NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 2259

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II - 2-CYCLOPROPYL-1-PENTENE, *cis* AND *trans* 2-CYCLOPROPYL-2-PENTENE AND 2-CYCLOPROPYLPENTANE

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SUMMARY

The hydrocarbons - 2-cyclopropyl-1-pentene, cis and trans 2-cyclopropyl-2-pentene, and 2-cyclopropylpentane - were synthesized in high purity and their physical properties and infrared spectra were determined. The olefins were isolated from the dehydration products of methyl-n-propylcyclopropylcarbinol, which was prepared by the reaction of n-propylmagnesium bromide with methylcyclopropyl ketone. Catalytic hydrogenation of the 2-cyclopropylpentenes yielded 2-cyclopropylpentane. The syntheses of these hydrocarbons are reported herein for the first time.

INTRODUCTION

In conjunction with an investigation of the effect of molecular structure on the velocity of flame propagation, a series of olefinic and paraffinic hydrocarbons containing the cyclopropyl ring were synthesized and purified at the NACA Lewis laboratory. 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 2-cyclopropylpropene and 2-cyclopropylpropane is reported by this laboratory in reference 1.

The present report describes the preparation and the purification of 2-cyclopropyl-1-pentene, cis and trans 2-cyclopropyl-2-pentene, and 2-cyclopropylpentane. The method of preparation was analogous to that reported in reference 1, and involved the synthesis of methyl-n-propylcyclopropylcarbinol from methylcyclopropyl ketone and n-propylmagnesium bromide, dehydration of the carbinol to yield a mixture of products from which the three 2-cyclopropylpentenes were isolated, and hydrogenation of the olefins to 2-cyclopropylpentane. None of these hydrocarbons has been previously prepared.

Methyl-n-propylcyclopropylcarbinol has been previously prepared by the reaction of methylmagnesium bromide with n-propylcyclopropyl ketone (reference 2). Neither the dehydration of methyl-n-propylcyclopropylcarbinol nor the hydrogenation of the resultant olefins has been previously reported.

DISCUSSION OF SYNTHESIS

The Grignard reagent, n-propylmagnesium bromide, was prepared in ether solution in a 30-gallon glass-lined reactor and the condensation reaction was accomplished by adding methylcyclopropyl ketone to the Grignard reagent. The desired reaction product, methyl-n-propylcyclopropylcarbinol, was found to be contaminated with a higher-boiling halogenated byproduct; treatment with an alcoholic solution of sodium hydroxide was required (reference 1) in order to remove the impurity.

The physical properties of the purified methyl-n-propylcyclopropylcarbinol are compared in the following table with values previously reported:

Reference	Boiling point (°C)	Index of refraction n_D^{20}	Density d^{20} (g/ml)
2	163.5 - 163.9 (761 mm)	1.44344	0.87721
Lewis laboratory	163.5 ±0.5[a] (760 mm)	1.4438	.87632

[a] Dehydration slowly occurred during the determination.

The dehydration of methyl-n-propylcyclopropylcarbinol gave a mixture of 2-cyclopropyl-1-pentene and cis and trans 2-cyclopropyl-2-pentene. Although all three olefins were isolated and purified, definite geometrical structure (cis or trans) was not assigned to the two 2-cyclopropyl-2-pentenes because of lack of corroborative data other than the physical constants.

The two methods of dehydrating methyl-n-propylcyclopropylcarbinol investigated were: (1) distilling in the presence of concentrated sulfuric acid, and (2) passing the carbinol over alumina at 225° to 250° C. The total yield of olefin was nearly the same for both methods; however, dehydration over alumina produced a greater amount of 2-cyclopropyl-1-pentene and of the higher-boiling isomer of 2-cyclopropyl-2-pentene. Distillation curves of the products from the two procedures are presented in figures 1 and 2.

By refractionating material having a refractive index range n_D^{20} 1.4360 to 1.4364 in a 22-millimeter by 6-foot column packed with 1/8-inch glass helices, 2-cyclopropyl-1-pentene was obtained in high purity. The geometrical isomers of 2-cyclopropyl-2-pentene were more difficult to purify because of the proximity of their boiling points (within 1.5° C) and their pronounced tendency to oxidize. In order to isolate the two 2-cyclopropyl-2-pentenes in high purity, it was necessary to resort to azeotropic fractionations with n-propanol in 6-foot Podbielniak columns.

The olefins were characterized by ozonolysis and catalytic hydrogenation of the ozonides (reference 3). The 2-cyclopropyl-1-pentene yielded the fragments formaldehyde and n-propylcyclopropyl ketone, whereas each of the isomers of 2-cyclopropyl-2-pentene gave the fragments propionaldehyde and methylcyclopropyl ketone. The 2,4-dinitrophenylhydrazones of the fragments were prepared and identified by mixed melting points with known derivatives or analysis for nitrogen or both.

The hydrogenation of each of the position isomers of the 2-cyclopropylpentene was investigated; it was observed that although the 2-cyclopropyl-1-pentene reacted readily with hydrogen at 100° to 110° C, the 2-cyclopropyl-2-pentene reacted very sluggishly even at 130° C. A comparison of the fractional distillation curves of the products (figs. 3 and 4) showed that the 2-cyclopropyl-1-pentene gave an essentially pure product, whereas the 2-cyclopropyl-2-pentene gave a product that contained an appreciable amount of an impurity, subsequently identified as 4-methylheptane.

Fractional distillation in Podbielniak columns operated at efficiencies in excess of 150 theoretical plates did not give a satisfactory separation of the 2-cyclopropylpentane and the 4-methylheptane, because the atmospheric boiling points differ by less than 0.1° C. By means of a series of azeotropic fractionations with n-propanol, which effectively removed the lower-boiling paraffin (figs. 5 and 6), 2-cyclopropylpentane was obtained in high purity.

The physical constants of the purified hydrocarbons were determined according to the methods described in reference 1. These data are presented in table I. The time-temperature melting curves from which the melting points were determined are presented in figure 7.

The infrared spectra of 2-cyclopropyl-1-pentene, each of the geometrical isomers of 2-cyclopropyl-2-pentene, and 2-cyclopropylpentane are shown in figures 8(a) to 8(d). 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 showed strong absorption at 9.8 microns, which appears to be characteristic of this type of cyclopropane hydrocarbon. Typical olefinic absorption at 6.0 to 6.1 microns appears in each of the olefin spectra. This band is shifted to a slightly lower wavelength and is decreased in intensity when the carbon-carbon double bond is moved from the 1- to the 2-position in the molecule.

EXPERIMENTAL DETAILS

Methylcyclopropyl Ketone

Commercial methylcyclopropyl ketone was fractionated and material having a range of n_D^{20} 1.4240 to 1.4246 was used in the Grignard reaction.

