NACA TN 2398 8798

TECH LIBRARY KAFB, NM
0065675

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 2398

SYNTHESIS OF CYCLOPROPANE HYDROCARBONS FROM METHYLCYCLOPROPYL KETONE

III - 2-CYCLOPROPYL-1-BUTENE, cis AND trans 2-CYCLOPROPYL-2-BUTENE, AND 2-CYCLOPROPYLBUTANE

By Vernon A. Slabey and Paul H. Wise

Lewis Flight Propulsion Laboratory
Cleveland, Ohio

Washington
June 1951

TECH LIBRARY KAFB, NM

0065675

2156

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 2398

SYNTHESIS OF CYCLOPROPANE HYDROCARBONS FROM METHYLCYCLOPROPYL KETONE

III - 2-CYCLOPROPYL-1-BUTENE, cis AND trans 2-CYCLOPROPYL-2-BUTENE, AND 2-CYCLOPROPYLBUTANE

By Vernon A. Slabey and Paul H. Wise

SUMMARY

The hydrocarbons - 2-cyclopropyl-1-butene, cis and trans 2-cyclopropyl-2-butene, and 2-cyclopropylbutane - were obtained from methylcyclopropyl ketone by reacting the ketone with ethylmagnesium bromide, dehydrating the resultant methylethylcyclopropylcarbinol to a mixture of olefins from which 2-cyclopropyl-1-butene and cis and trans 2-cyclopropyl-2-butene were isolated, and hydrogenating the olefins to 2-cyclopropylbutane. All four hydrocarbons were obtained in high purity for the first time; their physical constants and infrared spectra are presented.

INTRODUCTION

The preparation of a series of olefinic and paraffinic hydrocarbons that contain the cyclopropyl ring was undertaken at the NACA Lewis laboratory in order to provide pure hydrocarbon samples for an investigation of the effect of molecular structure on flame propagation. The synthesis program included those 2-cyclopropylalkenes up to C_9 in which the double bond was in either the 1- or 2-position, and the corresponding 2-cyclopropylalkanes. The preparation of the C_6 and C_8 hydrocarbons is already reported by the Lewis laboratory in references 1 and 2, respectively; the preparation of the C_7 hydrocarbons, 2-cyclopropyl-1-butene, cis and trans 2-cyclopropyl-2-butene, and 2-cyclopropylbutane, are described in the present report.

The methods for preparing the 2-cyclopropylbutenes and 2-cyclopropylbutane were analogous to those described in references 1 and 2, and involved the synthesis of methylethylcyclopropylcarbinol from methylcyclopropyl ketone and ethylmagnesium bromide, dehydration of the carbinol to yield a mixture of products from which the three 2-cyclopropylbutenes were isolated, and catalytic hydrogenation of the olefins to 2-cyclopropylbutane. 2156

The reaction of methylcyclopropyl ketone with ethylmagnesium bromide to give methylethylcyclopropylcarbinol was previously reported by Bruylants (references 3 and 4). Dehydration of the carbinol by the action of either acetic anhydride (reference 3) or concentrated sulfuric acid (reference 5), has been described, but the olefinic products have never before been obtained in sufficient quantity or purity for proper identification. In the present research, the separation of 2-cyclopropyl-1-butene and each of the geometrical isomers of 2-cyclopropyl-2-butene in high purity was accomplished. The catalytic hydrogenation of these olefins yielded 2-cyclopropylbutane, which has not previously been reported.

DISCUSSION OF SYNTHESIS

Methylethylcyclopropylcarbinol was prepared by the condensation of methylcyclopropyl ketone with ethylmagnesium bromide in ether solution, and the crude product was distilled at reduced pressure to avoid dehydration. A portion of the distilled material was treated with alcoholic sodium hydroxide to remove halogenated byproducts (reference 1), and fractionated to yield a product having the physical properties presented in the following table:

Reference	Boiling point (°C)	Index of refraction n_D^{20}	Density d^{20} (grams/ml)
4	143.4 - 143.8 (762 mm)	1.44163	0.88565
Lewis laboratory	142.3 ±0.5[a] (760 mm)	1.4412	.88068

[a]Dehydration slowly occurred during the determination.

The remainder of the carbinol was used for the dehydration reactions without further purification.

In addition to the desired carbinol, the reaction gave a higher boiling halogenated product, the elemental analysis of which agreed with that for methylethylcyclopropylcarbinyl bromide $C_7H_{13}Br$. Previous reports in the literature indicate that halides of this type are unstable and tend to rearrange although they disagree as to the structure of the rearranged products (references 6 and 7). The infrared spectrum of the bromide obtained in this research eliminated the possibility that the byproduct was a cyclopropylcarbinyl bromide, but indicated the basic structure to be that of an α,α,β-olefin; the isolated bromide was assumed to be 1-bromo-4-methyl-3-hexene.

The dehydration of methylethylcyclopropylcarbinol gave a mixture of products from which 2-cyclopropyl-1-butene and cis and trans 2-cyclopropyl-2-butene were isolated and purified; definite assignment of the cis and trans configurations to the 2-cyclopropyl-2-butene was not made, however, because of the unreliability of basing such assignments on physical properties alone.

The methods of dehydration investigated were: (1) distilling the carbinol in the presence of concentrated sulfuric acid, (2) passing the carbinol through alumina at 200° to 250° C, and (3) distilling the carbinol in the presence of oxalic acid. The yields of olefins for each method are presented in the following table:

Method	Yield, percent	
	2-Cyclopropyl-1-butene	2-Cyclopropyl-2-butene
1	23	56
2	32	47
3	12	38

The dehydrations with sulfuric acid or alumina (methods 1 and 2) gave no distillable products other than the olefins; typical distillations of the products are plotted in figures 1(a) and 1(b), respectively. These data indicate that although the sulfuric acid produced the same total yield of olefin as the alumina, the alumina gave the greater yield of 1-olefin and also the greater amount of the high-index (high-boiling) isomer in the 2-olefin fractions.

Oxalic acid was not so effective as the other two dehydrating agents; some of the methylethylcyclopropylcarbinol was consumed in a competing reaction that yielded a product, which was higher boiling than the olefins. The identity of this product was not proved, but by analogy to the isomerization of dimethylcyclopropylcarbinol when heated with oxalic acid to 2,2-dimethyltetrahydrofuran (reference 8), the product was possibly 2-methyl-2-ethyltetrahydrofuran.

Purification of the olefins was accomplished by fractional and azeotropic distillations in 22-millimeter by 6-foot columns, which were packed with 1/8-inch glass helices. Separation of the geometrical isomers of 2-cyclopropyl-2-butene required, in addition, azeotropic fractionations in 22-millimeter by 6-foot Podbielniak columns, which were operated at efficiencies in excess of 150 theoretical plates. After each fractionation the purity of selected samples of distillate was evaluated from visual inspection of time-temperature melting curves. The degree of purity desired was attained when the melting curves were considered to be indicative of purities of 99 to 100 mole percent.

The structures of the olefins were proved by ozonolysis and decomposition of the ozonides according to the procedure of reference 9. With the exception of formaldehyde, the ozonolysis fragments were identified by the infrared spectra, analysis of the 2,4-dinitrophenylhydrazones, or by mixed melting points with the corresponding derivatives of known materials.

