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TECHNICAL NOTE 2258

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I - 2-CYCLOPROPYLPROPENE AND 2-CYCLOPROPYLPROPANE

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SUMMARY

A method by which 2-cyclopropylpropene and 2-cyclopropylpropane can be prepared from methylcyclopropyl ketone is described. The synthesis involves the reaction of methylmagnesium chloride with methylcyclopropyl ketone to yield dimethylcyclopropylcarbinol, the dehydration of the carbinol to 2-cyclopropylpropene, and the hydrogenation of the olefin to 2-cyclopropylpropane. The physical constants and the infrared spectra of the purified hydrocarbons are presented.

INTRODUCTION

The synthesis and purification of a series of olefinic and paraffinic hydrocarbons, which contain the cyclopropyl ring, was undertaken at the NACA Lewis laboratory in conjunction with an investigation of the effect of molecular structure on the velocity of flame propagation. The synthesis program includes those 2-cyclopropylalkenes up to C_9 in which the double bond is in either the 1- or the 2-position and the corresponding 2-cyclopropylalkanes. The preparation and purification of the first members of the olefinic and paraffinic series, 2-cyclopropylpropene and 2-cyclopropylpropane, are described in this report.

When the synthesis program was started, it was considered desirable that the preparatory methods be generally suitable for preparing an homologous series of cyclopropane hydrocarbons rather than a specific member of such a series. The commerical availability of methylcyclopropyl ketone stimulated interest in the possibility of preparing an homologous series of methylalkylcyclopropylcarbinols by condensing the ketone with various Grignard reagents, dehydrating the carbinols to the cyclopropyl olefins, and subsequently hydrogenating the olefins to the cyclopropyl paraffins. If these processes could be carried out without rupturing the cyclopropyl ring, a method would be available for the preparation of an homologous series of cyclopropylalkenes and cyclopropylalkanes, nearly all members of which were heretofore unknown.

A review of the literature revealed that although several of the methylalkylcyclopropylcarbinols have been prepared by the condensation of alkylcyclopropyl ketones with Grignard reagents (reference 1), very little is known about the dehydration of the carbinols or the hydrogenation of the cyclopropyl olefins. Only the recent investigation of the dehydration of dimethylcyclopropylcarbinol and the hydrogenation of isopropenylcyclopropane (2-cyclopropylpropene) by Van Volkenburgh, Greenlee, Derfer and Boord (reference 2) contained sufficient experimental detail to be useful; prior reports of the dehydration reaction by Kizhner and Klavikordov and by others (references 3 and 4) were lacking in experimental detail.

In the present report, reaction conditions are described for the preparation of dimethylcyclopropylcarbinol from methylcyclopropyl ketone, dehydration of the carbinol to 2-cyclopropylpropene, and hydrogenation of the 2-cyclopropylpropene to 2-cyclopropylpropane. The two hydrocarbons were obtained in high purity by fractional-distillation methods, and the physical properties and the infrared spectra were determined.

DISCUSSION OF SYNTHESIS

The synthesis of 2-cyclopropylpropene and 2-cyclopropylpropane involved the condensation of methylcyclopropyl ketone with methylmagnesium chloride to yield dimethylcyclopropylcarbinol, the dehydration of the carbinol to 2-cyclopropylpropene, and the hydrogenation of the olefin to 2-cyclopropylpropane. The methylmagnesium chloride was prepared in ether from dry methyl chloride gas and magnesium turnings. The condensation reaction was accomplished by adding the methylcyclopropyl ketone to the methylmagnesium chloride.

No attempt was made to determine the conditions for optimum yield of carbinol; however, in those instances in which less than 50 percent of the theoretical amount of carbinol was obtained, significant quantities of the ketone were recovered or unusually large amounts of a halogenated byproduct were present in the products.

The physical properties and the yield of dimethylcyclopropylcarbinol prepared in the present investigation are compared in the following table with those previously reported:

Reference	Yield (percent)	Freezing point (°C)	Boiling point at 760 mm (°C)	Index of refraction n_D^{20}	Density d^{20} (g/ml)
5	54	-----	123[a]	1.4309[b]	0.8791[b]
2	68	-43.0	123.4	1.4337	.8842
Lewis laboratory	64	-----	123.7	1.4335	.8789

[a] At 740 mm.

[b] At 24° C.

