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SYNTHESIS AND EVALUATION OF BISBICYCLIC DIEPOXIDES

15 February 1962

Prepared under Navy, Bureau of Naval Weapons
Contract NOW 62-0475-d

Quarterly Progress Report No. 1

15 October 1961 - 15 January 1962

M.R.I. Project No. 2575-C

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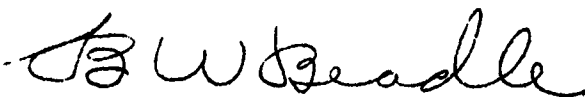
Midwest Research Institute
Kansas City 10, Missouri

PREFACE

The work discussed in this report was carried out by Mr. Thomas M. Medved and Mr. Howard W. Christie, project leader, under the supervision of Dr. F. V. Morriss, Head, Organic Chemistry Section. This report was prepared by Mr. Thomas M. Medved.

Approved for:

MIDWEST RESEARCH INSTITUTE

A handwritten signature in dark ink, appearing to read "B. W. Beadle". The signature is fluid and cursive, with the first letters of the first and last names being capitalized and prominent.

B. W. Beadle, Director
Chemistry Division

15 February 1962

ABSTRACT

Synthesis of bis [2-(bicyclo [2.2.1] heptane-5,6-epoxy)-methyl] oxide (diepoxide 262) was accomplished. The intermediate ether was obtained by the Williamson synthesis. The diepoxide can be cured with maleic anhydride and trimethylolethane to form a hard infusible resin. However, the resin obtained from this curing system is dark brown. A thin film of this same resin cured between salt plates was colorless. Curing temperature differences may account for the color differences noted between the two samples.

Cure of 5,6-epoxy bicyclo [2.2.2] octane-2-methyl-5',6'-epoxy bicyclo [2.2.2] octane-2-carboxylate, synthesized during an earlier program, with maleic anhydride and trimethylolethane yielded a dark brown, brittle, thermoplastic material.

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I. INTRODUCTION

The work discussed in this report is a continuation of the studies performed on Contract No. NOW 61-0673-d, "Development and Evaluation of High Temperature Resistant Composite Plastic Plates."

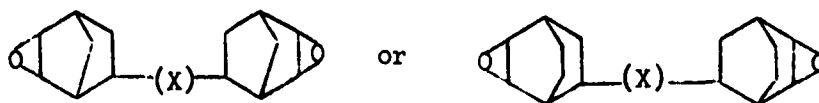
The goal of this program is the development of a castable transparent organic plastic suitable for use as a glazing material for supersonic aircraft. These plastics must withstand temperatures up to 500°F without discoloration or structural failure under supersonic flight conditions.

Work carried out in this program is involved with the synthesis of new diepoxide monomers and evaluation of the resins obtained from them. These compounds are based on the bicyclic [2.2.1] heptane and [2.2.2] octane structures.

Water white transparent resins have been achieved by selective methods of curing the diglycidylether of bisphenol A and also from resins derived from vinylcyclohexene dioxide. However, the latter was not usable because of the high notch sensitivity and brittleness of the cured resin.

It has been shown that epoxide resins containing the bicyclic structure are more thermally stable than most other types of epoxides.^{1/} Thermogravimetric analysis of various epoxides showed that resins containing the bicyclic structure were more thermally stable as measured by shape retention than other resin types, although epoxy-novolak resins gave smaller weight losses at high temperatures.

