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A Study Of The Formation Of Cyclic Allenes From 2,3-Dibromocycloalkenes

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A STUDY OF THE FORMATION OF CYCLIC ALLENES FROM 2,3-DIBROMOCYCLOALKENES

A Dissertation
Presented to
the Faculty of the Graduate School
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In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by
Michael John Millam
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This dissertation, written and submitted by

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CHAPTER I

INTRODUCTION AND REVIEW OF THE LITERATURE

Although allene (propadiene) and some of its homologues were prepared and characterized in the 1860's (allene itself was first prepared in 1865 (1); examples of homologues of allene are in references 2 and 3), the chemistry of allenes had been neglected until the last ten to fifteen years when a revival of interest in this field of organic chemistry began.

Allenes are the simplest of the "cumulenes"--compounds with cumulated double bonds; butatrienes and pentatetraenes are the next higher analogues in the cumulene series. The cumulated double bonds have some interesting chemical properties associated with them; for example, allenes are interconvertible with 1,3-dienes (of course, allene itself cannot be converted to 1,3-dienes) and acetylenes (4); a few such reactions were once widely used in industrial as well as laboratory work (5). Compounds with cumulated double bonds are found in nature (6-13).

One of the reasons that allenes have not been studied extensively until recently is that suitable methods for preparing pure allenes were not available. The recent literature contains a number of citations (14-19) wherein earlier reports are shown to be in error. Indeed, preparative procedures and physical constants for allenes prepared by earlier workers (before gas chromatography became a common tool for research) should be regarded with caution.

The ease with which allenes undergo rearrangement to acetylenes and conjugated dienes has long been one of the major problems faced by organic chemists in the synthesis of pure allenes; many preparations were mixtures of allenes and acetylenes. Often the allene was by far the predominant product but removal of the corresponding acetylene compound was usually difficult except in the case of terminal acetylenes which could be removed as a metal acetylide.

The author wishes to give a review of the literature but will mainly discuss the most recent publications because comprehensive reviews of the methods for preparing allenes (20) and of the chemical and physical properties of allenes (5) have been published in 1958 and 1964, respectively.

The classical method for preparing allenes is the method of Gustavson and Demjanov (21) which involves the debromination of 2,3-dibromopropanes in alcohol with zinc dust. However, the yields of allenes by this method are low, and the allenes are always contaminated with a number of side-reaction products, including methylacetylenes and 2-bromopropenes.

Slobodin and Khitrov (22) recently examined this method in detail and found, interestingly enough, that the use of butyl or isopentyl acetate as the solvent in the debromination of 2,3-dibromopropene gave 95-98% yield of allene and that the allene thus formed was free of the 2-bromopropene impurity which had been until now impossible to eliminate from the allene, even with a specially designed distillation apparatus (23).

In 1964 it was reported that treatment of 2,3-dihalopropenes with chromium (II) sulfate yielded allene (104). Optimum yields were obtained if the 2,3-dihalopropene contained a bromine (not a chemical) atom in the

2 position and if care was taken that the allene formed in the reaction was not reduced to propene by an excess of chromium (II) sulfate.

Allenes with a terminal allene group have been prepared by the reduction of 3-bromoprop-1-ynes or 1-bromo-1,2-alkadienes with a zinc-copper couple in alcohol (24) or with lithium aluminum hydride (25).

Upon reduction, many 1,3-disubstituted-propargyl halides (the substituents may be alkyl or aryl groups) undergo acetylene-allene rearrangement (4, 26-28) to give allenes in yields of up to 90%; the acetylene-allene rearrangement is also used advantageously in the preparation of 1,2-alkadienes by the addition of propargyl bromide to alkylmagnesium bromides (29). The acetylene side-product is removed from the reaction as the silver acetylide.