Four methods of dehydrating dimethylcyclopropylcarbinol were investigated: (1) refluxing the carbinol with traces of iodine, (2) passing the carbinol through alumina at 225° C, (3) distilling in the presence of dilute (1:2) sulfuric acid solution, and (4) distilling in the presence of concentrated sulfuric acid. The first method gave less than 15-percent dehydration as indicated by the amount of water and unconverted carbinol recovered. The yield of the second method, in which a pure sample of the carbinol was dissolved in twice its volume of toluene and passed through an alumina tower, was 54 percent. The third method gave a negligible amount of 2-cyclopropylpropene and 58 percent of 2,2-dimethyltetrahydrofuran, a product formed by ring expansion without the loss of water. With the proper selection of conditions, dehydration in the presence of concentrated sulfuric acid (method 4), produced 2-cyclopropylpropene in yields of more than 70 percent of the theoretical.

In the dehydrations with concentrated sulfuric acid, two procedures were followed:

(A) The carbinol and the acid were placed in a distilling flask and the products were distilled directly from the reactants into a downward condenser and a receiver. Fractional distillation of the products gave the following data:

Carbinol (moles)	Amount of acid (drops)	Yield (percent)		Unreacted carbinol (mole)
		2-Cyclopropylpropene	2,2-Dimethyltetrahydrofuran	
1.0	5	22	9	0.5
1.0	10	24	22	.4

(B) The carbinol and the acid were mixed in a flask, heated to boiling, and the products were distilled through a 4-foot glass helix-packed column as they formed. Yields were computed on the quantity of olefin purified by fractionation through a 22 millimeter (O.D.) by 6-foot glass column, which was packed with 1/8-inch glass helices. The distillation curve shown in figure 1 is typical of those obtained. The results of several experiments are summarized in the following table:

Carbinol (moles)	Amount of acid (drops)	Yield (percent)	
		2-Cyclopropylpropene	2,2-Dimethyltetrahydrofuran
[a]6.0	10	52	Traces
[a]6.0	20	65	do
[a]6.0	30	69	do
[a]6.0	40	61	Traces
[a]6.0	50	58	do
[a]6.0	60	45	do
[b]1.5	12	73	Traces

[a] Carbinol contained halogenated impurity.
[b] Halogen-free carbinol.

From these data and those presented for procedure (A), it is apparent that both the experimental procedure and the acid concentration influence the yield of 2-cyclopropylpropene. Refluxing the products through the 4-foot helix-packed column not only increases the conversion of the carbinol to the olefin, but has a pronounced effect on the quantity of 2,2-dimethyltetrahydrofuran formed. From the data obtained with the second method, it might also be inferred that the presence of halogen impurity decreases the quantity of acid required for optimum yield of olefin; however, this observation cannot be considered factual, because the number and the size of the experiments with halogen-free carbinol were insufficient to justify such a conclusion.

For the limited number of dehydrating methods and conditions investigated, it was found that 2-cyclopropylpropene was the only olefinic product obtained and that concentrated sulfuric acid was the most satisfactory dehydrating agent. In reference 2 it is suggested that the formation of 2-cyclopropylpropene is best explained by a carbonium-ion mechanism, and that as the acid strength of the catalyst is increased the carbonium-ion mechanism is favored.

Characterization of 2-cyclopropylpropene was accomplished by ozonolysis and catalytic reduction of the ozonide (reference 6). The fragments formaldehyde and methylcyclopropyl ketone were obtained. The ketone was identified by a mixed melting point of the 2,4 dinitrophenylhydrazone derivative with a known sample.

The hydrogenation of 2-cyclopropylpropene to 2-cyclopropylpropane was carried out in the presence of a barium-promoted copper chromite catalyst at an initial hydrogen pressure of 1500 pounds per square inch and at temperatures of 100° to 130° C. Under these conditions the hydrogenation was both rapid and complete, and the quantity of impurity in the product was so small that positive identification was impractical. A typical distillation curve of the hydrogenate is presented in figure 2. The impurity that appears in the last few fractions is probably 2-methylpentane, which is known to be formed when the hydrogenation is carried out in the presence of Raney nickel catalyst (reference 2). It is suggested in reference 2 that 2-methylpentane is formed by 1,4-addition of hydrogen to the "pseudo-conjugated" cyclopropylolefin.

Final purification of 2-cyclopropylpropane was accomplished by careful fractionation through a 6-foot Podbielniak column at an efficiency estimated to be better than 150 theoretical plates.