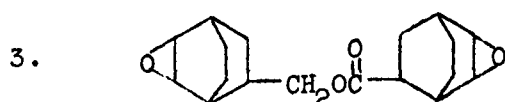
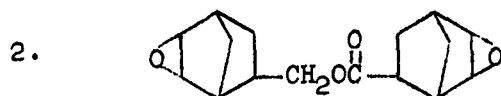
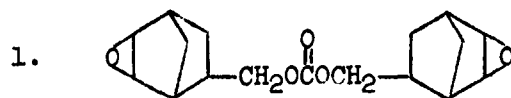
In order to study color formation, associated with the thermally stable bicyclic structure, a series of diepoxides containing various connecting groups between two bicyclic epoxide rings are being synthesized, examples are:



Bicyclic [2.2.1] heptane diepoxide Bicyclic [2.2.2] octane diepoxide

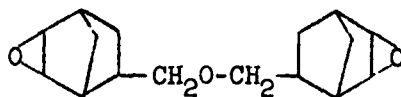
^{1/} Final Report, "Development and Evaluation of High Temperature Resistant Composite Plastic Plates," Contract NOW 61-0673-d, Midwest Research Institute, Kansas City, Missouri, 31 October 1961.

In earlier programs the following three diepoxides were synthesized and the properties of the resins prepared from some were described.



It was found that more color was generated in curing the ester connecting diepoxide than when curing the carbonate linked diepoxide.

The majority of effort during this quarter was spent on the synthesis of the diepoxide containing the ether linkage.



Bis [2-(bicyclo [2.2.1] heptane-5,6-epoxy)-methyl] oxide

The synthesis and cure of this diepoxide are described in the following sections.

II. DISCUSSION OF RESULTS

A. Cure of 5,6-Epoxy Bicyclo [2.2.2] Octane-2-Methyl-5',6'-Epoxy Bicyclo [2.2.2] Octane-2-Carboxylate (Diepoxide 304)

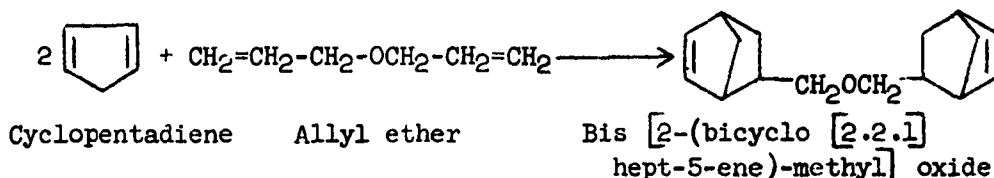
Approximately 100 g. of this diepoxide was synthesized as described in the Final Report.¹ Maleic anhydride and a polyol initiator were used as

the curing agents. Maleic anhydride with a polyol is the only curing agent found to give a satisfactory resin with these monomers. Other curing agents such as BF_3 react very rapidly with the diepoxides.

Diepoxide 304 did not give a completely cured resin in this attempt. At the elevated cure temperature the resin was soft, but after cooling a hard, brittle, amber colored resin was formed. This is the same way that the bicyclic [2.2.1] heptane ester linked diepoxide (276) behaved when cured. The infrared spectra taken at various intervals in the cure cycle showed the disappearance of hydroxyl (from the polyol initiator) and formation of a carboxylic acid group (by broadening of the band at $3,000 \text{ cm}^{-1}$). Disappearance of several bands between $1,800\text{-}2,000 \text{ cm}^{-1}$ indicated most of the anhydride was reacted. It was difficult to tell to what extent the epoxide band at 850 cm^{-1} reacted, as the sample cast between the salt plates was too thick, and did not resolve this band. Further curing experiments are necessary with this diepoxide.

B. Attempts to Synthesize Bis [2-(bicyclo [2.2.1] hept-5-ene)-methyl] Oxide by the Diels Alder Reaction

Several experiments with the Diels Alder type reaction were reported previously.^{1/} These involved the reaction of cyclopentadiene and allyl ether.

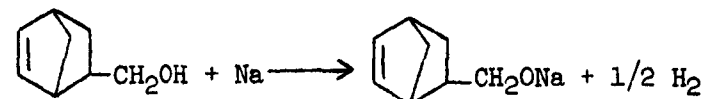


However, either all the starting material was recovered or polymerization took place.