Methyl-n-propylcyclopropylcarbinol

The Grignard reagent was prepared in a 30-gallon glass-lined reactor from 170 moles (4130 grams) of magnesium turnings and 165 moles (20,300 grams) of n-propyl bromide dissolved in 5 gallons of ether. The ether solution of the Grignard reagent was stirred overnight and then a solution of 150 moles (12,600 grams) of methylcyclopropyl ketone in 5 gallons of dry ether was added. The reaction mixture was stirred for 4 hours at reflux temperature and for 18 hours at room temperature. The Grignard complex was hydrolyzed by the addition of approximately 7 gallons of saturated ammonium chloride solution. The ether layer was separated and the ether removed by distillation. The product was distilled through a 25-millimeter by 4-foot helix-packed column at 60 millimeters to give 13,600 grams of crude carbinol and 1278 grams of a higher-boiling residue.

The crude carbinol contained a halogenated impurity, which was removed by refluxing with alcoholic sodium hydroxide (reference 1). Distillation at 60 millimeters gave 9792 grams (51-percent yield) of halide-free carbinol.

Dehydration of Methyl-n-propylcyclopropylcarbinol

Two methods of dehydration were investigated:

Concentrated sulfuric acid. - The carbinol (10 moles, 1282 grams) and the concentrated sulfuric acid (20 drops) were heated in a flask attached to a 4-foot helix-packed column. The dehydration products, which were distilled through the column as they formed, included 8 moles (146 grams) of water. The organic product was separated from the water, dried over anhydrous calcium sulfate, and fractionated through a 22-millimeter by 6-foot helix-packed column to give 207 grams (19-percent yield) of 2-cyclopropyl-1-pentene and 621 grams (56-percent yield) of 2-cyclopropyl-2-pentene.

Alumina. - The carbinol (14.3 moles or 1831 grams) was passed through a 2.5- by 120-centimeter pyrex column, which was packed with 8- to 14-mesh alumina and heated to 225° to 250° C. The quantity of water obtained in the process was 220 grams (85 percent yield). The organic product was dried over anhydrous calcium sulfate and fractionated in the described 6-foot helix-packed column. Nearly equal quantities, 614 grams (39-percent yield) of 2-cyclopropyl-1-pentene and 602 grams (38-percent yield) of 2-cyclopropyl-2-pentene, of the two olefins were obtained.

Purification of the Olefins

A description of a typical procedure for the isolation and the purification of the 2-cyclopropyl-1-pentene and each of the geometrical isomers of the 2-cyclopropyl-2-pentene follows:

The distillate from the preliminary fractionation of the crude dehydration products was combined into two parts: (1) material having an index range of n_D^{20} 1.4360 to 1.4364, and (2) n_D^{20} 1.4459 to 1.4487. The first part (1382 grams) was fractionated through a 6-foot (22 mm O.D.) column packed with 1/8-inch glass helices to give 774 grams of constant index product, which was combined into five samples. The melting points for each of the five samples were determined and found to differ by less than 0.1° C. The sample having the highest melting point was selected for the determination of the other physical constants (table I).

The second part (1400 grams) was combined with 2363 grams of n-propanol and azeotropically fractionated through the 6-foot helix-packed column to give concentrates of each of the geometrical isomers of 2-cyclopropyl-2-pentene. The concentrate of the lower-boiling isomer (538 grams) was azeotropically fractionated with 1262 grams of n-propanol in a 6-foot Podbielniak column to yield 398 grams of constant-index product. Peroxidation of the product occurred before the physical properties could be determined; a second azeotropic fractionation was therefore performed to obtain the purified low-boiling isomer.

The concentrate of the higher-boiling isomer (318 grams) was azeotropically fractionated with 1059 grams of n-propanol in a 6-foot

Podbielniak column to give 182 grams of product having a range of n_D^{20} 1.4496 to 1.4501. A second azeotropic fractionation gave the purified high-boiling isomer of 2-cyclopropyl-2-pentene.

Ozonolysis of 2-Cyclopropylpentenes

Ethanol solutions of each of the three olefin isomers were ozonized, the ozonides were decomposed by catalytic hydrogenation, and the fragments were separated by fractionation of the reduced products through a 0.9-by-47-centimeter column.

A 0.48-mole quantity (53 grams) of 2-cyclopropyl-1-pentene (n_D^{20} 1.4362) gave a white solid subliming above 85° C (presumably paraformaldehyde) and 23 grams (43-percent yield) of n-propylcyclopropyl ketone, which had the following properties: boiling point, 148° C; n_D^{20}, 1.4324; and d^{20}, 0.8795 gram per milliliter. The physical properties reported for n-propylcyclopropyl ketone (reference 4) are: boiling point, 151.0° to 151.4° C (754 mm); n_D^{20}, 1.43247; d^{20}, 0.88078 gram per milliliter. Analysis of the 2,4-dinitrophenylhydrazone of the ketone (melting point, 164.0° to 164.5° C (uncorrected)) - Calculated for $C_{13}H_{16}N_4O_4$: N, 19.17 percent. Found: N, 19.19 percent.

The infrared spectrum of the ketone is shown in figure 8(e).

From 0.3 mole (33 grams) of the low-index isomer of 2-cyclopropyl-2-pentene (n_D^{20} 1.4459 to 1.4461), there was obtained 3 grams (17-percent yield) of propionaldehyde and 11 grams (43-percent yield) of methylcyclopropyl ketone, the boiling point of which was 108° to 109° C. Mixed melting points of the 2,4-dinitrophenylhydrazones of the fragments with the corresponding derivatives of known materials showed no depression. Analysis of the 2,4-dinitrophenylhydrazone of the ketone - Calculated for $C_{11}H_{12}N_4O_4$: N, 21.21 percent. Found: N, 21.28 percent.

The high-index isomer of 2-cyclopropyl-2-pentene (0.3 mole or 33 grams, n_D^{20} 1.4500) gave 10.5 grams (60-percent yield) of propionaldehyde and 18.5 grams (73-percent yield) of methylcyclopropyl ketone. No depression in melting point was observed when the 2,4-dinitrophenylhydrazones of the fragments were mixed with the corresponding derivatives of known materials. Analysis of the derivative of the ketone - Calculated for $C_{11}H_{12}N_4O_4$: N, 21.21 percent. Found: N, 21.18 percent.

Hydrogenation of 2-Cyclopropyl-2-pentene

A charge of 6.2 moles (684 grams) of 2-cyclopropyl-2-pentene (the geometrical isomers were not separated in this instance, but the 2-cyclopropyl-1-pentene was essentially removed by preliminary fractionation, n_D^{20} 1.4442 to 1.4492), 140 grams of barium-promoted copper chromite catalyst, and 800 milliliters of ethanol was placed into a 3.4-liter rocker-type autoclave under an initial hydrogen pressure of 1750 pounds per square inch. The hydrogenation reaction was extremely sluggish at 130° C; after 160 hours only 5 moles of hydrogen had been consumed. The reaction was stopped at this stage, and the products were removed from the autoclave. An appreciable decrease in the volume of the reaction mixture was obvious; inspection of the exhaust lines showed that part of the charge had leaked into the exhaust system. Only 344 grams of products were recovered after the charge was filtered, washed with water to remove the alcohol, and dried. The distribution of the recovered products is indicated in the distillation curve presented in figure 3.