The physical properties of 2-cyclopropylpropene and 2-cyclopropylpropane are presented in table I. The melting curves (fig. 3(a and b)) and the boiling points were determined with a platinum resistance thermometer and a G-2 Mueller bridge. The accessory equipment and the method for determining the melting points were those of references 7 and 8, respectively. The boiling-point apparatus was modified from that of reference 9, and the system was pressurized with dry air from a surge tank, which was held at constant pressure by adjusting a continuous bleed. The gravimetric balance described in reference 10 was used for determining the densities. The refractive indices were measured with a Bausch and Lomb precision oil-model instrument, the prism of which was maintained at the desired temperature by means of a constant-temperature bath. The heats of combustion were measured in an oxygen-bomb calorimeter according to the method described in reference 11.

The magnitude of the uncertainties and the precision of the measurements are estimated, respectively, as follows: for the melting points, 0.02° and ±0.003° C; boiling points, 0.1° and ±0.04° C; densities, 0.00005 gram per milliliter and ±0.00002 to ±0.00003 gram per milliliter; refractive indices, 0.0002 and ±0.0001; and heat of combustion, 100 Btu per pound (5 kcal/mole) and ±50 Btu per pound.

The infrared spectra of the hydrocarbons are presented in figure 4(a) and (b). The spectra were taken with a double-beam automatic recording spectrometer, the wavelength accuracy of which is estimated to be ±0.03 micron. A detailed analysis of the spectra was not made; however, characteristic olefinic absorption at 6.05 microns is observed in the spectrum of 2-cyclopropylpropene, and both the hydrocarbons showed a strong absorption at 9.8 microns, which appears to be characteristic of this type of cyclopropane hydrocarbon. Characteristic cyclopropane absorption in substituted cyclopropanes has been observed at 9.8 to 10.0 microns (reference 12).

EXPERIMENTAL DETAILS

Methylcyclopropyl ketone

Commercial methylcyclopropyl ketone was fractionated and distillate having a refractive-index range of n_D^{20} 1.4246 to 1.4249 was used in the Grignard reaction. A 1-liter quantity of this distillate was refractionated in order to obtain a purer sample which had the following physical properties: freezing point, -68.40° C; boiling point, 112.1° C (760 mm); n_D^{20}, 1.4252; and d^{20}, 0.8988 gram per milliliter. The infrared spectrum is shown in figure 5.

Dimethylcyclopropylcarbinol

Ten gallons of dry ether and 170 moles (4130 grams) of magnesium turnings were placed into a 30-gallon glass-lined reactor, and dry methyl chloride gas was added below the surface of the ether through a 1/4-inch copper tube. The reaction was initiated by introducing 100 grams of methyl iodide and was kept at refluxing temperature during the addition of the methyl chloride. Periodically, the amount of unreacted magnesium was ascertained by sampling with a long-handled spoon. After 25 hours, only a thick sludge was detectable. Consequently, 150 moles (12,616 grams) of methylcyclopropyl ketone dissolved in 5 gallons of ether was added at a rate such that a vigorous reflux was maintained. The reaction mixture was kept at the reflux temperature for 1 hour after the addition of the ketone was completed, and then stirred at room temperature for an additional 20 hours.

The hydrolysis of the reaction product was accomplished by adding a saturated solution of ammonium chloride to the point of salt precipitation (approximately 7 gal). The ether solution was siphoned from the precipitated salts and distilled. The dimethylcyclopropylcarbinol was collected between 58° to 62° C at 60 millimeters to give 8316 grams of product. An additional 1318 grams of carbinol was obtained by dissolving the salt cake in dilute sulfuric acid and distilling the organic material that had been absorbed in it. The yield of carbinol, based on methylcyclopropyl ketone, was 64 percent of the theoretical.

The removal of halide contamination from the dimethylcyclopropylcarbinol was accomplished in the following manner: The carbinol (17.1 moles or 1714 grams) was refluxed for 4 hours with a mixture of 200 grams of sodium hydroxide and 1 liter of ethanol. A white solid, presumably sodium chloride, was precipitated during the process. The reaction mixture was thoroughly extracted with water to remove the caustic and distilled at 60 millimeters. The small amount of halide contaminant still present was completely removed by distilling the carbinol from 1 percent of its weight of sodium metal.

2-Cyclopropylpropene

Four methods of dehydrating dimethylcyclopropylcarbinol were tried:

Iodine. - Five moles (500 grams) of the carbinol was refluxed for 20 hours over 5 grams of iodine in a 2-liter flask. Less than 15-percent dehydration occurred as shown by the amount of water collected and the recovery of 468 grams of material, which was principally unconverted carbinol.