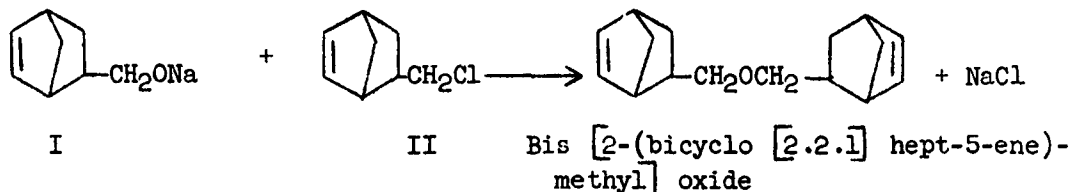
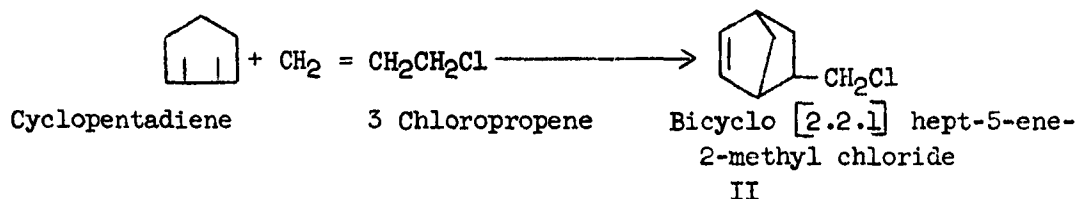
During this quarter three more reactions were tried in an autoclave at temperatures of 150° , 250° , and 280°C . The reaction planned for 230°C was interrupted by a leak in the autoclave. The maximum temperature was 150° and all of the starting material was recovered. The reaction at 280°C gave a polymerized rubbery material while 90 per cent of the starting material was recovered from the reaction at 250°C . Fractionation of the remaining 10 per cent gave several distinct compounds. Two of these compounds had an ether band in the spectra, but neither of these compounds analyzed correctly for the desired ether.

C. Williamson Synthesis of Bis [2-(bicyclo [2.2.1] hept-5-ene)-methyl]
Oxide

This synthesis involves the following reactions.



Bicyclo [2.2.1] hept-5-ene-2-methanol I



Two difficulties were encountered in previous attempts to synthesize the ether by the Williamson method. The first involved difficulty in reaction of the bicyclo [2.2.1] hept-5-ene-2-methanol with sodium or potassium. Secondly, reaction of the alkoxide with the halide did not give a pure product identifiable as the sought ether. To overcome the difficulty of the alkoxide coating the alkali metal, several reactions using sodium dispersions were tried. These dispersions were made in xylene, toluene, and the reacting alcohol. Complete reaction of the sodium was achieved.

After successful formation of the alkoxide was achieved the bicyclo [2.2.1] hept-5-ene-2-methyl chloride was added slowly to the alkoxide. Several experiments were run in which the halide was added to the alkoxide at temperatures between the gel point of the alkoxide, 50°C, and the refluxing temperature of xylene, 144°C. Most of the starting materials were recovered from these experiments.

Disappearance of the alkoxide was followed by titration of hydrolyzed samples. It was found after several runs the only condition in which the alkoxide would disappear was if the reaction mixture was heated to a temperature of 195°C. The solvents were stripped off in order to attain this higher temperature.

At a pot temperature of 195°C the mixture started refluxing. This refluxing material could not be identified as any of the starting materials. The alkoxide disappeared after 6 hr. of refluxing at which time it was also noticed that the refluxing material disappeared. During this refluxing period the temperature dropped to 180°C. The mixture was taken up in ether, washed with water, and distilled. The ether was obtained in about 33 per cent yield. The infrared spectrum of the product did not coincide with any of the fractions obtained from the Diels Alder reaction.