Hydrogenation of 2-Cyclopropyl-1-pentene

Five moles (555 grams) of 2-cyclopropyl-1-pentene (n_D^{20} 1.4360 to 1.4362), 55 grams of barium-promoted catalyst, and 500 milliliters of ethanol were charged to the autoclave under a pressure of 1500 pounds per square inch of hydrogen. The reaction was completed at 100° to 110° C within 8 hours. The products were filtered through a filter aid to remove the catalyst, washed with water to remove the ethanol, dried over anhydrous calcium sulfate, and fractionated to give the data presented in figure 4. The distillate was essentially pure 2-cyclopropylpentane and totaled 448 grams or 80 percent of the theoretical.

Purification of 2-Cyclopropylpentane

The fractionated products from several hydrogenations of both the 2-cyclopropyl-1-pentene and 2-cyclopropyl-2-pentene were combined into two parts: (1) n_D^{20} 1.4008 to 1.4093, and (2) 1.4099 to 1.4111. Each of these parts was azeotropically fractionated with n-propanol 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 n-propanol was removed by extraction with water. These data from the first part are plotted against the percentage by weight of distillate in figure 5. The low-index impurity was identified as 4-methylheptane from its physical properties and infrared spectrum.

The data from the azeotropic fractionation of the second part are presented in figure 6. The 4-methylheptane impurity was removed in the first few fractions of the distillation. The remainder of the distillate was essentially pure 2-cyclopropylpentane. Refractionation of the constant-index material (n_D^{20} 1.4111 to 1.4112) gave 2-cyclopropylpentane in high purity.

RESULTS

From the dehydration products of methyl-n-propylcyclopropylcarbinol, 2-cyclopropyl-1-pentene and *cis* and *trans* 2-cyclopropyl-2-pentene were isolated and purified. The catalytic hydrogenation of these olefins yielded 2-cyclopropylpentane. The physical properties and the infrared spectra of the hydrocarbons were determined.

Lewis Flight Propulsion Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, August 1, 1950.

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, 1950.

2. Bruylants, P.: Contribution à l'étude des composés cycliques triméthyléniques. Bull. Soc. Chim. Belgique, T. 36, No. 1, Jan. 1927, P. 153-164.

3. 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.

4. Bruylants, P.: Contribution à l'étude des composés cycliques triméthyléniques. Bull. Soc. Chim. Belgique, T. 36, No. 11, Nov. 1927, P. 519-532.

TABLE I - PHYSICAL CONSTANTS OF 2-CYCLOPROPYLPENTENES AND 2-CYCLOPROPYLPENTANE

		2-Cyclopropyl-1-pentene	2-Cyclopropyl-2-pentene, low-boiling isomer	2-Cyclopropyl-2-pentene, high-boiling isomer	2-Cyclopropyl-pentane
Melting point, °C		-113.87	-113.65	-107.61	-118.46
Boiling point, °C at 760 mm		123.94	128.61	129.98	117.74
Index of refraction, n_D^{20}		1.4362	1.4458	1.4502	1.4112
Density, d^{20}, grams/ml		0.77660	0.78402	0.79077	0.74295
Net heat of combustion, kcal/mole		1148	1153	-------	1191
Percent carbon	Found	87.27	87.16	87.14	85.55
	Calculated	87.20	87.20	87.20	85.63
Percent hydrogen	Found	12.90	12.80	12.73	14.40
	Calculated	12.80	12.80	12.80	14.37

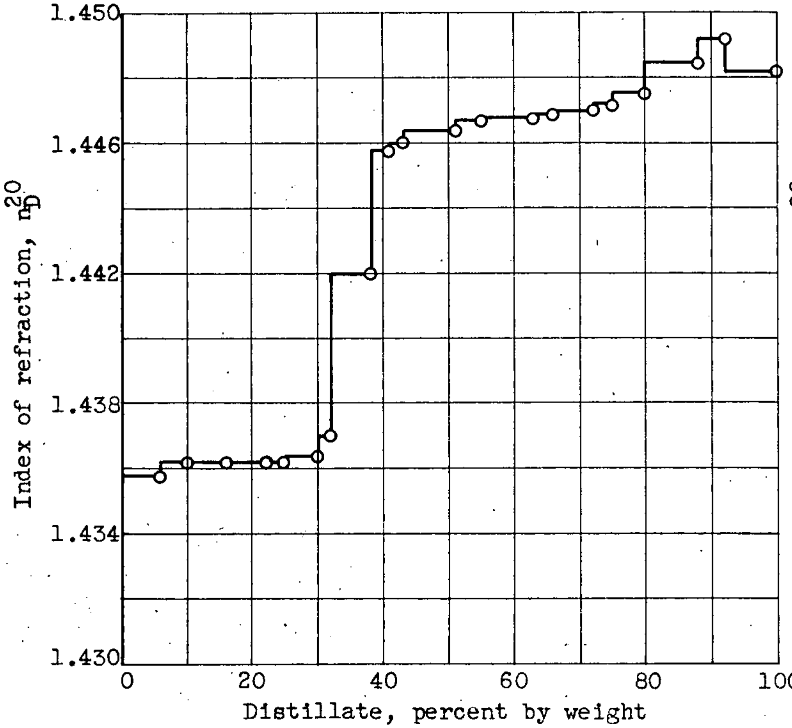


Figure 1. - Distillation of products from dehydration of methyl-n-propylcyclopropyl carbinol with concentrated sulfuric acid. Distillate, 926 grams.

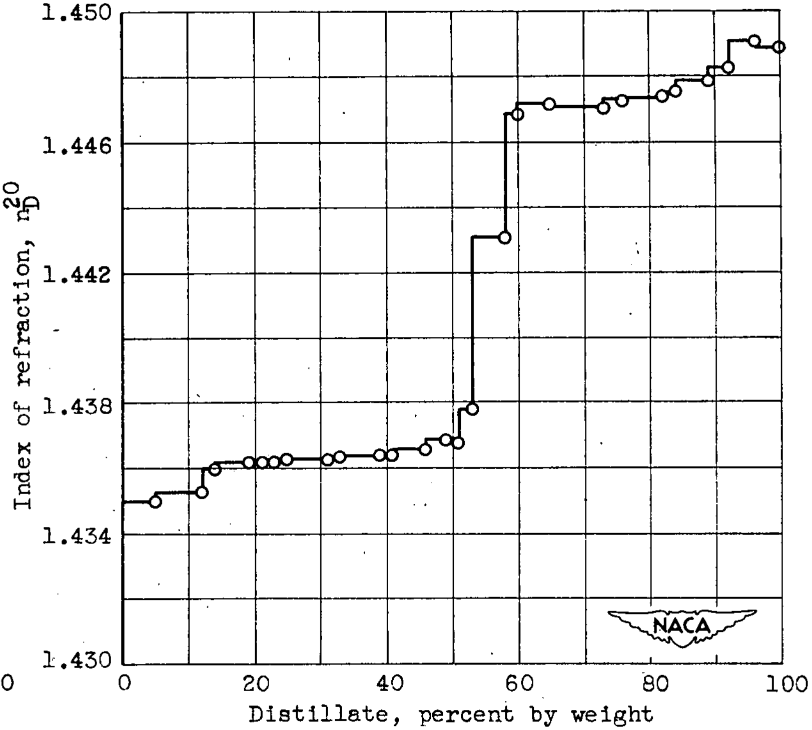


Figure 2. - Distillation of product from dehydration of methyl-n-propylcyclopropyl carbinol over alumina at 225° to 250° C. Distillate, 1236 grams.