Hydrogenation experiments were run on each of the position isomers of 2-cyclopropylbutene. It was observed that 2-cyclopropyl-1-butene readily hydrogenated at 100° to 130° C to give a product of relatively constant index of refraction (fig. 2(a)), whereas 2-cyclopropyl-2-butene under the same conditions hydrogenated slowly and gave a product that contained significant quantities of a paraffinic impurity. When the reaction temperature was raised to 150°, the hydrogenation of 2-cyclopropyl-2-butene was completed in considerably less time, and the product contained no greater amount of the impurity. A distillation curve of the product obtained at the higher reaction temperature is shown in figure 2(b).

The 2-cyclopropylbutane was purified by fractional and azeotropic distillations in 6-foot Podbielniak columns. The purification was especially difficult because of the presence of the paraffinic impurity subsequently identified as 3-methylhexane, which boiled approximately

2156

1° higher than the desired hydrocarbon. A separation was finally effected by azeotropically fractionating with ethanol; although the boiling points of the two hydrocarbon azeotropes are very close to one another, the 3-methylhexane azeotrope is the lower boiling and the impurity is removed in the early fractions.

The physical constants of the purified hydrocarbons, which were determined by the methods described in reference 1, are presented in table I. The time-temperature melting curves from which the melting points were estimated are shown in figure 3. Despite repeated efforts to freeze 2-cyclopropylbutane, a crystalline form of the hydrocarbon could not be obtained.

The infrared spectra of 2-cyclopropyl-1-butene, each of the geometrical isomers of 2-cyclopropyl-2-butene, and 2-cyclopropylbutane are presented in figures 4(a), (b), (c), and (d), respectively. These data were obtained with a double-beam automatic recording spectrometer, the wavelength accuracy of which was estimated to be ±0.03 micron. All the hydrocarbons show strong absorption at 9.8 microns, which appears to be characteristic of this type of cyclopropane (references 1 and 2). Typical carbon-carbon double-bond absorption at 6.0 to 6.1 microns appears in each of the olefin spectra, and the intensity of this absoprtion is decreased and the band is shifted to a lower wavelength as the double bond is changed from the 1- to the 2-position. A similar observation has been previously made from the spectra of the 2-cyclopropylpentenes (reference 2).

EXPERIMENTAL DETAILS

Methylcyclopropyl Ketone

Commercial methylcyclopropyl ketone was fractionated, and distillate having a refractive index range of n_D^{20} 1.4245 to 1.4250 was used in the Grignard reaction.

Methylethylcyclopropylcarbinol

For a typical reaction, 25 moles (608 grams) of magnesium turnings and 23 moles (2507 grams) of ethyl bromide in 2 gallons of dry ether were reacted in a 10-gallon glass-lined reactor. The reaction mixture was kept at reflux temperature for 1 hour after the addition of the ethyl bromide was completed and the methylcyclopropyl ketone (20 moles, 1686 grams) dissolved in 1 gallon of dry ether was added to the

ethylmagnesium bromide at a rate sufficient to maintain rapid reflux. The reaction mixture was stirred at room temperature for 18 hours and then hydrolyzed by the slow addition of 2 liters of saturated ammonium chloride solution. The ether solution of product was separated from the water layer, the ether was removed by distillation, and the methylethylcyclopropylcarbinol was fractionated at 60 millimeters to yield 1767 grams (77-percent yield) of carbinol. A small quantity (approximately 5 percent by weight) of a halogenated product was also obtained from the reaction. The physical properties of the byproduct were: boiling point, 91° to 92° C (54 mm); n_D^{20} 1.4775; and d^{20}, 1.1873 grams per milliliter. Analysis - Calculated for $C_7H_{13}Br$: C, 47.47 percent; H, 7.40 percent; Br, 45.13 percent. Found: C, 47.61 percent; H, 7.39 percent; Br, 44.89 percent.

2156

Dehydration of Methylethylcyclopropylcarbinol

Three methods of dehydration were investigated:

Oxalic acid. - A total of 2 moles (228 grams) of the carbinol and 100 grams of oxalic acid dihydrate were heated to boiling and the reaction products were stripped off as formed. Approximately 2 moles of water was collected in addition to the organic products. Fractionation of the organic material gave 24 grams boiling from 98° to 108° (principally 2-cyclopropyl-1-butene), 73 grams boiling at 108° (2-cyclopropyl-2-butene), and 30 grams boiling from 108° to 122° C. The yield of olefin was 97 grams (50-percent yield). The major portion of the last cut, boiling point 122° C, and n_D^{20} 1.4202, was probably 2-methyl-2-ethyltetrahydrofuran.

Concentrated sulfuric acid. - An 8-mole (912 grams) quantity of the carbinol was mixed with 1 milliliter of concentrated sulfuric acid and heated to boiling in a flask attached to a 4-foot helix-packed column. The products, which were removed from the top of the column as they formed, included 7 moles (126 grams) of water. The organic products were dried over anhydrous calcium sulfate and fractionated through a 22-millimeter by 6-foot helix-packed column to give 177 grams (23-percent yield) of 2-cyclopropyl-1-butene and 430 grams (56-percent yield) of 2-cyclopropyl-2-butene.

2156

Alumina. - The methylethylcyclopropylcarbinol, 14.7 moles (1685 grams) was passed at a rate of 50 milliliters per minute through a 2.5- by 120-centimeter pyrex column, which was packed with 8- to 14-mesh alumina and heated to 200° to 250° C. The weight of water removed by the process was 13.1 moles (236 grams). The organic products were dried over calcium chloride and fractionated in the 6-foot column previously described to give 452 grams (32-percent yield) of 2-cyclopropyl-1-butene and 664 grams (47-percent yield) of 2-cyclopropyl-2-butene.

Purification of Olefins

After preliminary fractionation of the crude dehydration products, fractions were combined on the basis of refractive index to obtain concentrates of each of the position isomers. Fractionation of the 2-cyclopropyl-1-butene concentrate (739 grams) through the 6-foot helix-packed column yielded 422 grams of product of constant refractive index n_D^{20} 1.4321. While the physical constants of selected samples of this material were being determined, the density values increased about 0.0001 unit every 24 hours, presumably because of rapid oxidation. Consequently, a small portion (110 grams) of the constant-index material was azeotropically fractionated with ethanol, and the physical constants were determined immediately after the distillate was removed from the column, washed with water, and dried.

The concentrate of 2-cyclopropyl-2-butene (1500 grams) was refractionated into two parts: (1) n_D^{20} 1.4437 to 1.4449, and (2) n_D^{20} 1.4451 to 1.4478.

The first part (868 grams) was azeotropically fractionated with ethanol in the previously described helix-packed column to obtain 490 grams of higher concentrate, n_D^{20} 1.4428 to 1.4433. A second azeotropic fractionation gave 225 grams of constant-index material, n_D^{20} 1.4428; however, the time-temperature melting curve of this material was not indicative of the required degree of purity. Consequently, a third azeotropic distillation was performed in a 6-foot Podbielniak column to give 115 grams of the low-boiling isomer of 2-cyclopropyl-2-butene.