Alumina. - Two moles (200 grams) of the carbinol was dissolved in 400 milliliters of toluene, and the solution was passed through a 2.5-centimeter (O.D.) by 120-centimeter pyrex column packed with 8 to 14 mesh alumina. The column was heated by resistance wire elements to 175° C. Little, if any, dehydration occurred at this temperature. The column was then heated to 225° C, and the carbinol solution was passed through a second time. In addition to the organic products, approximately 1.7 moles of water was collected. The organic layer was dried over anhydrous calcium sulfate and fractionated through the 6-foot helix-packed column previously mentioned. The yield of 2-cyclopropylpropene was 89 grams or 54 percent of the theoretical.

Dilute sulfuric acid. - One mole (100 grams) of carbinol was mixed with 170 milliliters of 1:2 sulfuric acid and water. Distillation of the mixture directly from the flask into a downward condenser and a receiver produced a high-boiling residue and a 58-percent yield of 2,2-dimethyltetrahydrofuran, which had the following properties: freezing point, -114.46° C; boiling point, 92.25° C (760 mm); n_D^{20}, 1.4068; and d^{20}, 0.84019 gram per milliliter. Analysis - Calculated for $C_6H_{12}O$: C, 71.94 percent; H, 12.08 percent. Found: C, 71.55 percent; H, 12.10 percent. The quantity of olefin in the products was negligible.

Concentrated sulfuric acid. - Procedure (A) was similar to the method described for dilute sulfuric acid. Distillation of the product from 1 mole (100 grams) of the carbinol and 10 drops of concentrated sulfuric acid gave 20 grams (24-percent yield) of 2-cyclopropylpropene, 22 grams (22-percent yield) of 2,2-dimethyltetrahydrofuran, and 0.4 mole of unreacted carbinol.

In a typical experiment (procedure (B)), 6 moles (602 grams) of dimethylcyclopropylcarbinol and 30 drops of concentrated sulfuric acid were mixed in a 2-liter flask. The flask was then attached to a 4-foot glass column packed with 1/8-inch glass helices, and the reaction mixture was heated to reflux temperature. The products were distilled through the column as they formed. The distillate was washed with two 1-liter portions of cold water, dried over anhydrous calcium sulfate, and fractionated through the 6-foot helix-packed column previously mentioned. The yield of 2-cyclopropylpropene was 340 grams (69-percent yield), n_D^{20} 1.4254 to 1.4256.

Ozonolysis of 2-Cyclopropylpropene

Three-tenths mole (25 grams) of 2-cyclopropylpropene in 150 milliliters of ethanol was ozonized and the ozonide was decomposed by hydrogen. The reduced product was fractionated through a 1.4-centimeter (O.D.) by 45-centimeter column packed with 3/32-inch glass helices. Formaldehyde was detected only by its odor and by the appearance of a white amorphous solid that sublimed into the still head above 85° C (presumably paraformaldehyde). The presence of the paraformaldehyde made isolation of the other fragment difficult, but a sufficient amount of product boiling from 108° to 110° C was obtained to form a 2,4-dinitrophenylhydrazone, which had a melting point of 147.5° to 148.0° C (uncorrected). A mixed melting point with a sample of the corresponding derivative of methylcyclopropyl ketone showed no depression.

2-Cyclopropylpropane

In a typical hydrogenation 8.0 moles (658 grams) of 2-cyclopropylpropene (n_D^{20} 1.4255), 66 grams of barium-promoted copper chromite catalyst and 500 milliliters of absolute ethanol were charged to a 3.4-liter rocker-type autoclave. After hydrogen was admitted to 1500 pounds per square inch, the vessel was heated to 100° C. Hydrogenation began at this temperature; the heat of reaction increased the temperature to a maximum of 130° C. After this initial rise, the temperature was maintained at 120° C for 20 hours. The absorption of hydrogen was negligible after the first 8 hours. The total amount of hydrogen consumed was calculated to be 7.9 moles.

The products were removed from the autoclave when they had cooled to room temperature, filtered through a filter-aid to remove the catalyst, washed with three 2-liter portions of cold water to remove the ethanol, and dried over anhydrous calcium sulfate. The dried product, which weighed 567 grams (84-percent recovery), was fractionated through the 6-foot helix-packed column. The yield of 2-cyclopropylpropane was 540 grams or 80 percent of the theoretical. With the exception of 13 grams of residue, this yield represented all the product recovered.