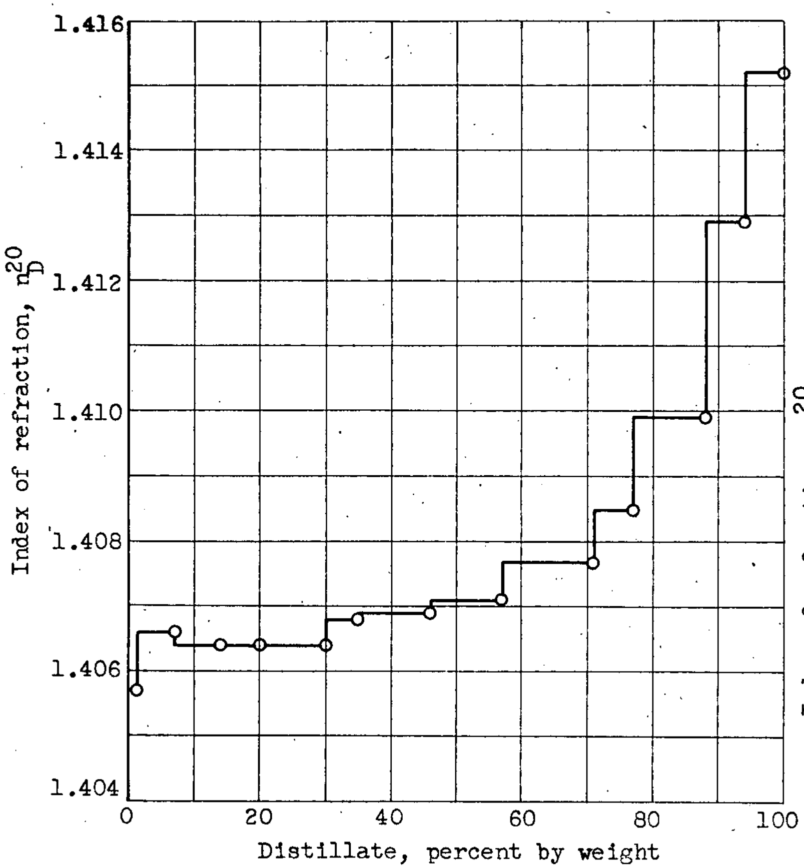


Figure 3. - Distillation of products from hydrogenation of 2-cyclopropyl-2-pentene at temperature of 130° C. Distillate, 284 grams.

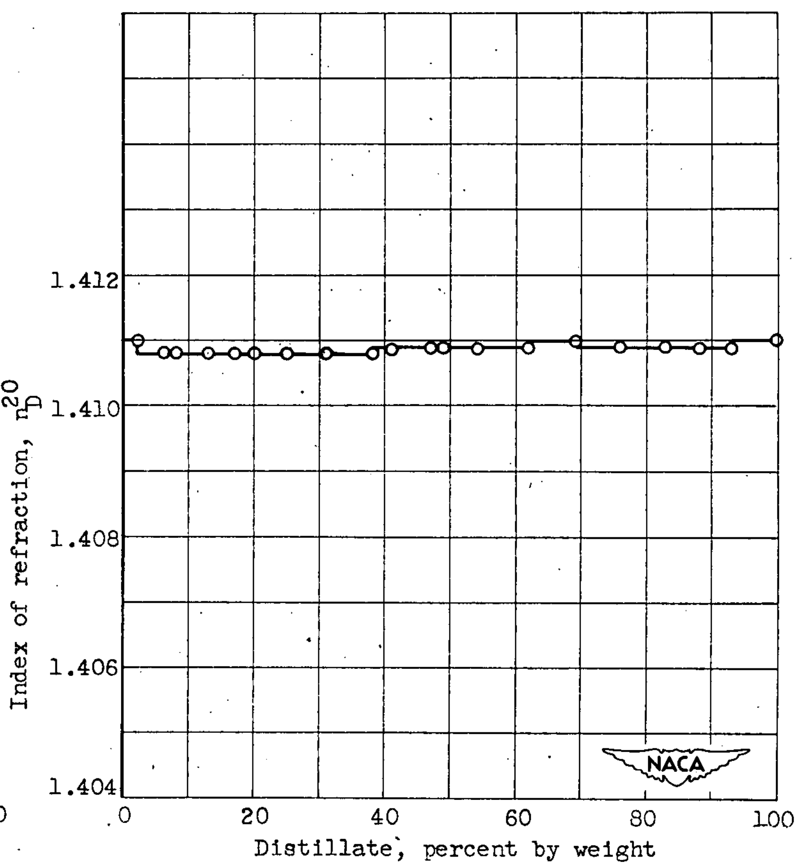


Figure 4. - Distillation of products from hydrogenation of 2-cyclopropyl-1-pentene at temperatures of 100° to 110° C. Distillate, 448 grams.