D. Synthesis of Bis [2-(bicyclo [2.2.1] heptane-5,6-epoxy)-methyl]
Oxide (Diepoxide 262)

Difficulty was encountered in epoxidizing with perbenzoic in benzene (procedure reported earlier).¹ A compound was obtained with an epoxide band at 850 cm.⁻¹ but the spectrum also showed a carbonyl band at 1,750 cm.⁻¹ in all fractions obtained. Aromatic character was noted in the spectrum. It appears that the benzoic acid reacted with some of the epoxide groups. The sought diepoxide was obtained by epoxidizing with perbenzoic acid in ether at low temperatures (-5°C). Analysis of the material obtained after the first distillation was fairly satisfactory.

The infrared spectrum has a large epoxide band at 850 cm.⁻¹ and a large ether band 1,100 cm.⁻¹. A carbonyl band was noted in some of the fractions obtained. A slight trace of carbonyl is present in the twice distilled diepoxide.

E. Cure of Diepoxide 262

Maleic anhydride and a polyol initiator were used to cure a small sample of the diepoxy ether. The maleic anhydride and trimethylolethane were melted together, the diepoxide was added and mixed thoroughly. The temperature was about 180°F during mixing. A drop was cast between salt plates for infrared studies, the remainder was placed in a 180°F oven. Gellation took place in about 1 hr. and the resin was hard after 4 hr. This mixture turned an amber color. Further curing was done at 250°F for 15 hr. Infrared analysis showed disappearance of hydroxy, anhydride and epoxide bands; carboxylic acid appeared during curing but after 15 hr. at 250°F, the carboxylic acid disappeared and hydroxyl reappeared. The epoxide band in the infrared spectra of the cured resin showed almost complete reaction.

By dissolving away the salt plates from the cast sample, the film of cured diepoxide was obtained. This film was colorless. The reason for absence

of color in this film may be due to a slightly different curing cycle. For about 20 min. the sample was at considerably lower temperature than the parent mixture from which it was taken.

This diepoxide showed the greatest reactivity of those synthesized thus far. Synthesis of a larger quantity and further curing experiments will be done in the next quarter.

III. EXPERIMENTAL

A. Cure of 5,6-Epoxy Bicyclo [2.2.2] Octane-2-Methyl 5',6'-Epoxy Bicyclo [2.2.2] Octane-2-Carboxylate (Diepoxide 304)

A mixture consisting of 3 g. of diepoxide 304, 1.5 g. maleic anhydride, and 0.3 g. trimethyloethane (0.9 mole, 1.5 moles, 0.2 mole) was cured in the following manner.

The maleic anhydride and trimethyloethane were melted together and not allowed to rise above 180°F in temperature. The diepoxide was dissolved in the molten mixture and was stirred thoroughly. A sample was cast between salt plates for infrared studies.

The sample was cured according to the following schedule:

5 hr. at 180°F;

19 hr. at 225°F; and

3 hr. at 275°F.

A continual increase in viscosity was noted throughout the entire cure cycle, however, a rigid resin was not obtained until the sample was cooled to room temperature. At room temperature the resin was very brittle.

The infrared spectra taken at various intervals throughout the cure cycle showed disappearance of anhydride, epoxide and hydroxyl character, and the formation of carboxylic acid character. Since the diepoxide is an ester the formation of new ester groups through polymerization could not be followed.

B. Attempt to Synthesize Bis [2-(bicyclo [2.2.1] hept-5-ene)-methyl]
Oxide by the Diels Alder Reaction

Three experiments utilizing 1 mole of allyl ether and 1 mole of dicyclopentadiene were run in a steel autoclave at 150°C, 250°C, and 280°C. After 15 hr. at temperature, the autoclave was cooled and the contents analyzed. All starting material was recovered from the 150°C run while the run at 280°C gave a polymerized mass. Distillation of the 250°C run gave 90 per cent recovery of the starting materials and a residue which gave the following fractions.