CONCLUDING REMARKS

The preparation of 2-cyclopropylpropene and 2-cyclopropylpropane from methylcyclopropyl ketone is described. The synthesis involves the reaction of methylmagnesium chloride with methylcyclopropyl ketone to yield dimethylcyclopropylcarbinol, the dehydration of the carbinol to 2-cyclopropylpropene, and the hydrogenation of the olefin to 2-cyclopropylpropane. The physical constants of the purified hydrocarbons have been determined by precise measurements. The infrared spectra of 2-cyclopropylpropene, 2-cyclopropylpropane, and methylcyclopropyl ketone are presented.

Lewis Flight Propulsion Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, July 28, 1950.

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TABLE I - PHYSICAL PROPERTIES OF 2-CYCLOPROPYLPROPENE AND 2-CYCLOPROPLYPROPANE

		2-Cyclopropyl-propene	2-Cyclopropyl-propane
Melting point, °C		-102.34	-112.97
Boiling point, °C at 760 mm		70.33	58.31
Index of refraction, n_D^{20}		1.4255	1.3865
Density, d^{20}, grams/ml		0.75153	0.69858
Net heat of combustion, kcal/mole		865.8	898.9
Percent carbon	Found	87.55	85.58
	Calculated	87.73	85.62
Percent hydrogen	Found	12.20	14.33
	Calculated	12.27	14.38

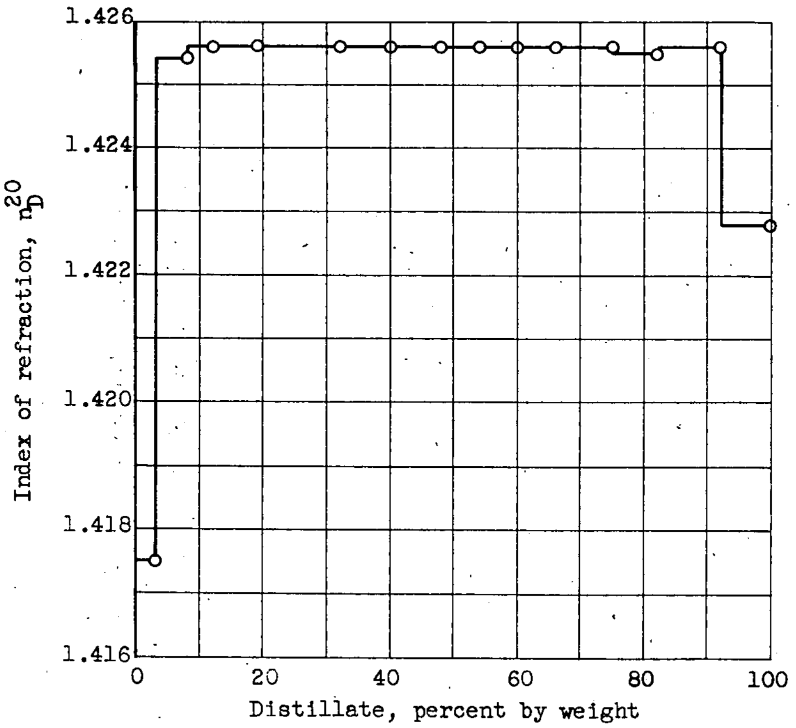


Figure 1. - Distillation of product from dehydration of dimethylcyclopropylcarbinol with concentrated sulfuric acid. Distillate, 378 grams.