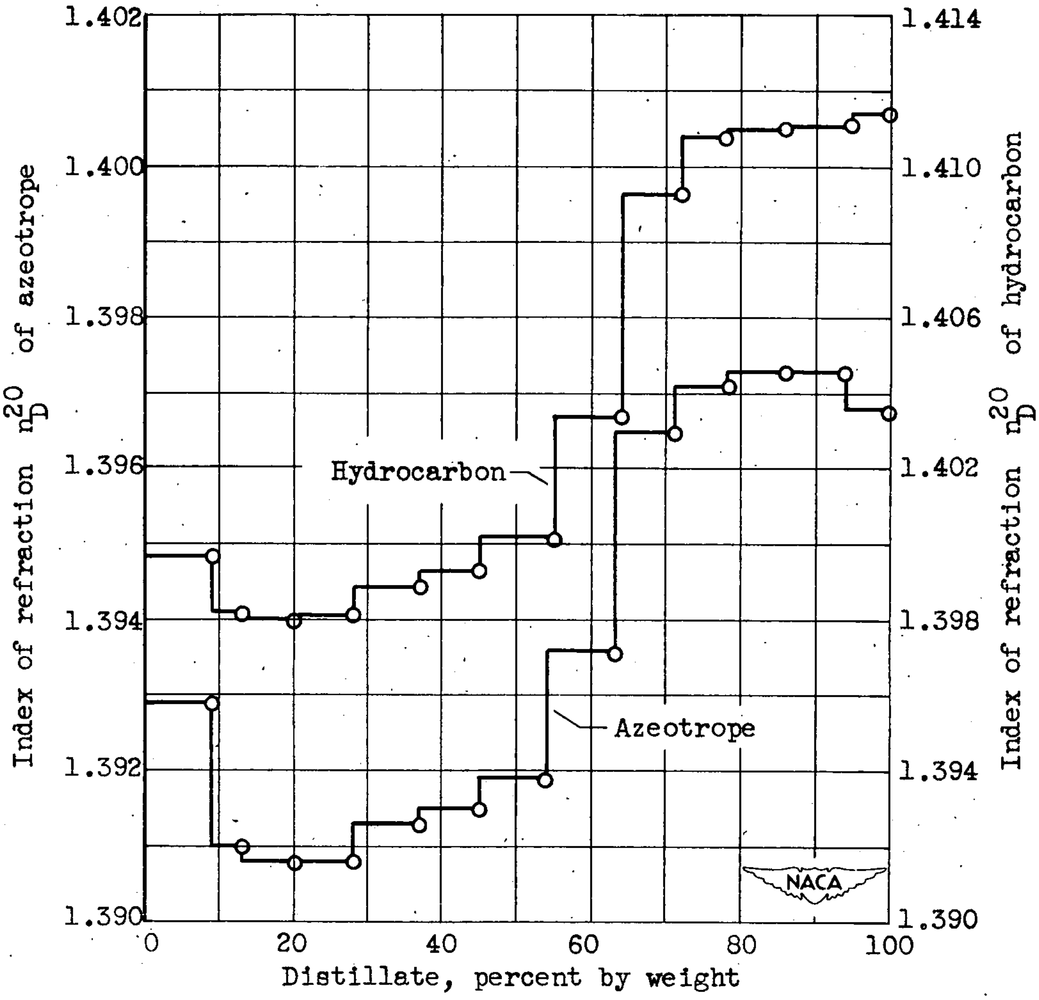


Figure 5. - Azeotropic distillation of low-index products, n_D^{20} 1.4008 to 1.4093, from hydrogenation of 2-cyclopropylpentenes. Hydrocarbon distillate, 255 grams; azeotrope distillate, 539 grams.

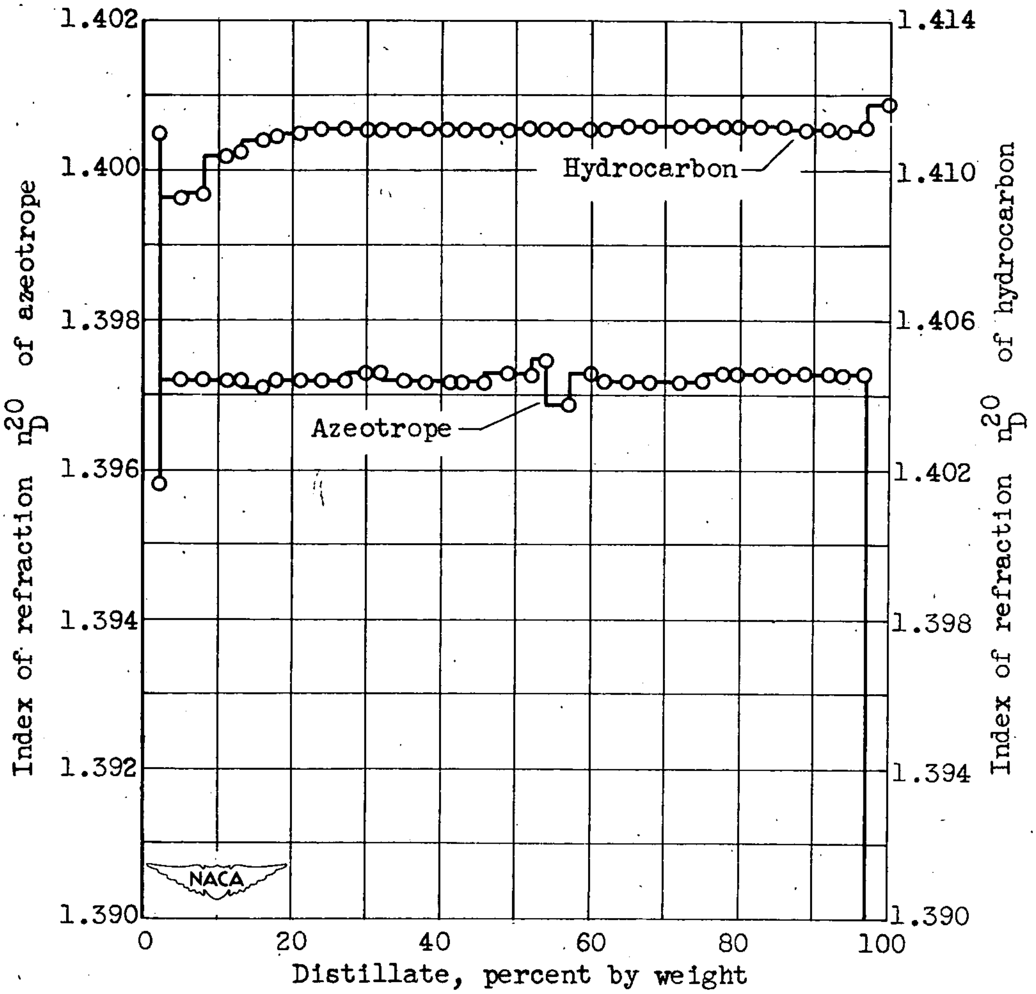
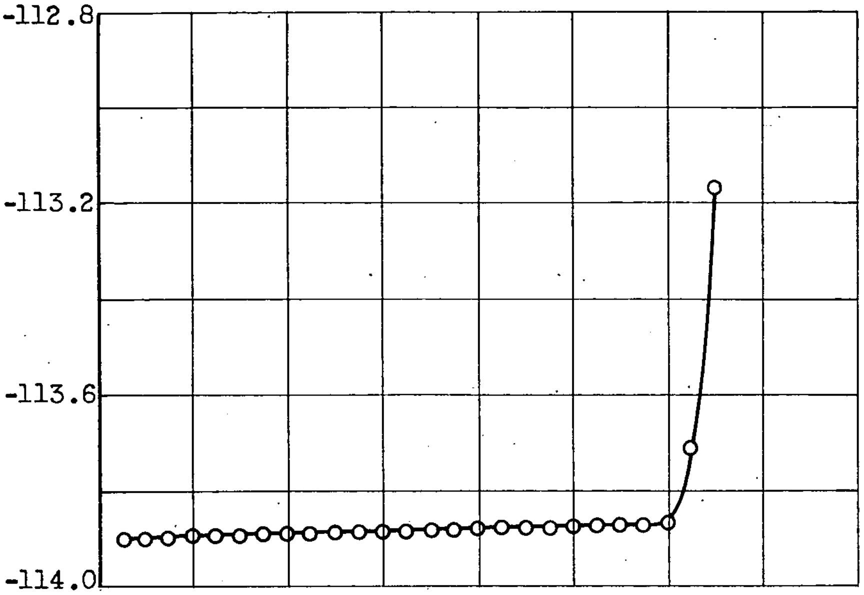
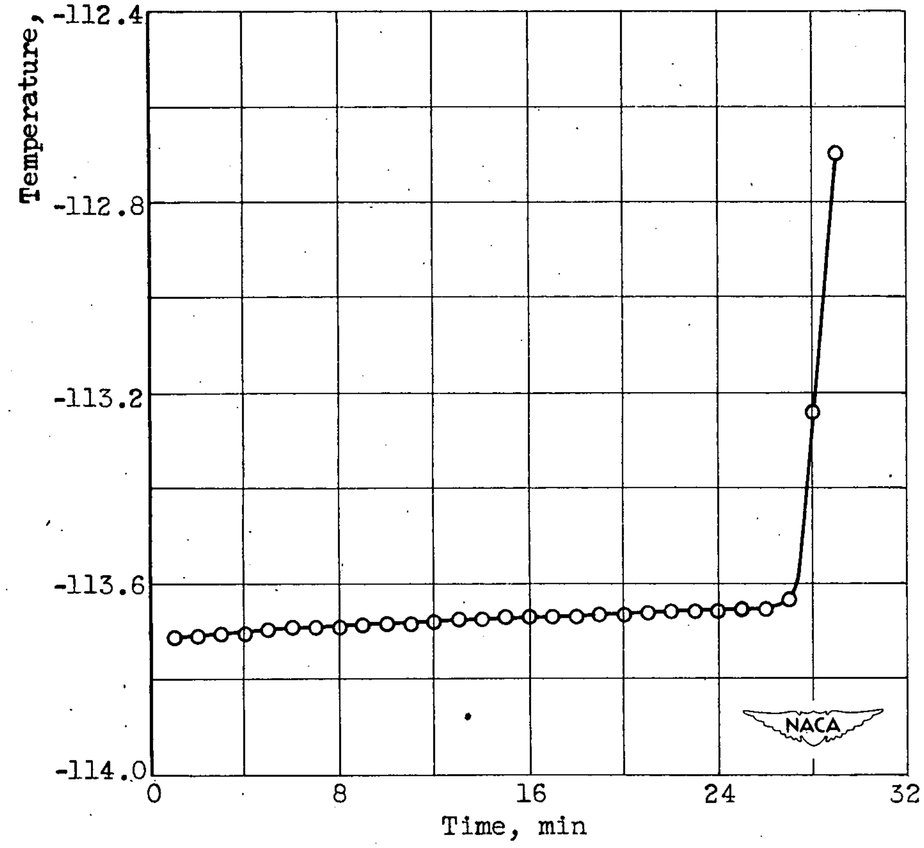