1. 58-62°C/3.7 mm Hg;
2. 62-112°C/3.7 mm Hg;
3. 112-113°C/3.7 mm Hg;
4. 119-127°C/3.7 mm Hg;
5. 127-148°C/3.7 mm Hg; and
6. 148°C/3.7 mm Hg - white solid solidified in condenser.

Fractions 3 and 4 were the only fractions with ether bands in their spectra. Redistillation of fraction 3 gave a compound boiling at 105°C/3.5 mm Hg, which solidified to a white solid upon standing at room temperature. Redistillation of fraction 4 gave a compound boiling at 125-125.5/3.5 mm Hg. Analysis of these compounds indicated that the desired ether was not obtained.

C. Williamson Ether Synthesis of Bis [2-(bicyclo [2.2.1] hept-5-ene)-
methyl] Oxide

Several unsuccessful attempts to synthesize the ether were done using the following procedure. A sodium dispersion was made in a 4-neck Morton flask equipped with a high speed stirrer, stainless steel condenser, addition funnel, and nitrogen inlet tube. The sodium (4.5 g.) was dispersed in toluene or xylene. Addition of 24 g. (0.193 mole) bicyclo [2.2.1] hept-5-ene-2-methanol to the Na dispersion caused a color change from grey to white. Bicyclo [2.2.1] hept-5-ene-2-methyl chloride, 27.6 g. (0.193 mole), was added to the alkoxide at the refluxing temperature of the solvent used in that run. The white color turned to a dark brown upon addition of the halide. Several reactions were tried using the above technique including one reaction in which a copper catalyst was employed. No ether was obtained from these experiments.

The successful procedure used to obtain the ether was as follows. Sodium (4.5 g.) was added to a large excess of bicyclo [2.2.1] hept-5-ene-2-methanol (300 ml.) contained in a Morton flask equipped as previously described. The temperature was raised to the melting point of sodium and stirring was used to keep the particles of sodium from becoming coated with the alkoxide. After all the sodium was reacted 27.6 g. (0.193 mole) of bicyclo [2.2.1] hept-5-ene-2-methyl chloride was added rapidly to the hot alkoxide. The temperature was then raised to 195°C at which point refluxing of the material began. The temperature of reflux gradually dropped to 180°C. Titration of a hydrolyzed sample of the mixture showed all the alkoxide was gone after about 6 hr. The mixture was taken up in ether and washed with water and distilled. The product (33 per cent yield) distilled at 72°C/0.05 mm Hg. The infrared spectrum is shown in Fig. 1.

Anal. Calcd. for: $C_{16}H_{22}O$; C, 83.5, H, 9.58

Found: C, 83.8; H, 9.62; $n_D^{25} = 1.5100$

$\rho = 1.0105$ g/cc at 25°C

D. Synthesis of Bis [2-(bicyclo [2.2.1] heptane-5,6-epoxy)-methyl]
Oxide (Diepoxide 262)

Epoxidation with perbenzoic acid in benzene as described previously¹ failed to give the diepoxide compound. Epoxidation with perbenzoic acid in ether at a lower temperature (-5°C - 0°C) appears to have produced a 50 per cent yield of the diepoxide, b.p. 124°C/0.05 mm Hg.

Anal. Calcd. for $C_{16}H_{22}O_3$; C, 73.3; H, 8.45

Found: C, 72.6; H, 8.23

The infrared spectrum is shown in Fig. 2.

E. Cure of Diepoxide 262

Curing of the crude diepoxide was accomplished using maleic anhydride and trimethylolethane. Maleic anhydride (2.0 g.) and 0.1 g. of trimethylolethane were heated until a solution was obtained. The temperature was held at 180°F while 3.2 g. of diepoxide 262 was added. After mixing, a drop was cast between salt plates for study by infrared analysis. The cure cycle was 15 hr. at 180°F and 15 hr. at 250°F. After 1 hr. at 180°F the resin was gelled.