The second part (300 grams, n_D^{20} 1.4451 to 1.4478) was azeotropically fractionated with ethanol in a 6-foot Podbielniak column to obtain 131 grams of high-boiling isomer of 2-cyclopropyl-2-butene.

Ozonolysis of 2-Cyclopropylbutenes

Samples of each of the three purified olefin isomers were ozonized in ethanol solution. The reduced ozonolysis products were fractionated through a 0.9- by 47-centimeter column to separate the fragments.

From 0.28 mole (27 grams) of 2-cyclopropyl-1-butene there was obtained formaldehyde (identified only by its odor and the appearance of a white solid, presumably paraformaldehyde, which sublimed into the distilling head), and 11 grams (39-percent yield of ethylcyclopropyl ketone, which had the following properties: boiling point, 130° C (atmospheric pressure); n_D^{20} 1.4284. (The corresponding properties reported for ethylcyclopropyl ketone in reference 10 are 131.8° C (769 mm) and n_D^{20} 1.42986.) The 2,4-dinitrophenylhydrazone of the ketone was prepared and found to melt at 160.4° to 160.5° C.

Analysis of the 2,4-dinitrophenylhydrazone - Calculated for $C_{12}H_{14}N_4O_4$: N, 20.13 percent. Found: N, 20.17 percent.

The infrared spectrum of the ethylcyclopropyl ketone fragment is shown in figure 4(e).

A 0.42-mole quantity (41 grams) of the low-boiling isomer of 2-cyclopropyl-2-butene gave 6.3 grams (33-percent yield) of acetaldehyde boiling from 24° to 25° C, and 14.3 grams (40-percent yield) of methylcyclopropyl ketone boiling from 109° to 110° C, n_D^{20} 1.4246. The methylcyclopropyl ketone was identified by comparing its infrared spectrum with that of an authentic sample.

Analysis of the 2,4-dinitrophenylhydrazone of the acetaldehyde fragment - Calculated for $C_8H_8N_4O_4$: N, 25.00 percent. Found: N, 25.06 percent.

Analysis of the 2,4-dinitrophenylhydrazone of the ketone fragment - Calculated for $C_{11}H_{12}N_4O_4$: N, 21.21 percent. Found: N, 21.36 percent.

From 0.38 mole (37 grams) of 2-cyclopropyl-2-butene (high-boiling isomer) there was obtained 5.5 grams (33-percent yield) of acetaldehyde, boiling range 20° to 30° C, and 13 grams (40-percent yield) of methylcyclopropyl ketone, boiling point 109° to 110° C, n_D^{20} 1.4240; the second fragment was again identified from its infrared spectrum. Mixed melting points of both the aldehyde and ketone 2,4-dinitrophenylhydrazone derivatives with known materials showed no depressions.

2156

Hydrogenation of 2-Cyclopropyl-1-butene

A charge consisting of 4.1 moles (394 grams) of 2-cyclopropyl-1-butene (n_D^{20} 1.4319 to 1.4321), 500 milliliters of ethanol, and 40 grams of a barium-promoted copper chromite catalyst was placed into a 3.4-liter rocker-type autoclave under an initial hydrogen pressure of 1600 pounds per square inch. Hydrogenation began at a temperature of 100° C and was completed within 7 hours; maximum temperature attained during the reaction was 130° C. The products were filtered through Celite to remove the catalyst, washed with water to remove the ethanol, and dried over anhydrous calcium sulfate. Fractionation of the 339 grams of products (fig. 2(a)) gave 271 grams of essentially constant index material. Infrared examination of the 43 grams of residue from the fractionation showed it to be principally the same as the distillate with traces of olefin as an impurity.

Hydrogenation of 2-Cyclopropyl-2-butene

A hydrogenation charge consisting of 4.8 moles (461 grams) of mixed 2-cyclopropyl-2-butene isomers (n_D^{20} 1.4430 to 1.4468), 500 milliliters of ethanol, and 46 grams of barium-promoted copper chromite catalyst was placed in the described autoclave. Hydrogenation was barely perceptible at 110° C. After 48 hours the temperature was increased to 130°. The total time required for consumption of the theoretical amount of hydrogen was 127 hours.

A second charge of the olefin (4.2 moles or 401 grams), 500 milliliters of ethanol and 40 grams of the catalyst, was hydrogenated at 150° C; the theoretical quantity of hydrogen was consumed within 50 hours. The products were treated as previously described. The distribution of the 283 grams of distillate is shown in figure 2(b).

Purification of 2-Cyclopropylbutane

The products from several hydrogenations were combined after the preliminary fractionation into two parts: (1) n_D^{20} 1.3912 to 1.3998, and (2) n_D^{20} 1.4000 to 1.4026. Each of these parts was azeotropically fractionated with ethanol in Podbielniak columns, which were estimated to have efficiencies in excess of 150 theoretical plates. The refractive index of each fraction was determined before and after the ethanol was removed by extraction with water. These data from part 1 are plotted

against the percent by weight of distillate in figure 5(a). The impurity in the 2-cyclopropylbutane appeared in the first half of the distillate and was identified conclusively as 3-methylhexane from the infrared spectrum. 2156

The data from the azeotropic fractionation of part 2 are presented in figure 5(b). Several low-index fractions were obtained, indicating that more of the 3-methylhexane impurity was removed from this material. The middle fractions were essentially pure 2-cyclopropylbutane, and the last fraction contained an olefinic impurity. By refractionation of the constant-index middle fractions, the pure 2-cyclopropylbutane was isolated.

RESULTS

From the dehydration products of methylethylcyclopropylcarbinol, 2-cyclopropyl-1-butene, and cis and trans 2-cyclopropyl-2-butene were isolated and purified. The structures of the olefins were proved by ozonolysis, and in the course of identifying 2-cyclopropyl-1-butene a new derivative of ethylcyclopropyl ketone, the 2,4-dinitrophenylhydrazone, was obtained. Catalytic hydrogenation of the 2-cyclopropylbutenes yielded 2-cyclopropylbutane, which is reported herein for the first time. The physical properties of the four hydrocarbons were measured by precise methods and the infrared spectra of the hydrocarbons and ethylcyclopropyl ketone were determined.

Lewis Flight Propulsion Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, February 8, 1951.

2156

REFERENCES

1. Slabey, Vernon A., and Wise, P. H.: Synthesis of Cyclopropane Hydrocarbons from Methylcyclopropyl Ketone. I - 2-Cyclopropylpropene and 2-Cyclopropylpropane. NACA TN 2258, 1951.

2. Slabey, Vernon A., and Wise, P. H.: Synthesis of Cyclopropane Hydrocarbons from Methylcyclopropyl Ketone. II - 2-Cyclopropyl-1-pentene, cis and trans 2-Cyclopropyl-2-pentene and 2-Cyclopropylpentane. NACA TN 2259, 1951.

3. Bruylants, Pierre: Contribution à l'étude des composés cycliques triméthyléniques du type $\begin{matrix} H_2C \\ H_2C \end{matrix}\!\!>CH\text{-}R$. Rec. des Travaux Chim. des Pays-Bas et Belgique, T. XXVIII, 1909, P. 224-226.

4. Bruylants, P.: Contribution à l'étude des composes cycliques triméthyléniques. Bull. Soc. Chim. Belg., Vol. 36, No. 1, Jan. 1927, P. 154-155.