Figure 6. - Azeotropic distillation of products, n_D^{20} 1.4099 to 1.4111, from hydrogenation of 2-cyclopropylpentenes. Hydrocarbon distillate, 747 grams; azeotrope distillate, 1626 grams.

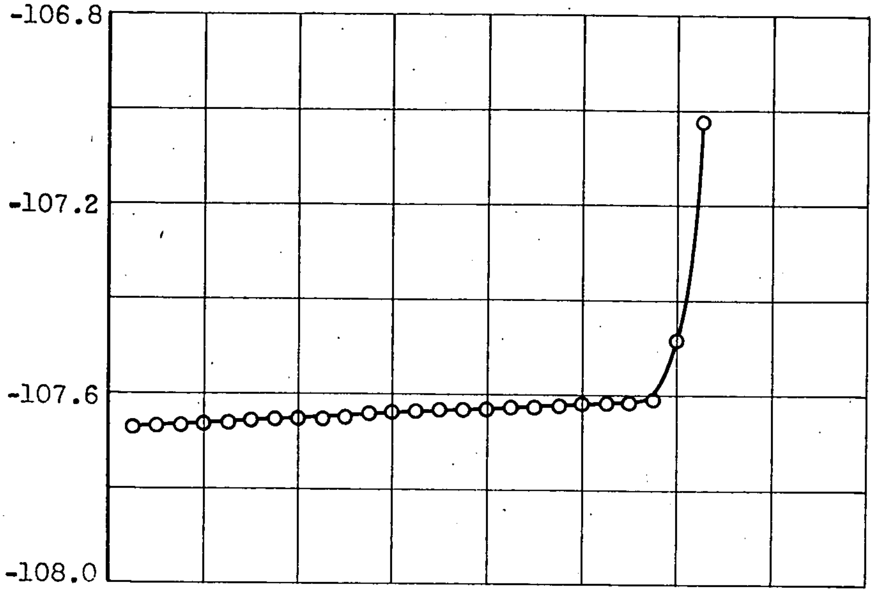


(a) 2-Cyclopropyl-1-pentene.

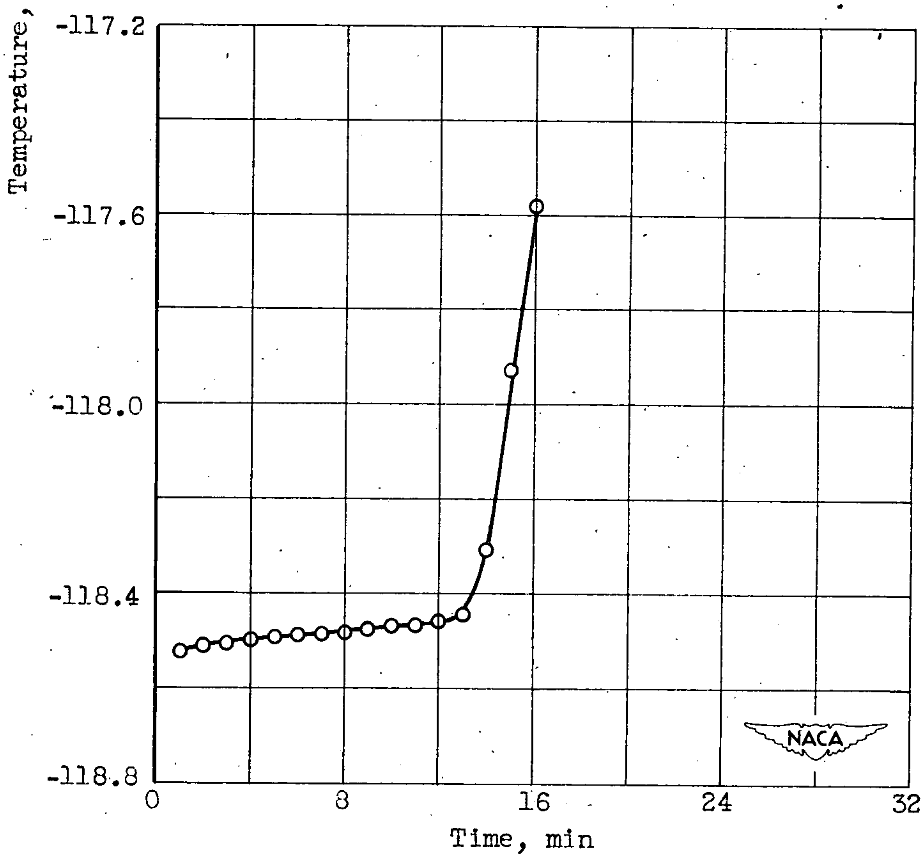


(b) 2-Cyclopropyl-2-pentene (low-boiling isomer).