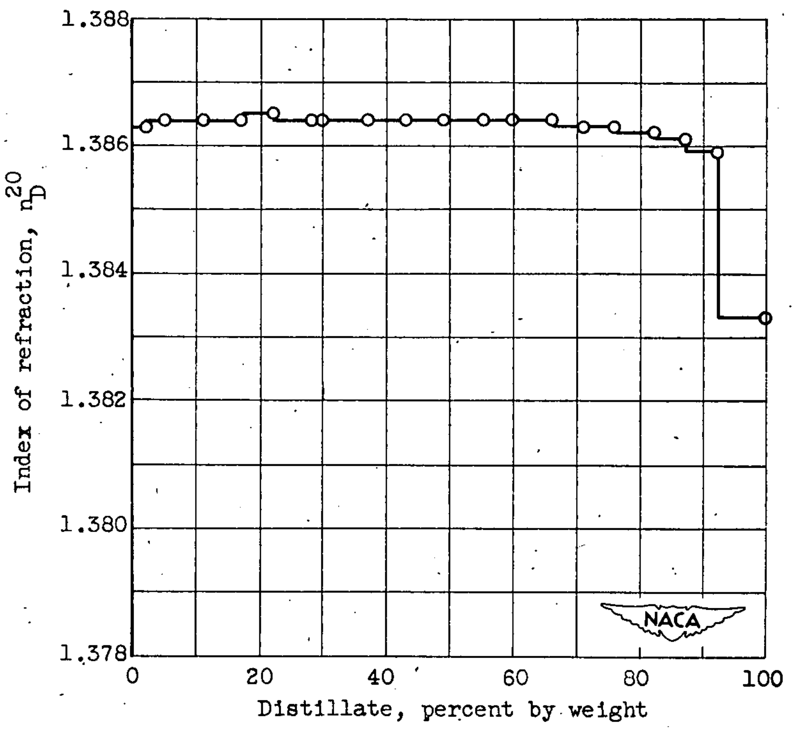
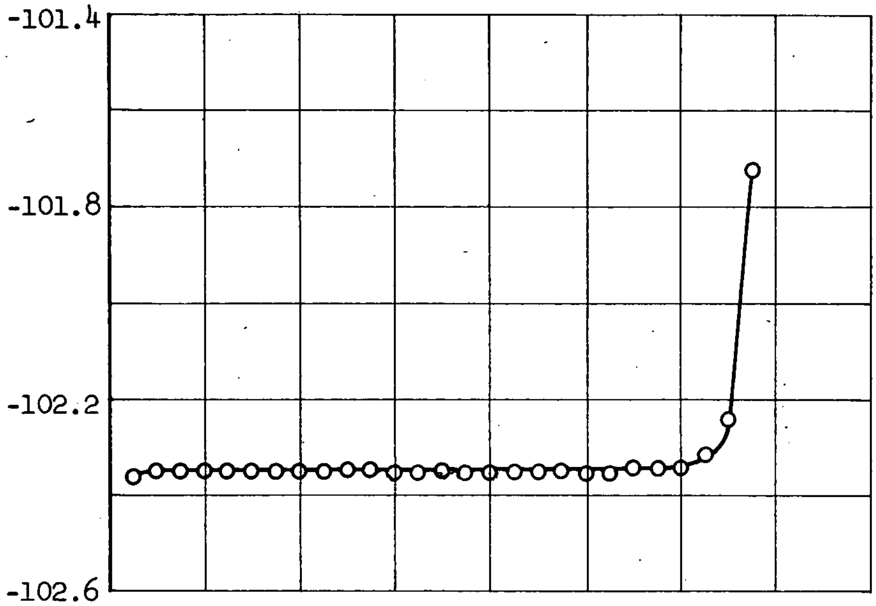
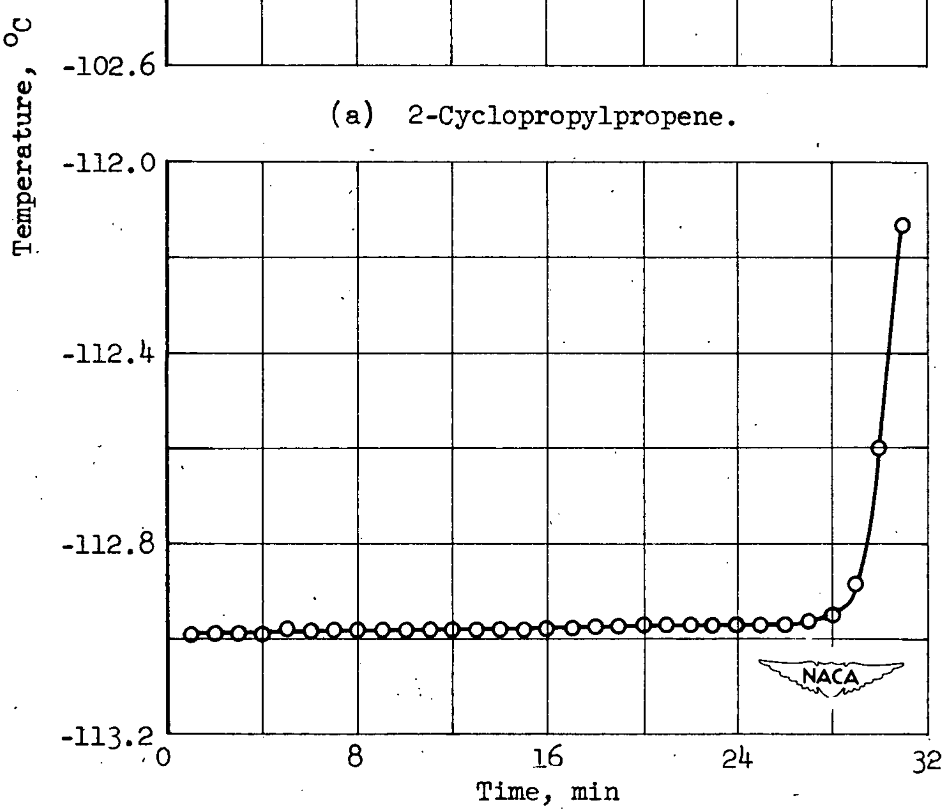