5. Van Keersbilk, N.: Contribution à l'étude des composes cyclopropaniques. Bull. Soc. Chim. Belg., Vol. 38, No. 6, Juin 1929, P. 210.

6. Bruylants, P., and Dewael, A.: Contribution à l'étude des composes cyclopropaniques. Bull. Sci. Acad. Roy. Belg., T. XIV, 1928, P. 140-153.

7. Favorskaya, T. A.: Transition from Derivatives of Ethylenic Hydrocarbons to Derivatives of Simplest Polymethylene Rings. I. Preparation of Methylethylcyclopropylcarbinol and Properties of the Chloride Derived from It. Chem. Abs., vol. 42, pp. 1210-1211.

8. Zelinsky, N.: Ueber Isomerisation des Dimethylcyclopropylcarbinols. Ber. d. D. chem. Gesellschaft, Jahrg. XXXIV, Bd. III, 1901, S. 3887-3889.

9. Henne, Albert L., and Perilstein, Warren L.: The Preparation of Aldehydes and Ketones by Ozone Oxidation. Jour. Am. Chem. Soc., vol. 65, no. 11, Nov. 1943, pp. 2183-2185.

10. Bruylants, P.: Contribution à l'étude des composés cycliques triméthylénique. Bull. Soc. Chim. Belg., Vol. 36, No. 11, Nov. 1927, P. 519-532.

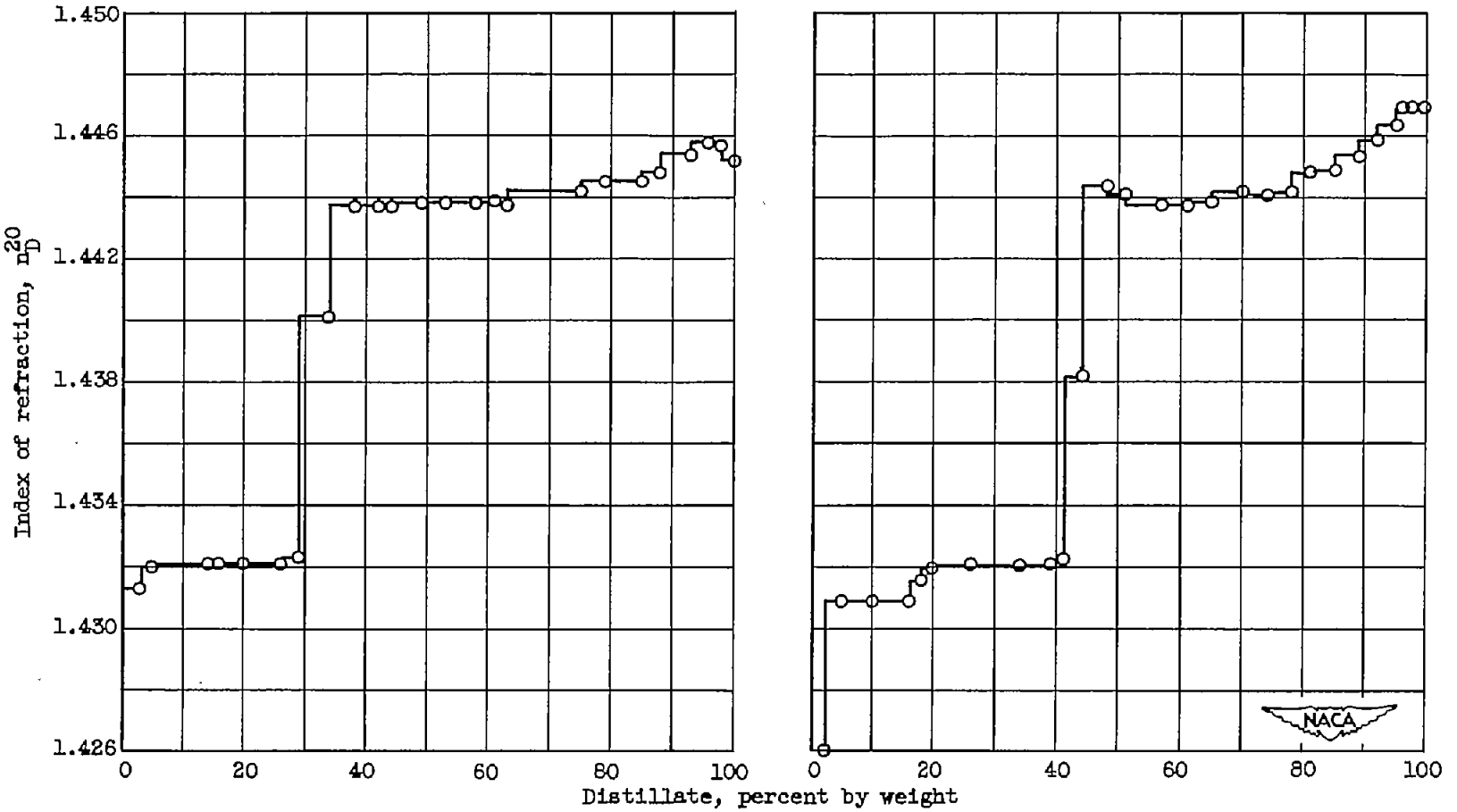
TABLE I - PHYSICAL CONSTANTS OF 2-CYCLOPROPYL-1-BUTENE, cis AND trans

2-CYCLOPROPYL-2-BUTENE, AND 2-CYCLOPROPYLBUTANE

		2-Cyclopropyl-1-butene	2-Cyclopropyl-2-butene, L.B.[a]	2-Cyclopropyl-2-butene, H.B.[a]	2-Cyclopropyl-butane
Melting point, (°C)		-119.55 and -121.94[b]	-97.83	-74.07	Glass
Boiling point, (°C at 760 mm)		98.57	106.55	107.46	90.98
Index of refraction n_D^{20}		1.4319	1.4428	1.4474	1.4024
Density, d^{20}, (grams/ml)		0.76820	0.78100	0.78745	0.72830
Net heat of combustion (kcal/mole)		1023	1021	-------	1047
Percent carbon	Found	87.49	87.41	87.31	85.55
	Calculated	87.42	87.42	87.42	85.63
Percent hydrogen	Found	12.54	12.56	12.56	14.33
	Calculated	12.58	12.58	12.58	14.37

[a]Abbreviations L.B. and H.B. designate low and high boiling isomers, respectively.