In 1958, von Doering and La Flamme (30) reported that 1,1-dibromocyclopropanes, which are prepared from olefins and bromoform by the method of von Doering and Hoffman (31), react with magnesium or highly dispersed sodium to yield allenes in reasonable yields; however, the products are usually contaminated with acetylenes and cyclopropanes (32). Subsequently, Moore and Ward (33) showed that alkyllithium reagents, specifically methyllithium and butyllithium, react with 1,1-dibromocyclopropanes even at -78°C to give allenes in 70-80% yields and of high purity; in most cases, no acetylenes or other contaminants could be detected. 1,1-Dichlorocyclopropanes are inert to methyllithium but react slowly with butyllithium (34) to yield a mixture of products (16) including allenes, which were found to be the main product. Generally, methyllithium and 1,1-dibromocyclopropanes gave the best results as butyllithium has a slightly greater tendency to produce acetylenic compounds and because difficulties have occasionally been encountered in gaining complete separation of butylbromide from the allene. Skattebol (35) has shown the utility of the reaction by synthesizing a number of allenes, including 1,2-cyclononadiene, from 1,1-dibromocyclopropanes. Moore and Ward (34) extended their work by synthesizing a number of other allenes, including 1,2-cyclodecadiene and 1,2-cycloundecadiene.

Recently, Untch, et. al. (36), reported that allenes could be prepared in one step from olefins by treating a fourfold excess of olefin with one equivalent of carbon tetrabromide and two equivalents of methyllithium in ether. The use of butyllithium resulted in lower yields of the allene. The yields are good (70-80% over-all as determined by gas chromatography) by this method; and the method is convenient. However, this author experienced difficulty removing the excess olefin from the allene with the equipment available. It is possible that efficient fractionating devices can be used to overcome that difficulty.

Treating gem-dibromocyclopropanes with alkyllithium reagents is obviously a very successful, general method for preparing allenes; however, it is of interest to note that tetramethylallene has not been successfully prepared by this method (16). Instead of finding tetramethylallene in the reaction mixture, Skattebol (16) found that 95% of the reaction mixture consisted of 1-methyl-1-isopropenylcyclopropane.

Recently, however, tetramethylallene and other tetraalkylallenes have been prepared by pyrolyzing 2,2,4,4-tetraalkyl-3-hydroxy-3-butenoic acid β-lactones (17, 37); and allene itself has been prepared in 16% yield by heating diketene to 550°C under a nitrogen atmosphere in a copper reactor (38).

A novel method for preparing certain allenes is illustrated by the preparation of 1,1- and 1,3-diphenylallene. By treating N-(2,2-diphenylcyclopropyl)-N-nitrosourea in heptane at $0^{o}C$ with sodium ethoxide (or simply by heating the N-(2,2-diphenylcyclopropyl)-N-nitrosourea in heptane) 1,1-diphenylallene is formed (39). Using the same procedure on (-) N-(trans-2,3-diphenylcyclopropyl)-N-nitrosourea yields optically active 1,3-diphenylallene ($[\alpha]_{D}^{24} = + 797^{o}$) (40).

Favorsky (41) was the first to report the synthesis of a cyclic allene when he reported that 1,2-cycloheptadiene was the product obtained when 1-chloro-2-bromocycloheptene in ether solution was treated with sodium metal. Following the report by Favorsky, there were a number of attempts (42-44) by other investigators to prepare 1,2-cyclohexadiene; all these attempts ended in failure. Then in 1948, Domnin (44) reported the synthesis of 1,2-cycloheptadiene and 1,2-cyclooctadiene by the method of Favorsky (41). However, Ball and Landor (45) later showed that the works of both Favorsky and Domnin on the preparation of 1,2-cycloheptadiene and 1,2-cyclooctadiene were in error.

Finally, Blomquist, _et_. _al_. (23, 46) were in 1952 able to successfully prepare 1,2-cyclononadiene and 1,2-cyclodecadiene but then only as a mixture with the analogous cyclic acetylene. However, pure 1,2-cycloalkadienes may be prepared by treating the appropriate _gem_-dibromocyclopropane with an alkyllithium reagent (33).

