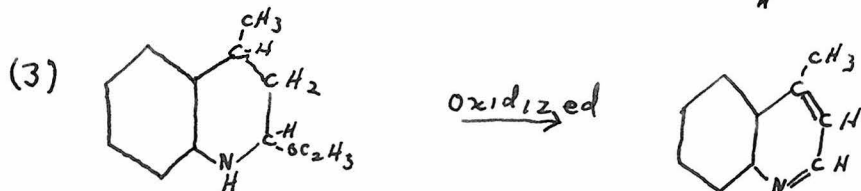
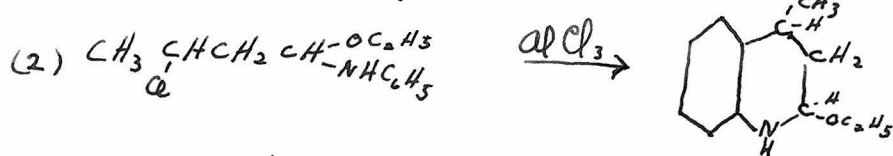
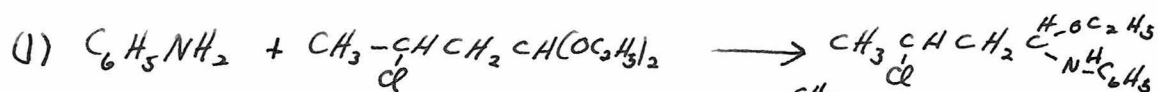
It was planned to make the bromamide by a method similar to that used for preparing acetbromamide.⁹ However, great difficulties were encountered in the purification of the compound. The crystals usually came down intermingled with an oil which had about the same solubility as the bromamid. Several modifications of the method were tried. The reaction was carried out in various solvents; ether, CCl_4 , methyl alcohol and glacial acetic acid. Whenever a solvent was used the result was for the most part an uncrystallizable oil.

The best results were obtained by adding the bromine to the amide in a flask cooled with a freezing mixture, and slowly adding 50% KOH until the mixture was pale yellow. The paste was then filtered, extracted with hot benzene and crystallized from benzene and ligroin. The product from the first crystallization was white needles melting about 100° . By repeated fractional crystallization the melting point was raised to a constant value of 118°C . The yield of the pure material so obtained was 2%, based on the amount of amid used.

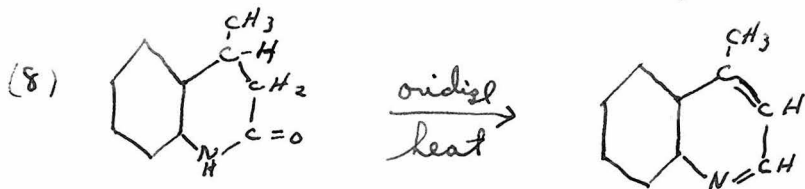
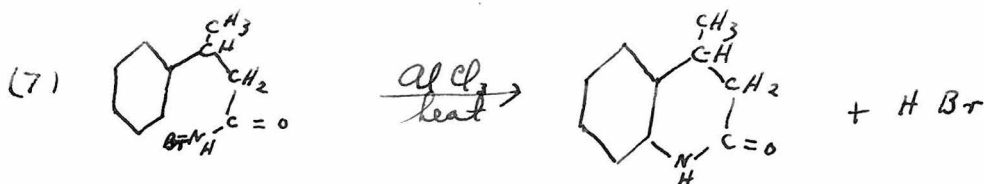
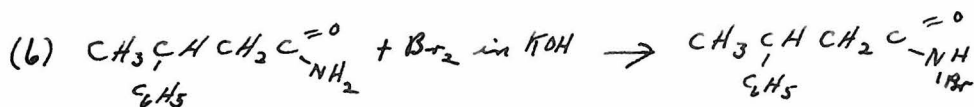
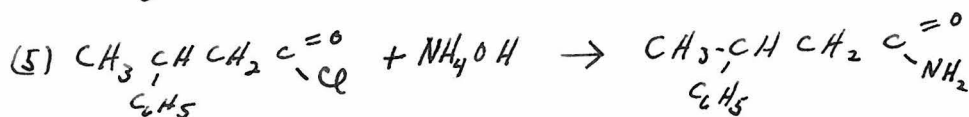
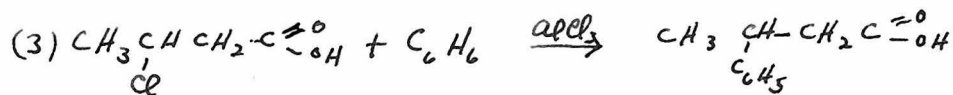
First Method



Second Method



Third Method



An analysis of the bromamid gave results as follows;

$C_{10}H_{12}ONBr$			
Nitrogen	calculated for bromamid	5.45	Found 5.56
Halogen	calculated	31.05	Found 31.4

The compound is definitely established as B-phenyl butyric bromamid. It is a white crystalline solid, melting point $118^{\circ}C$. It is insoluble in water or ligroin, soluble in benzene. It liberates iodine very slowly from potassium iodide, showing some characteristics of an oxidizing bromine group. It has a molecular weight of 258. Its structural formula is $CH_3(C_6H_5)CHCH_2CONHBr$.

On account of the small amount of bromamid obtained, the last two steps in the production of lepidine were not attempted.

SUMMARY

The synthesis of lepidine was undertaken in three ways: (1) by use of B-chlor butyraldehyde and aldehyde, (2) by condensation of aniline with B-chlor butyraldehyde, (3) by ring closure of B-phenyl butyric bromamide. A hitherto unprepared compound, B-phenyl butyric bromamide was prepared in small amount and was analyzed.

It seems probable that lepidine can be prepared from B-phenyl butyric bromamide by ring closure brought about by treatment with $AlCl_3$, with subsequent oxidation to lepidine.

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