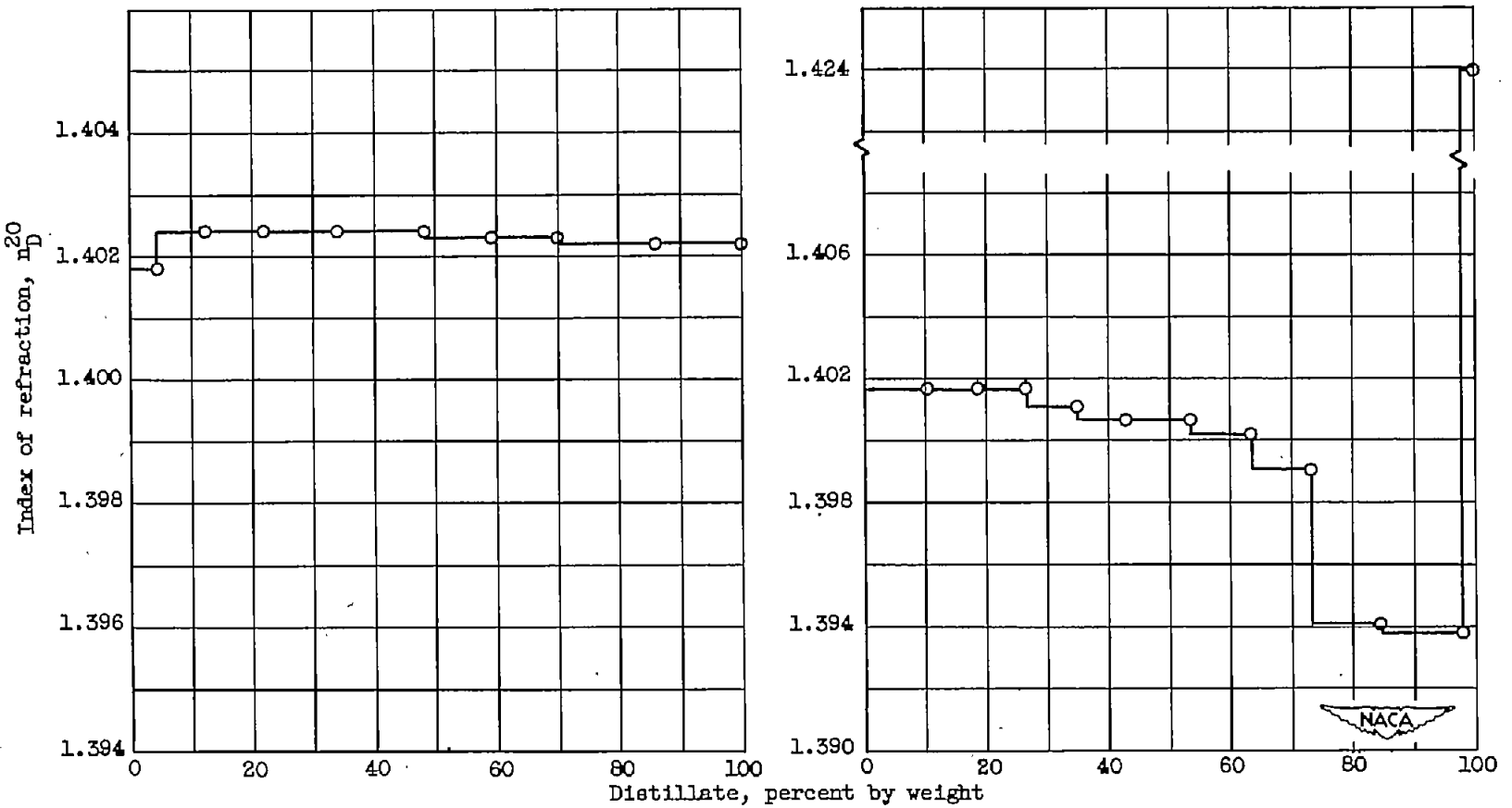
[b]Two crystalline modifications were observed.



(a) Sulfuric acid (distillate, 608 grams).

(b) Alumina (distillate, 1187 grams).

Figure 1. - Distillation of products from dehydration of methylethylcyclopropylcarbinol.



(a) Hydrogenation of 2-cyclopropyl-1-butene at 100° to 130° C (distillate, 271 grams).

(b) Hydrogenation of 2-cyclopropyl-2-butene at 150° C (distillate, 283 grams).

Figure 2. - Distillation of products from hydrogenation of 2-cyclopropylbutenes.