The preparation of allenes containing halogen, oxygen, and nitrogen is described in a review by Pansevich-Kolyada (47).

Since the chemical properties of allenes have been discussed in the review of Petrov and Fedorova (5), this author will briefly discuss those chemical properties which are essential to this investigation and review the contents of some of the most recent literature.

Allene itself is non-polar because of its symmetry; however, in reactions of allene with hydrogen halides, water, alcohols, free radicals, and 1,3-dipoles (e.g., benzonitrile oxide), allene undergoes electrophilic attack at one of the terminal carbon atoms and nucleophilic attack at the central carbon atom. However, the above generalization does not appear to apply to the addition of mixed halogens, hypohalous acids, and their derivatives to allene. Thus, the addition of compounds to allene remains of theoretical and of practical interest.

It is still more difficult to explain the course of addition to homologues of allene. Addition to allene homologues usually leads to a mixture of the possible isomers; the explanation for this probably lies in the geometry of the allene molecule and in the mechanism of the addition.

It has long been known that allenes react with bromine in chloroform and carbon tetrachloride to give tetrabromides. However, it has been shown recently that, while the addition of the first mole of bromine to allenes is fast, the addition of a second mole of bromine takes place quite slowly (48). Therefore, the dibromides may be isolated. Thus, one mole of bromine adds to allene to form 2,3-dibromopropene; and 2,3-nonadiene and 6-methyl-2,3-heptadiene in chloroform at -40°C react with bromine to yield mixtures from which 70% yields of 3,4-dibromo-2-nonene and 3,4-dibromo-6-methyl-2-heptane, respectively, may be obtained (49).

As one might expect, allenes take part in Diels-Alder reactions. The cumulated double bonds of allenes act as if they were isolated from one another; and because only one of the two double bonds of an allene reacts with the diene, cyclic hydrocarbons with an attached methylene group are the products. For example, allene reacts with a pentane solution of cyclopentadiene to yield 5-methylenebicyclo [2.2.1] hept-2-ene (50). Cyclopentadiene reacts with 2,3-butadienoic acid to yield 3-methylenebicyclo [2.2.1] hept-5-ene-2-carboxylic acid (51).

One very interesting recent development in the field of allene chemistry is that allenes have been found to form complexes with certain metals (52-56). A number of workers have reported the preparation of allenic acids from the appropriate propargyl halide with the aid of nickel tetracarbonyl and carbon monoxide (57-59); other workers have used the action of nickel-containing catalysts on allene to prepare several interesting cyclic compounds (60). A ruthenium carbonyl-allene complex has been used to prepare methyl methacrylate (61). Decomposition of the allene-palladium chloride complex with ethanol and carbon monoxide gives ethyl 2-chloro-2-propenoate (62); and the interaction of a benzene solution of tetraphenylallene with dicobalt octacarbonyl and carbon monoxide yields a mixture of 1,1,3-triphenylindene, 2-diphenylmethyl-3-phenylindenone, and 2,2,4-triphenylnaphthalenone (63).

A number of very interesting allenes have been prepared by treating lithioallene compounds with various reagents (64); for example, the addition of benzoic acid to the 3-lithio-3,4-octadiene yields 3-benzoyl-3,4-octadiene, the addition of benzonitrile to the same lithioallene yields 2,4,6-triphenyl-2-(3,4-octadien-3-yl)-1,2-dihydrotriazine whereas the addition of phenyl isocyanate to 3-lithio-3,4-octadiene yields N-phenyl-2-ethyl-2,3-heptadienamide. The addition of pyridine to the same lithioallene under anhydrous conditions yields 3-(α-pyridyl)-3,4-octadiene; however, if water is added to the reaction mixture after the pyridine has been added to the lithioallene, 3-(1,2-dihydro-α-pyridyl)-3,4-octadiene is the product.

Reaction of the organo-zinc, aluminum or magnesium compound from propargyl bromide with tributyl borate yields the dibutyl allenylboronate (65).