Figure 7. - Time-temperature melting curves.

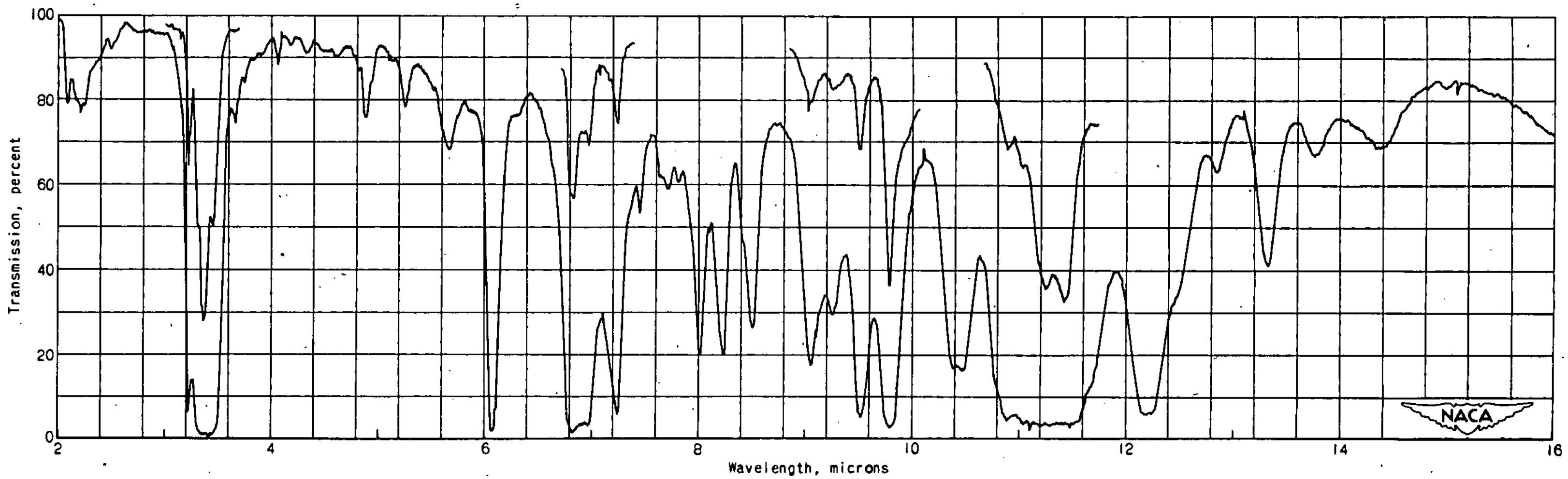


(c) 2-Cyclopropyl-2-pentene (high-boiling isomer).



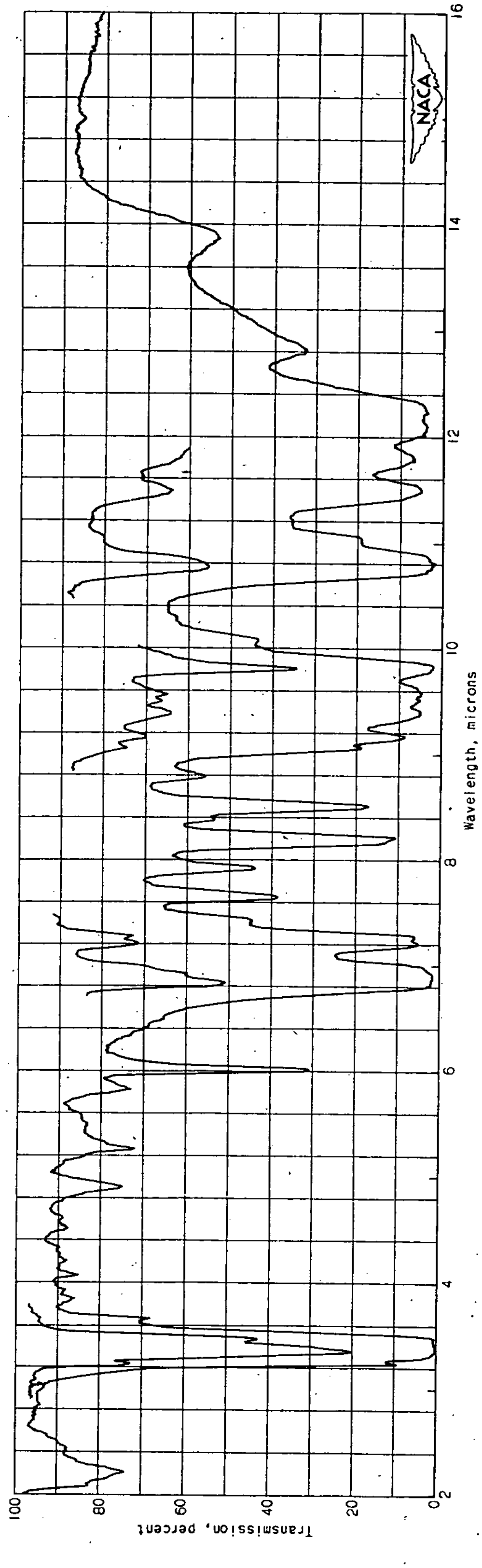
(d) 2-Cyclopropylpentane.

Figure 7. - Concluded. Time-temperature melting curves.



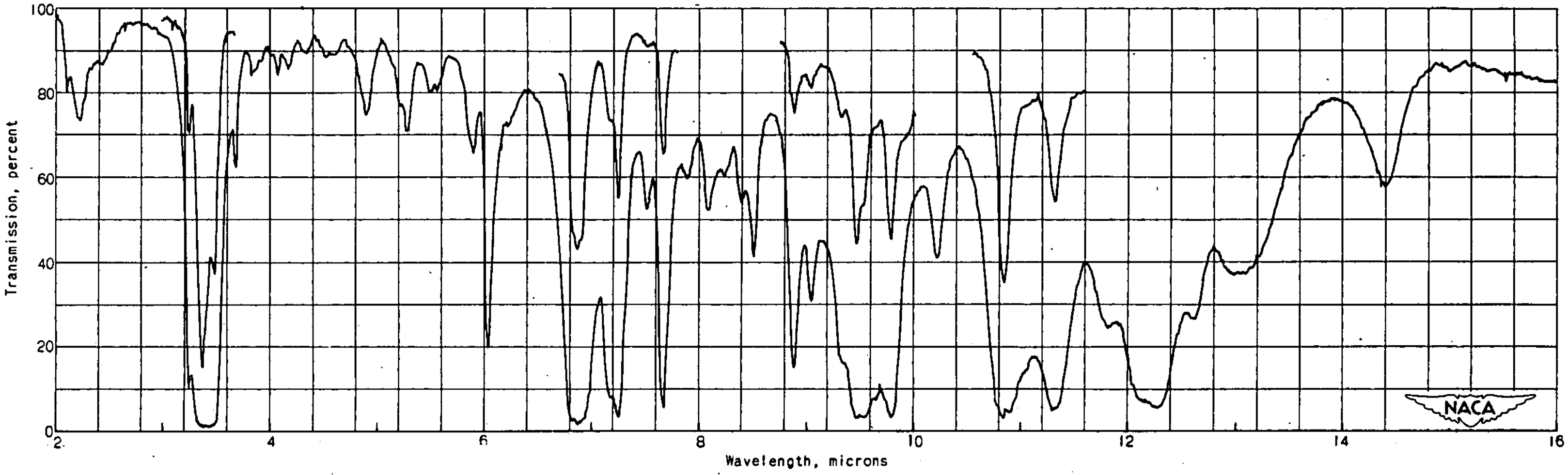
(a) 2-Cyclopropyl-1-pentene.