2156

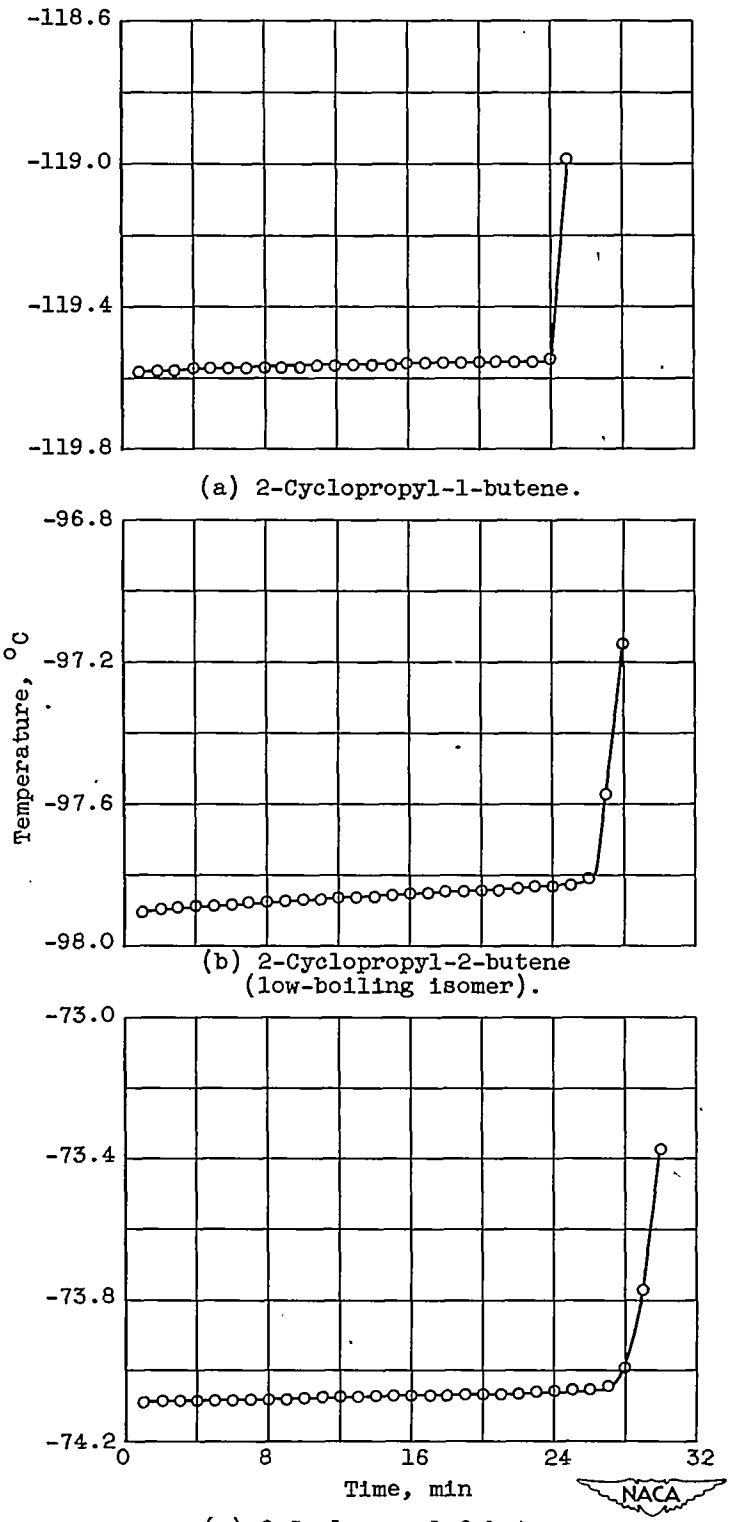
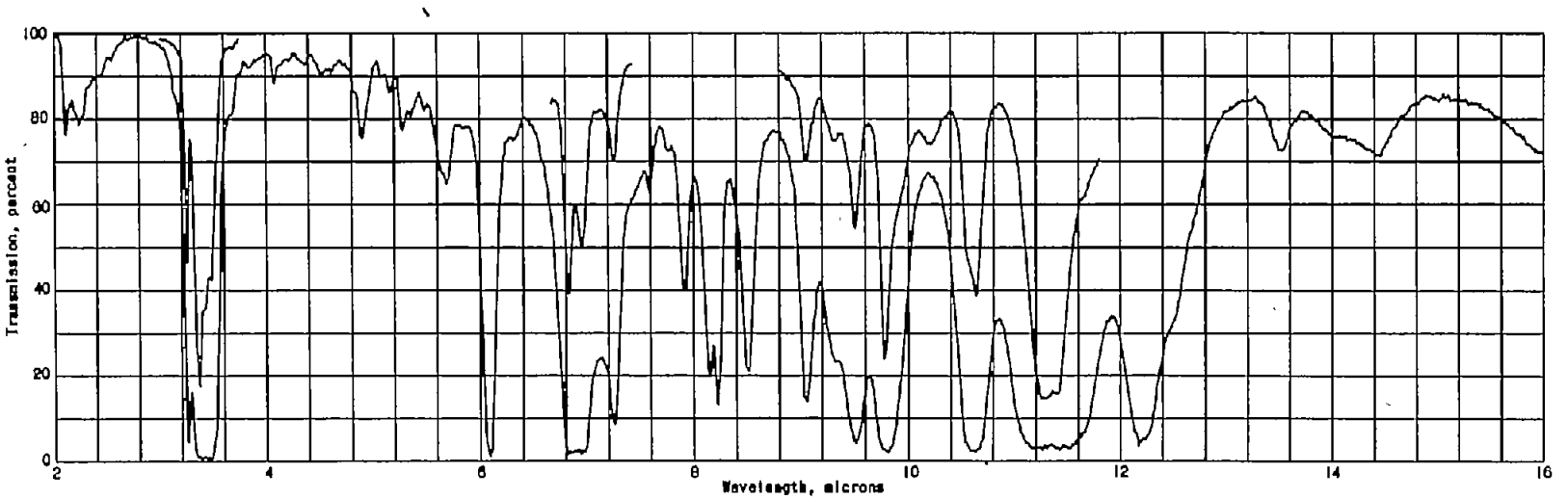
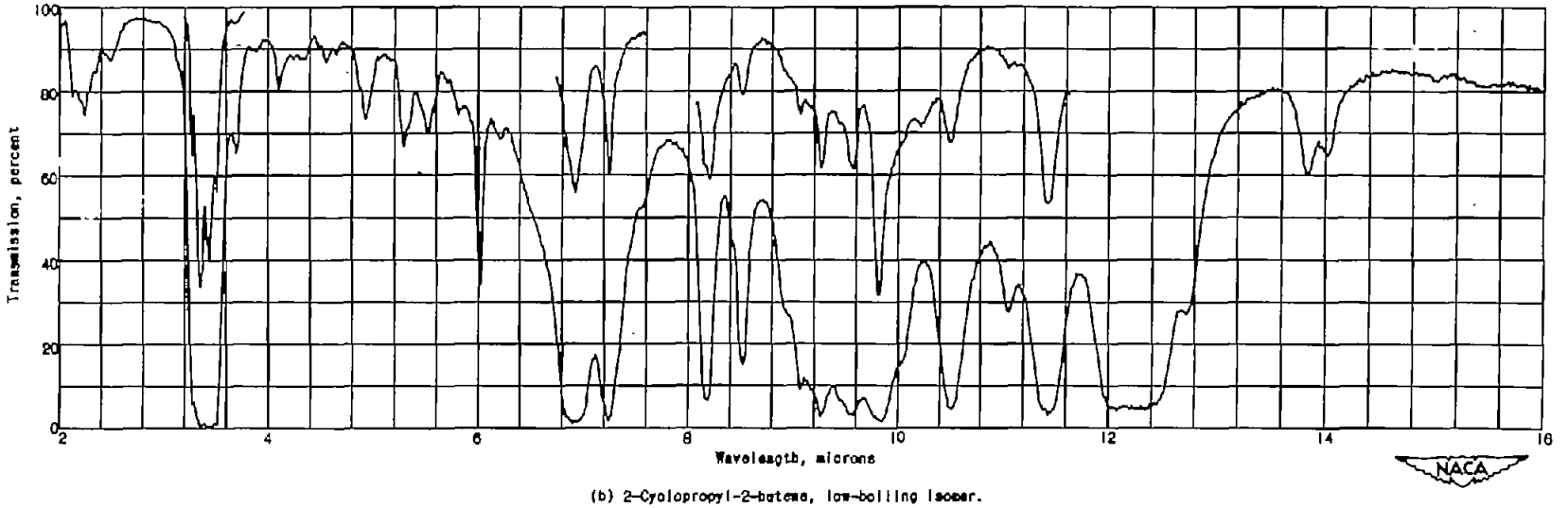


Figure 3. - Time-temperature melting curves.



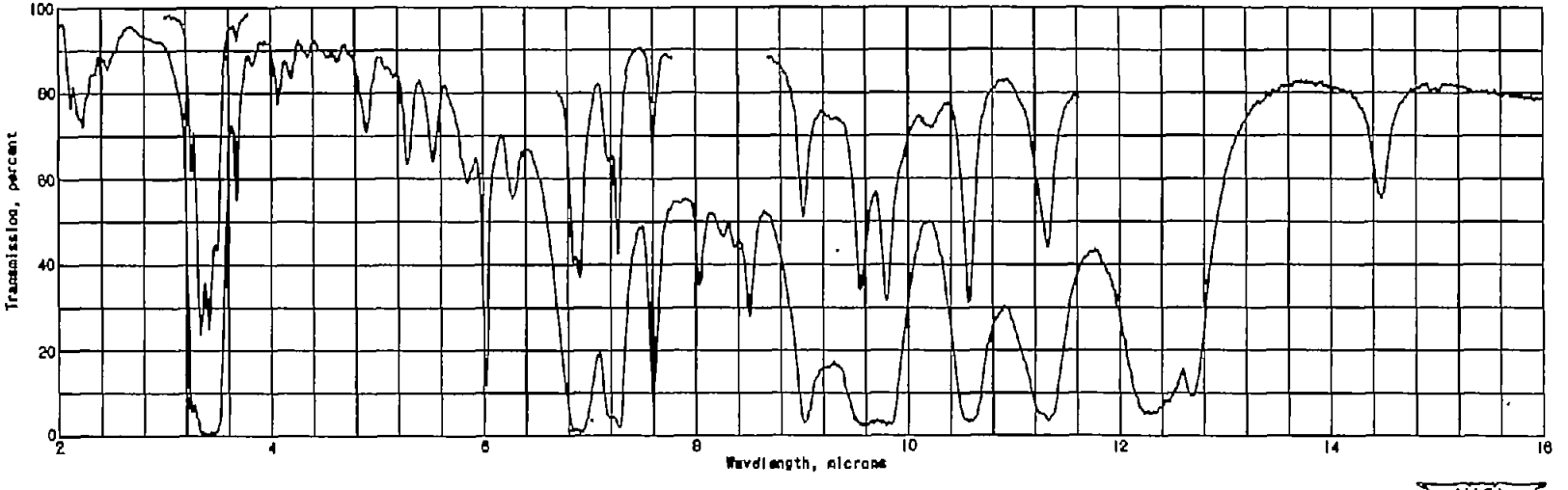
(a) 2-Cyclopropyl-1-butene.