The recent literature shows that allenes may be used with a variety of reagents to prepare compounds that are otherwise difficult to prepare. Diborane reacts with allene to give an interesting cyclic compound, 1,2-trimethylenediborane (66). 1,3-Dibenzoylallene is easily dimerized to 2-benzoylmethyl-3-benzoyl-4-benzoyl-methylene-6-phenyl-γ-pyran (67).

Triphenylallene when treated with acid gives the interesting dimer, 2-(1,3,3-triphenylallyl)-1,3-diphenylindene (68). The allene, 4-bromo-1,2-butadiene, is the starting material for the sterospecific synthesis of the natural product, hypoglycine A, which is probably (+)-2-(S),-4-(S)-2-amino-4,5-methylene-5-hexenoic acid (69).

At -78 °C, tetramethylallene adds oxygen diflouride to give a mixture of 2,4-difluoro-2,4-dimethyl-3-pentanone and 2-fluoro-2,4-dimethylpent-4-en-3-one (70). Ethylene adds to the epoxide of tetracyanoethylene with cleavage of the C--C bond between the $C(CN)_2$-groups to yield 2,2,5,5-tetracyanotetrahydrofuran; allene reacts in a similar manner to give 3-methlene-2,2,5,5-tetracyanotetrahydrofuran (71).

Allenic ketones have been shown to add hydrazine to yield 3-5-disubstituted pyrazoles; for example, 3,4-pentadien-2-one reacts with hydrazine in alcohol solution to give 3,5-dimethyl-4H-pyrazole (72). Substituted hydrazines react with allenic ketones to give N-substituted pyrazoles; for example, the reaction of 3,4-hexadien-2-one with 2,4-dinitrophenylhydrazine gives 3-methyl-5-ethyl-1-(2,4-dinitrophenyl)-4H-pyrazole (73).

Substituted-methylene cyclobutanones may be prepared by treating the appropriate ketene with a suitable allene under a nitrogren atmosphere; for example, tetramethylallene reacts with diphenylketene to form 2-isopropylidene-3,3-dimethyl-4,4-diphenylcyclobutane (74).

Benzonitrile oxide adds to allene in the manner typical of 1,3-dipoles to yield 3,3'-diphenyl-5,5'-spirobi-(4H, 5H-isoxazoline) and a small amount of diphenylfuroxan (75).

Diazomethane is another 1,3-dipole whose addition to allene is completely orientation specific. D'yankanov (76) was the first to add diazomethane to allene but was uncertain as to the position of the substituent. Recently, however, the structure of the adduct, 4-methylene-1-pyrazoline, was determined independently by two investigators (77,78).

In a slightly different reaction, benzoyldiazomethane reacts with cyanoallene to produce 3-benzoyl-5-cyano-4-methylpyrazole, which may add a second molecule of cyanoallene to yield N-(1-cyanopropen-2-yl)-3-benzoyl-5-cyano-4-methylpyrzole (79).

CHAPTER II

STATEMENT OF THE PROBLEM

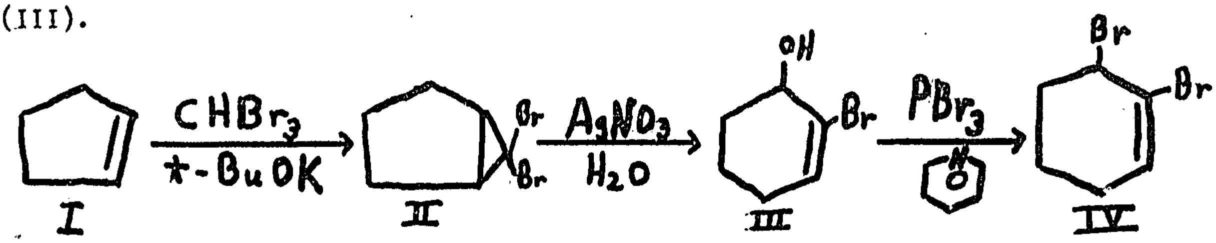
This investigation was undertaken in an attempt to form strained cyclic allenes and to study their chemistry. The method chosen for the attempted formation of strained cyclic allenes was the debromination of the corresponding 2,3-dibromocycloalkene. 2,3-Dibromocyclononene was synthesized during the course of this investigation so that its debromination to the 1,2-cyclononadiene, which is the smallest stable, 1,2-cycloalkadiene, could be studied as a model for the debromination of smaller 2,3-dibromocycloalkenes. An exploration of methods for making smaller 2,3-dibromocycloalkenes was initiated. The formation of 1,2-cyclohexadiene was attempted by the debromination of the 2,3-dibromocyclohexene. Evidence for the presence of this unstable intermediate was sought via the use of trapping agents.