Figure 8. - Infrared spectra. Cell width, 0.1 millimeter; sample undiluted and diluted 1:10 with carbon tetrachloride.



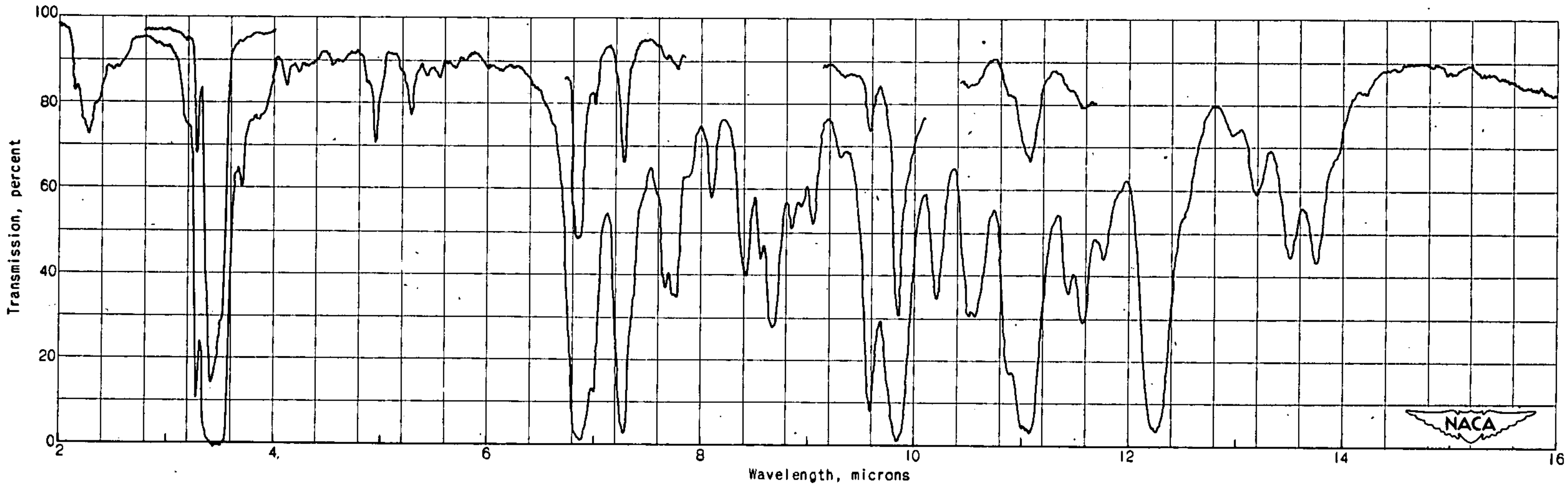
(b) 2-Cyclopropyl-2-pentene (low-boiling isomer).

Figure 8. - Continued. Infrared spectra. Cell width, 0.1 millimeter; sample undiluted and diluted 1:10 with carbon tetrachloride.



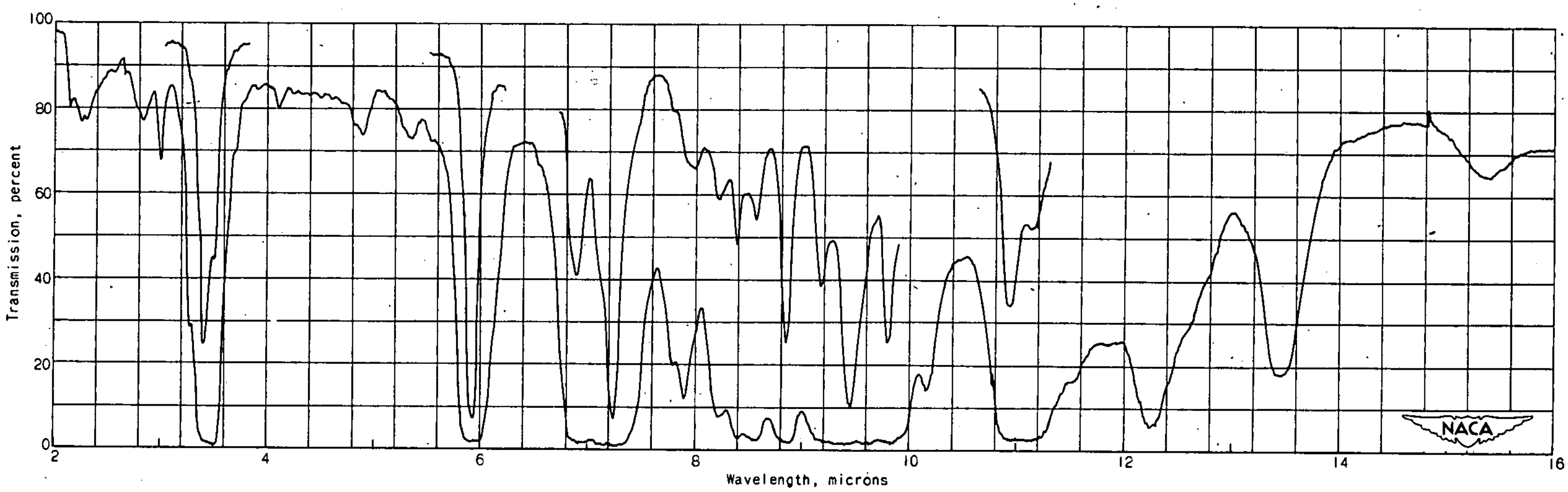
(c) 2-Cyclopropyl-2-pentene (high-boiling isomer).

Figure 8. - Continued. Infrared spectra. Cell width, 0.1 millimeter; sample undiluted and diluted 1:10 with carbon tetrachloride.



(d) 2-Cyclopropylpentane.

Figure 8. - Continued. Infrared spectra. Cell width, 0.1 millimeter; sample undiluted and diluted 1:10 with carbon tetrachloride.



(e) n-Propylcyclopropyl ketone.

Figure 8. - Concluded. Infrared spectra. Cell width, 0.1 millimeter; sample undiluted and diluted 1:10 with carbon tetrachloride.

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