Figure 2. - Distillation of product from hydrogenation of 2-cyclopropylpropene at temperature of 100° to 130° C. Distillate, 548 grams.

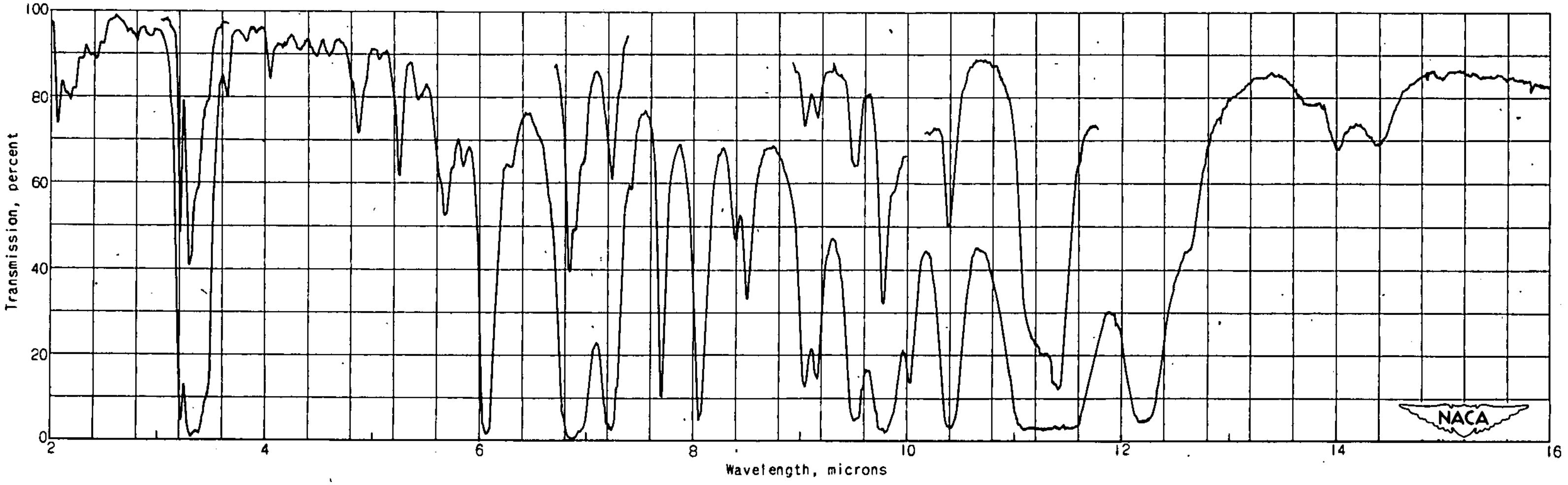


(a) 2-Cyclopropylpropene.