CHAPTER III

RESULTS AND DISCUSSION

I. PREPARATION OF 2,3-DIBROMOCYCLOHEXENE

2,3-Dibromocyclohexene (IV) was prepared from cyclopentene (I) via 6,6-dibromobicyclo[3.1.0]hexane (II) and 2-bromo-3-hydroxycyclohexene (III).



6,6-Dibromobicyclo[3.1.0]hexane was prepared from cyclopentene by the method of von Doering and Hoffmann (31) in which a solution of potassium t-butoxide in t-butyl alcohol was added to a solution of cyclopentene, bromoform, and pentane* in t-butyl alcohol at 0°C. Yields of up to 56% of the 6,6-dibromobicyclo[3.1.0]hexane were obtained with this method. The use of this method is complicated by certain definite problems. First, yields are lowered by the reaction of potassium t-butoxide with t-butyl alcohol as was shown by the fact that solutions of potassium t-butoxide turned orange on standing for about 24 hours. Second, with the amounts of reagents utilized, the addition of the t-butyl alcohol solution of potassium t-butoxide took 18 hours. And third, it was found to be necessary to wash the pentane* solution of the product with twice the quantity of water specified in the original literature in order to remove all of the t-butyl alcohol. A slightly modified method, in which a solution of bromoform in pentane* is added to a slurry of potassium _t_-butoxide and the olefin in pentane*, eliminated most of the problems. Yields of up to 72% were obtained by this modified method.

2-Bromo-3-hydroxycyclohexene was prepared by the method of Sonnenberg and Winstein (80) in which 6,6-dibromobicyclo [3.1.0] hexane was treated with aqueous silver nitrate. The crude product was purified by distillation followed by crystallization from petroleum ether on a dry ice-acetone bath. The petroleum ether filtrate from the above crystallization gave a positive test for nitrogen. Analysis of the liquid by gas chromotography showed that it contained about 20% of a liquid which showed infrared absorptions characteristic of a nitrate ester. This material was probably 2-bromo-2-cyclohexen-1-yl nitrate (80). This result is contrary to the findings of Sonnenberg and Winstein who found that no covalent nitrate formed in this reaction. However, they used very small amounts of reagents (2.5 mmoles of 6,6-dibromobicyclo [3.1.0] hexane and 5 ml. of 1 _M_ aqueous silver nitrate) and a one hour reaction time in contrast to this author's use of 0.329 moles of 6,6-dibromobicyclo [3.1.0] hexane and 660 ml. of 1 _M_ aqueous silver nitrate with a reaction of 7½ hours. During the reaction, the reaction mixture becomes acidic because of the accumulation of nitric acid (the final concentration of the acid is 0.5 _M_, assuming complete conversion of the 6,6-dibromobicyclo [3.1.0] hexane to 2-bromo-3-hydroxycyclohexene). It seems likely that this discrepancy is explained by nitric acid nitrating some of the 2-bromo-3-hydroxycyclohexene during the extended reaction period. While the yield of 2-bromo-3-hydroxycyclohexene obtained by this author is fairly satisfactory, it is possible that the yield might be improved by keeping the pH of the reaction mixture around pH 7 with the aid of a "pH stat." Since hydrolysis of nitrate esters leads to carbonyl compounds and other undesirable side products (81, 82), it would not be profitable to attempt to hydrolyze the 2-bromo-2-cyclohexene-1-yl nitrate formed during the conversion of 6,6-dibromobicyclo[3.1.0]hexane to 2-bromo-3-hydroxycyclohexene. However, the use of silver acetate as the Lewis acid to remove one of the bromine atoms from the 6,6-dibromobicyclo[3.1.0]hexane might eliminate the problem of ester formation since any acetate ester which formed should be easily hydrolized to 2-bromo-2-hydroxycyclohexene by sodium hydroxide. Sonnenberg and Winstein (80) also prepared 2-bromo-3-hydroxycyclohexene by refluxing 6,6-dibromobicyclo[3.1.0]hexane in aqueous acetone for 24 hours. However, the infrared spectrum of the product showed that it was contaminated with a small amount of a substance with a carbonyl group. This author did not evaluate this procedure for preparing 2-bromo-3-hydroxycyclohexene.