Figure 4. - Infrared spectra. Cell width, 0.1 millimeter; sample undiluted and diluted 1:10 with carbon tetrachloride.



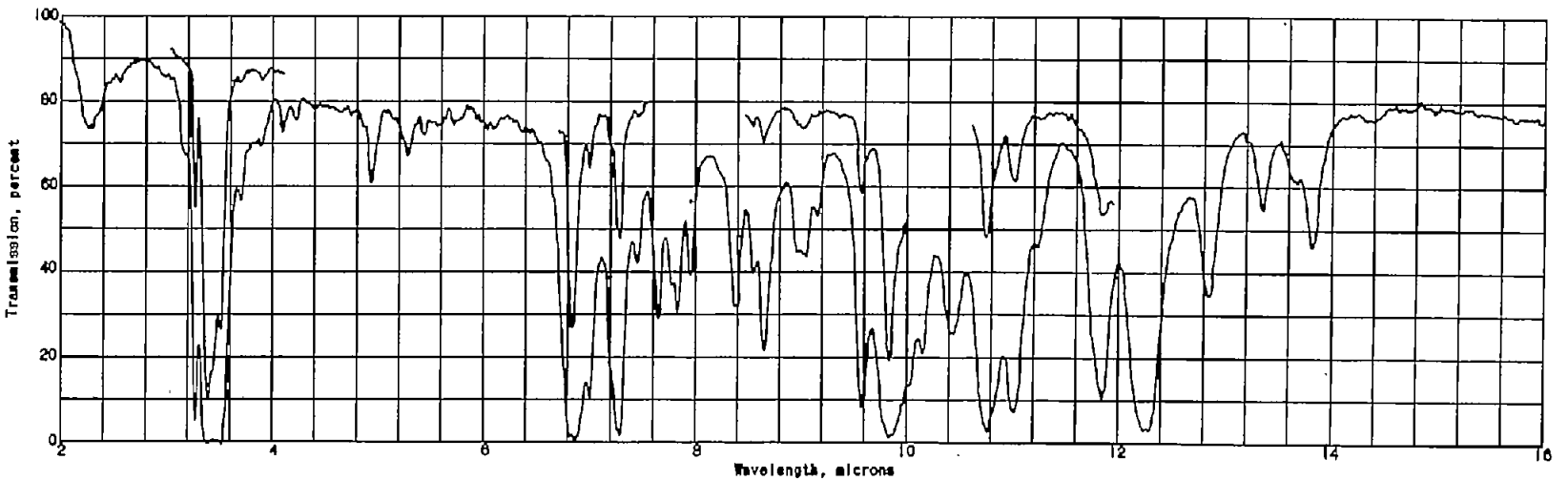
(b) 2-Cyclopropyl-2-butene, low-boiling isomer.

Figure 4. - Continued. Infrared spectra. Cell width, 0.1 millimeter; sample undiluted and diluted 1:10 with carbon tetrachloride.



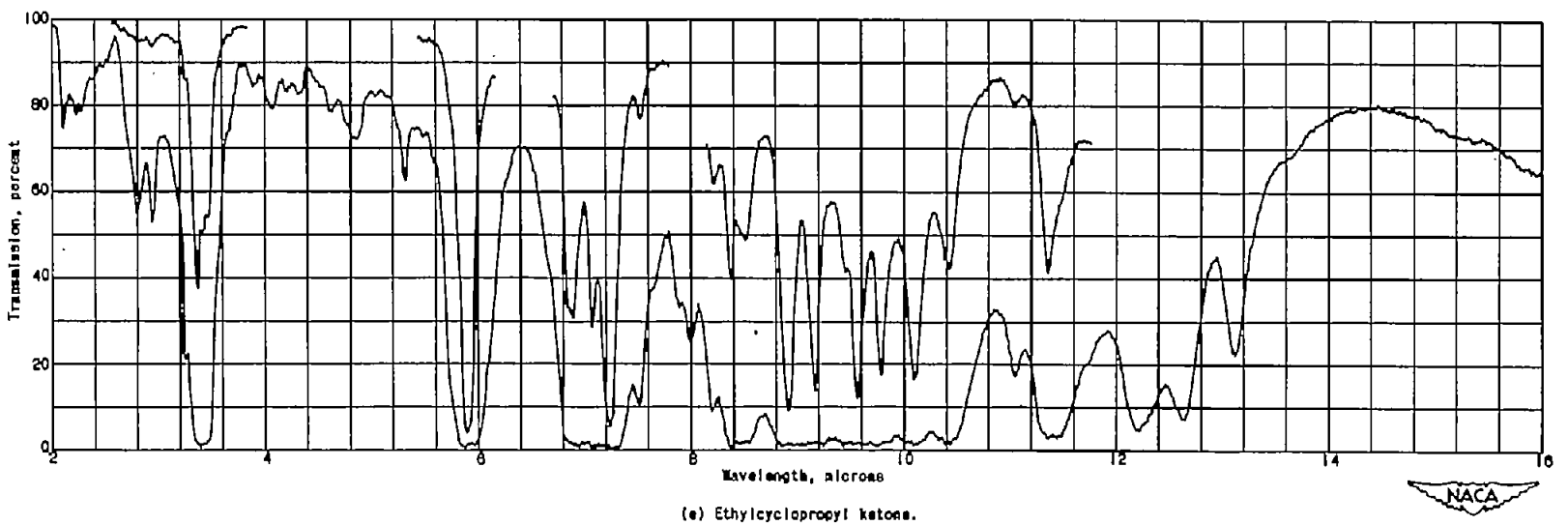
(c) 2-Cyclopropyl-2-butene, high-boiling isomer.

Figure 4. - Continued. Infrared spectra. Cell width, 0.1 millimeter; sample undiluted and diluted 1:10 with carbon tetrachloride.