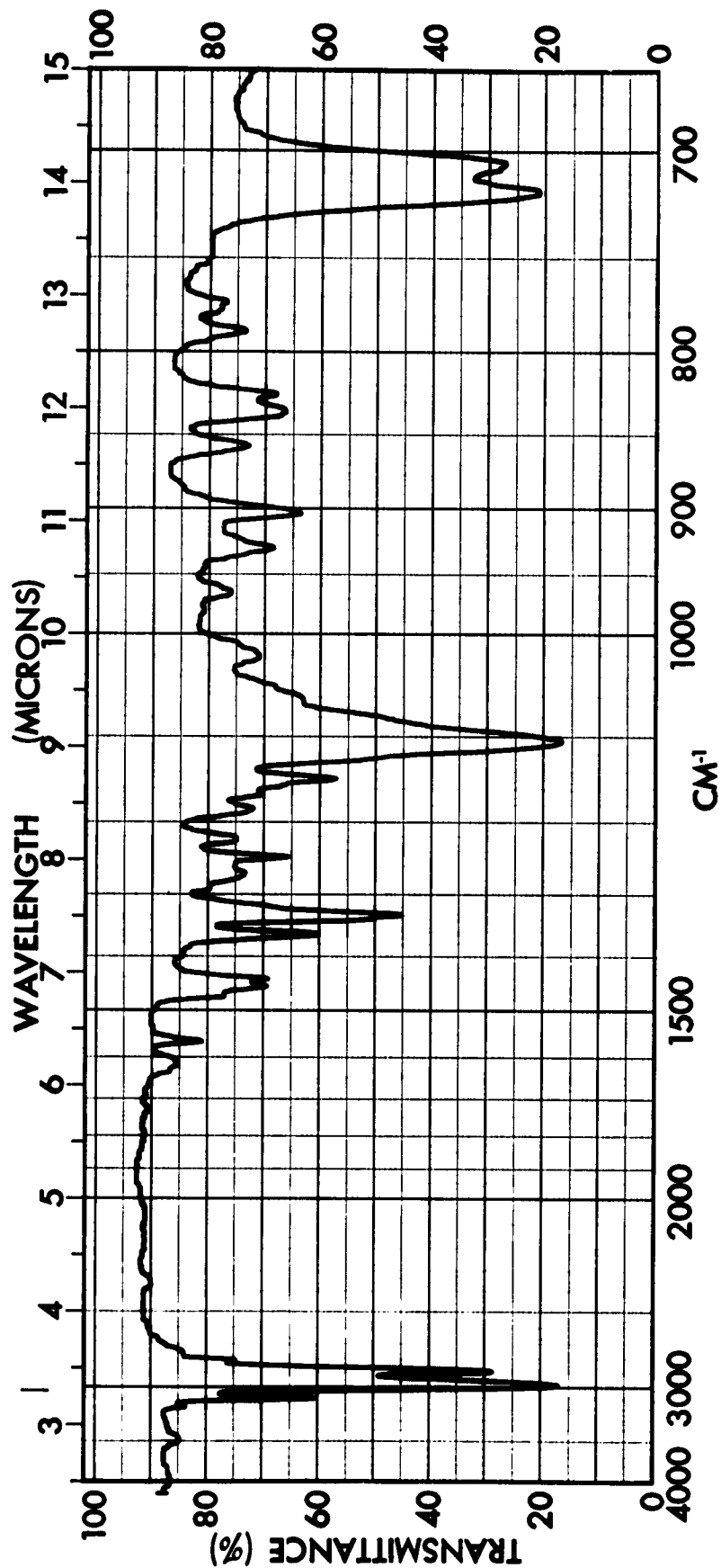


Fig. 1 - Infrared Spectra of Bis 2-(bicyclo 2.2.1 hept-5-ene)-methyl Oxide

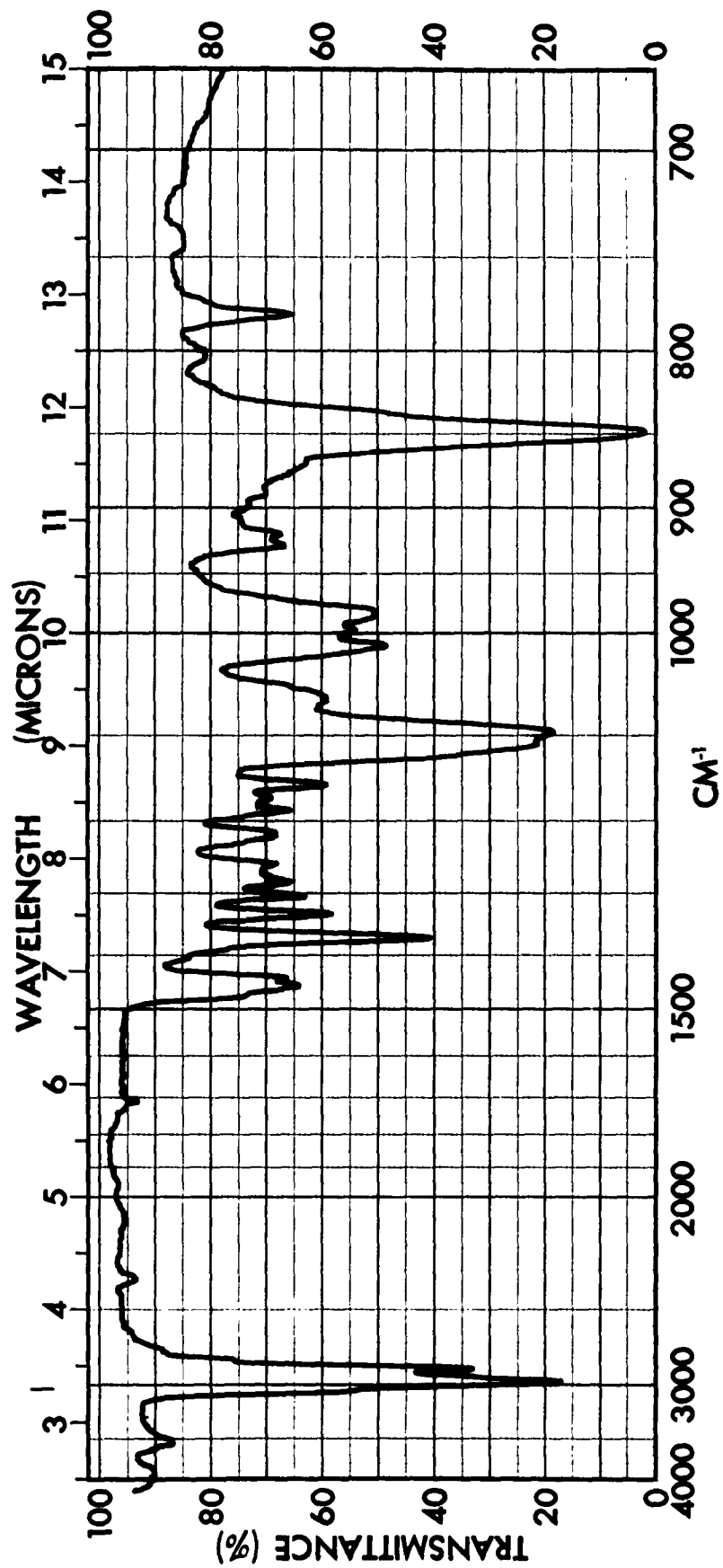


Fig. 2 - Infrared Spectra of Bis 2-(bicyclo 2.2.1 heptane-5,6-epoxy)-methyl Oxide

After about 4 hr. at 180°F the resin was hard. The infrared spectrum showed complete disappearance of the hydroxyl, anhydride, and almost complete disappearance of the epoxide character. The formation of ester linkage was readily apparent.