2,3-Dibromocyclohexene was prepared by treating an ether solution of 2-bromo-3-hydroxycyclohexene and pyridine with phosphorous tribromide. It is of interest to note that Sonnenberg and Winstein (80) have shown that 2,3-dibromocyclohexene may be obtained directly by heating 6,6-dibromobicyclo[3.1.0]hexane; indeed, Stevens and Valicenti (83) obtained 2,3-dibromocyclohexene from 6,6-dibromobicyclo[3.1.0]hexane in 27% over-all yield by this method. However, this author obtained a higher (as much as 37% over-all) yield by preparing 2,3-dibromocyclohexene in two steps via 2-bromo-3-hydroxycyclohexene.

II. ATTEMPTED PREPARATION OF 2,3-DIBROMOCYCLOHEPTENE

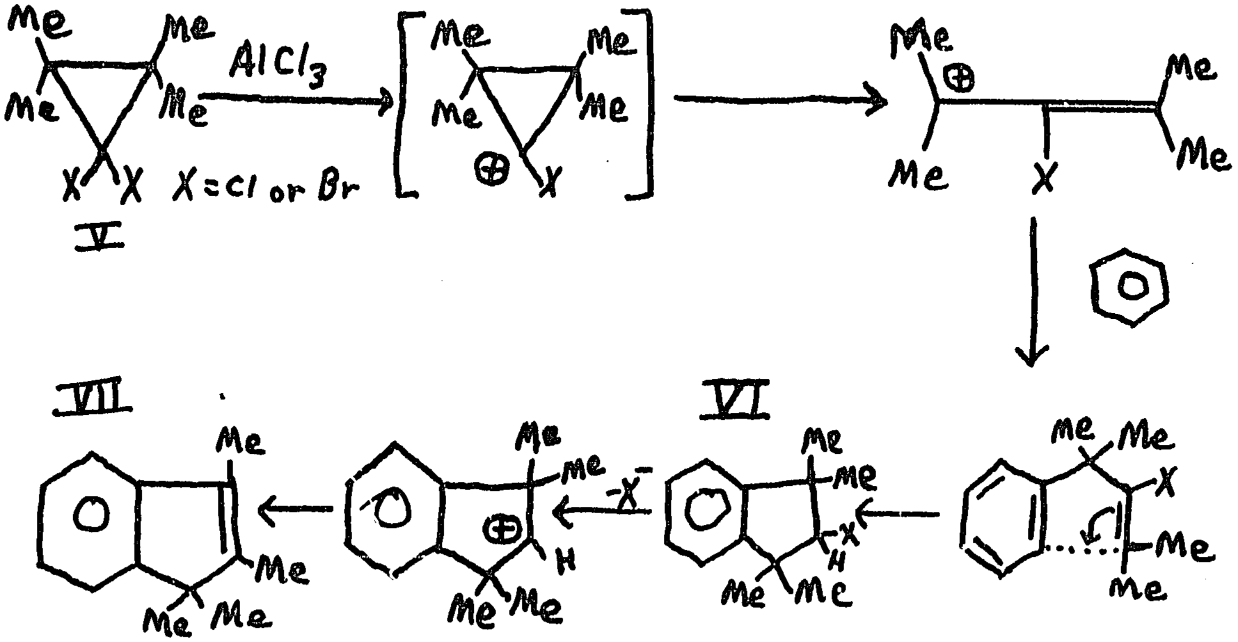
Among the original aims of this investigation was the synthesis of the series of 2,3-dibromocycloalkenes: 2,3-dibromocyclohexene, 2,3-dibromocycloheptene, 2,3-dibromocyclooctene, and 2,3-dibromocyclononene. When this investigation was begun, only 2,3-dibromocyclohexene had been reported.