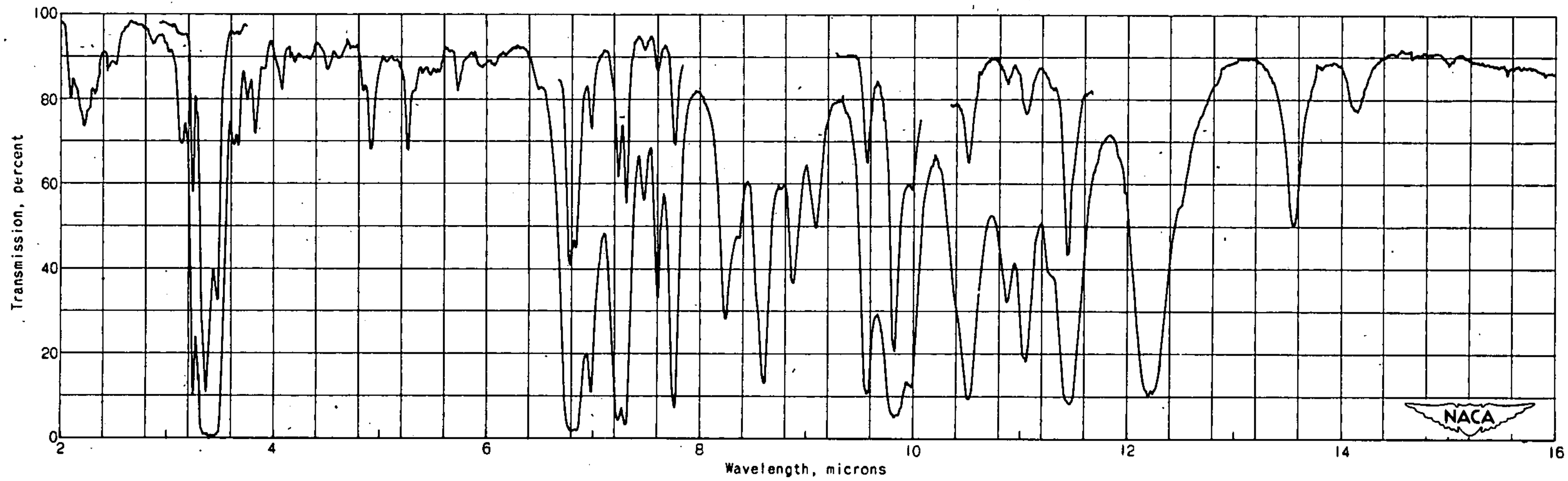
(b) 2-Cyclopropylpropane.

Figure 3. - Time-temperature melting curve.



(a) 2-Cyclopropylpropene.

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



(b) 2-Cyclopropylpropane.

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

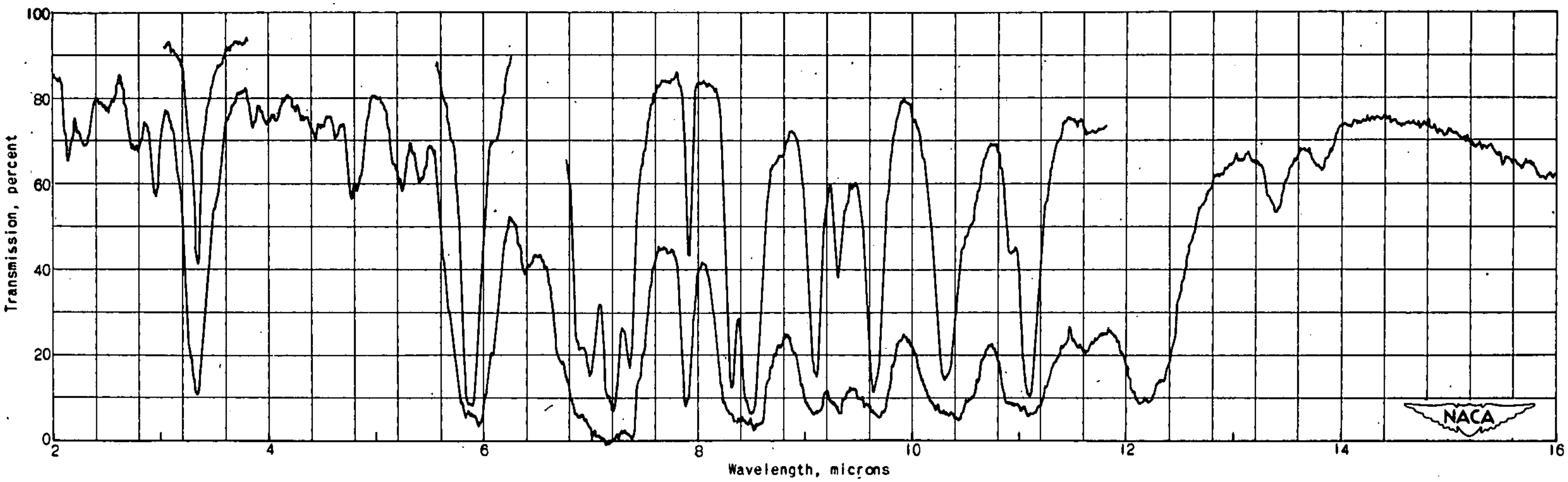


Figure 5. - Infrared spectrum of methylcyclopropyl ketone. Cell width, 0.1 millimeter; sample undiluted and diluted 1:5 with carbon tetrachloride.