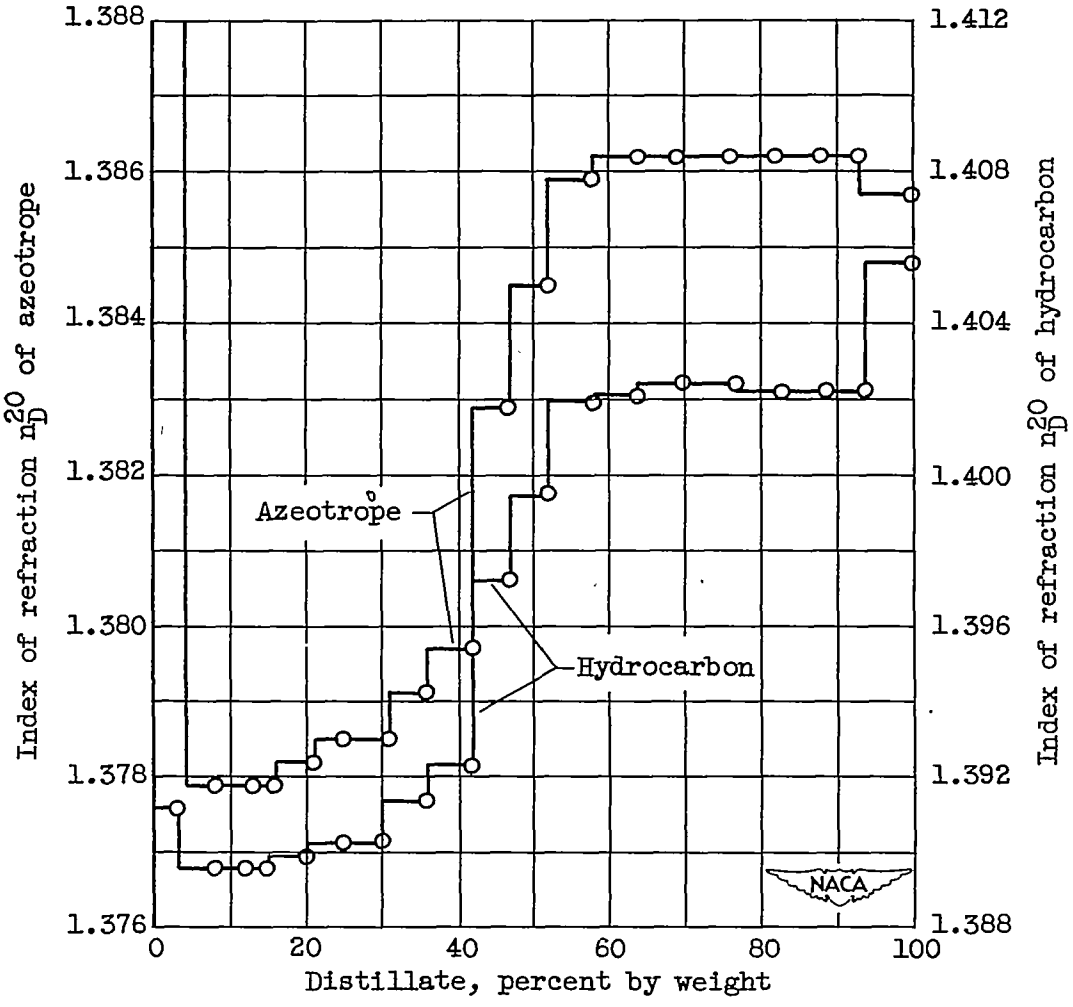
(d) 2-Cyclopropylbutane.

Figure 4. - Continued. Infrared spectra. Cell width, 0.1 millimeter; sample undiluted and diluted 1:10 with carbon tetrachloride.



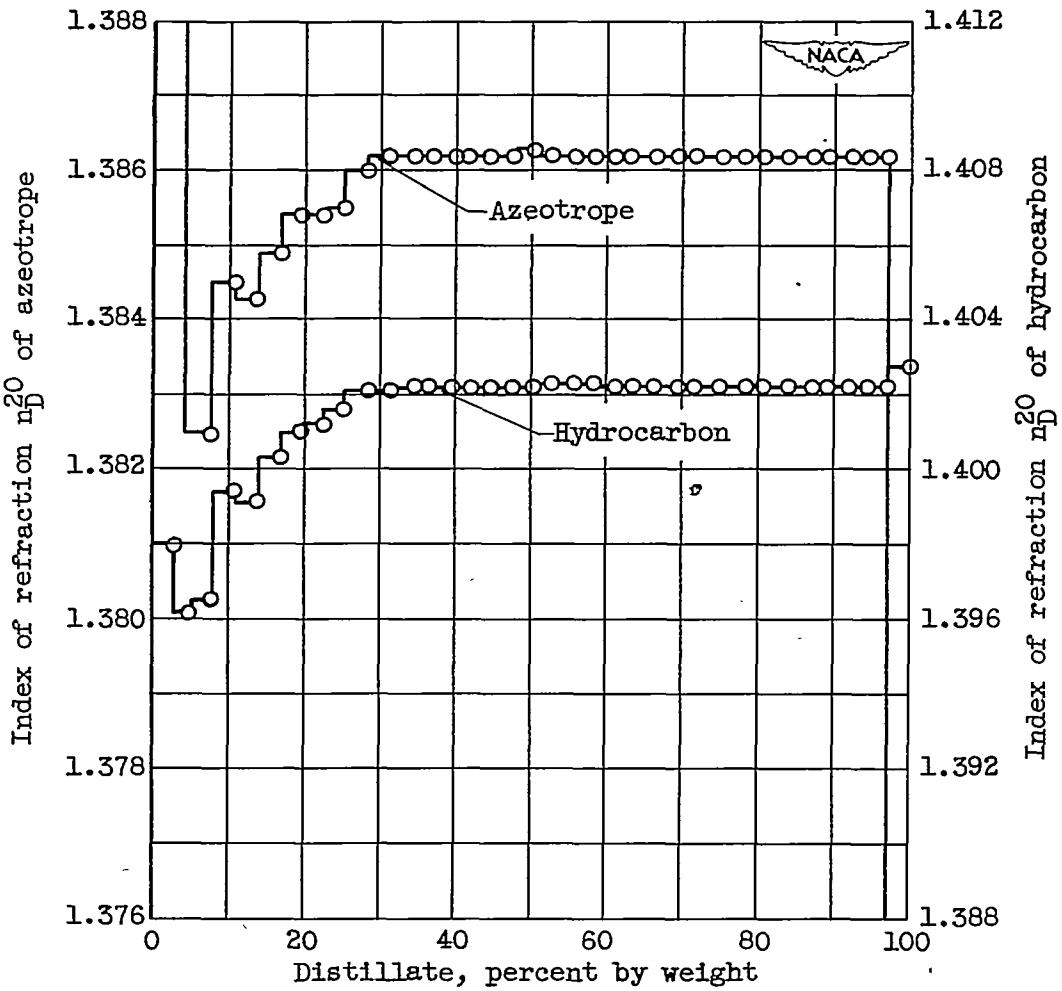
(e) Ethylcyclopropyl ketone.

Figure 4. - Concluded. Infrared spectra. Cell width, 0.1 millimeter; sample undiluted and diluted 1:10 with carbon tetrachloride.



(a) Low-index products, n_D^{20} 1.3912 to 1.3998; hydrocarbon distillate, 446 grams; azeotrope distillate, 756 grams.

Figure 5. - Azeotropic distillation of products from hydrogenation of 2-cyclopropylbutenes.



(b) High-index products, n_D^{20} 1.4000 to 1.4026; hydrocarbon distillate, 866 grams; azeotrope distillate, 1456 grams.

Figure 5. - Concluded. Azeotropic distillation of products from hydrogenation of 2-cyclopropylbutenes.

NACA-Langley - 6-25-51 - 1000