7,7-Dibromobicyclo [4.1.0] heptane was prepared by the method of von Doering and Hoffman (31). The same problems that were encountered in the preparation of 6,6-dibromobicyclo[3.1.0] hexane by this method were encountered in the preparation of 7,7-dibromobicyclo [4.1.0] heptane.

A report by Skell and Sandler (84) indicated that the reaction of aqueous silver nitrate with gem-dibromocyclopropanes to give 2-bromo-3-hydroxyalkenes was a general reaction. They reported that the rate of reaction of aqueous silver nitrate with 6,6-dibromobicyclo [3.1.0] hexane was 200 times the rate of reaction of aqueous silver nitrate with 7,7-dibromobicyclo [4.1.0] heptane. Therefore, it seemed reasonable to expect that 7,7-dibromobicyclo [4.1.0] heptane would react with aqueous silver nitrate to yield 2-bromo-3-hydroxycycloheptene, which could be brominated with phosphorous tribromide to 2,3-dibromocycloheptene. Accordingly, several experiments were carried out in an attempt to apply this procedure to 7,7-dibromobicyclo [4.1.0] heptane. However, when a mixture of aqueous silver nitrate and 7,7-dibromobicyclo [4.1.0] heptane was stirred at room temperature for six days, only starting material and a very small amount (about 0.01 g.) of a black precipitate were obtained. When aqueous silver nitrate and 7,7-dibromobicyclo [4.1.0] heptane were refluxed for 2½ days, only a very small amount (about 0.2 g.) of a yellow liquid which quickly turned black, and a small amount (about 0.1 g.) of a black precipitate were obtained. In neither experiment was any silver bromide formed.

In preliminary experiments, this author observed some silver bromide precipitate when 7,7-dibromobicyclo [4.1.0] heptane was treated with aqueous silver nitrate; however, when 7,7-dibromobicyclo [4.1.0] heptane was purified by two careful distillations, no precipitate of silver bromide was observed upon treatment with aqueous silver nitrate. It seems likely that the 7,7-dibromobicyclo [4.1.0] heptane used by Skell and Sandler (84), when they determined the rates of reaction of 6,6-dibromobicyclo [3.1.0] - hexane and 7,7-dibromobicyclo [4.1.0] heptane with aqueous silver nitrate, was impure.

In a recent report, Skattebol and Boulette (85) reported the preparation of some substituted indenes by treating gem-dihalocyclopropanes in benzene solution with anhydrous aluminum chloride. During the reaction, the gem-dihalocyclopropane underwent ring opening to an allylic carbonium ion which added to benzene and then cyclized. 2-Haloindenes (VI) which could be isolated when the proper conditions were employed, were postulated

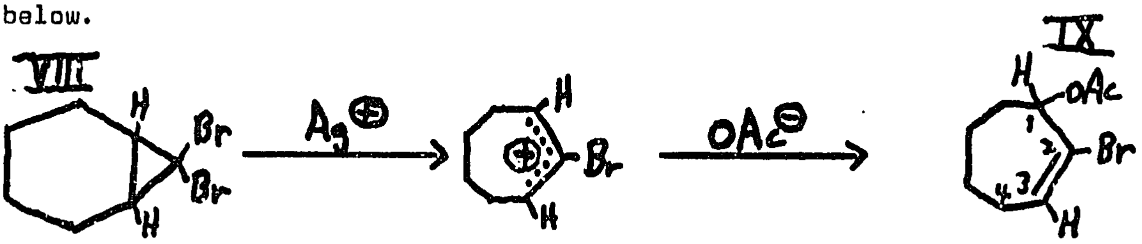


as intermediates. It seemed reasonable, therefore, that the reaction of 7,7-dibromobicyclo [4.1.0] heptane with anhydrous aluminum bromide might lead to 2,3-dibromocycloheptane. However, the addition of a pentane* solution of 7,7-dibromobicyclo [4.1.0] heptane to an equimolar amount of anhydrous aluminum bromide in pentane* gave only a tar and a small amount (about 0.5 g.) of a very smelly liquid, which quickly turned black. The addition of a similar solution of 7,7-dibromobicyclo [4.1.0] heptane to anhydrous aluminum bromide (one tenth mole per mole of the gem-dibromide) in pentane* gave only starting material and a small amount (about 0.1 g.) of a low-boiling, black liquid. Two similar experiments using ether as the solvent instead of pentane* were performed. In both cases, however, the 7,7-dibromobicyclo [4.1.0] heptane was recovered unchanged.

III. PREPARATION OF AND ASSIGNMENT OF STRUCTURE TO 2-BROMO-2-CYCLOHEPTEN-1-YL ACETATE

2-Bromo-2-cyclohepten-1-yl acetate was prepared by refluxing 7,7-dibromobicyclo [4.1.0] heptane with silver acetate in concentrated acetic acid. The yield of the acetate was low (21.2%) and the acetate was shown by gas chromatography to be contaminated with about 10% of lower-boiling substances even after two fractional distillations. It should be noted, however, that the gem-dibromide starting material was contaminated with as much as 5% low-boiling material since this 7,7-dibromobicyclo [4.1.0]-heptane was recovered from previous attempts to prepare 2,3-dibromocycloheptene. However, the most important reasons for the low yield of 2-bromo-2-cyclohepten-1-yl acetate were handling errors and errors in the work up. A small amount of the reaction mixture was spilled. However, the attempt to neutralize the concentrated acetic acid with solid sodium bicarbonate was the most serious procedural error. Not only did the neutralization process consume a large amount of sodium bicarbonate but increased spattering may have contributed to the loss of product. The following procedure is recommended. Reflux the concentrated acetic acid with a few mililiters of acetic anhydride to remove water from the acid before the other reagents are added. Reflux the reaction mixture for a longer period of time (perhaps 48 hours). Remove the precipitated silver bromide by filtration and remove the excess acid under reduced pressure. Add ether and remove the last traces of acid with sodium bicarbonate solution. The 2-bromo-2-cyclohepten-1-yl acetate may then be purified in the conventional manner.

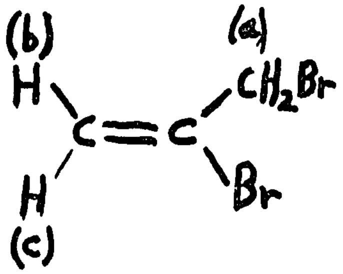
A mechanism which would account for the rearrangement of 7,7-dibromobicyclo [4.1.0] heptane to 2-bromo-2-cyclohepten-1-yl acetate is given below.

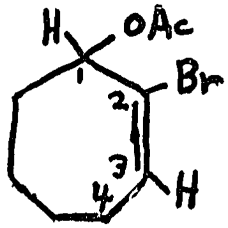


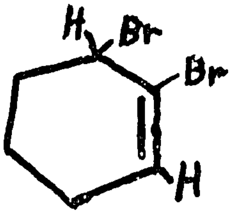
The assignment of the structure, IX, to the product of the rearrangement reaction is based on the following data: a satisfactory elemental analysis for the empirical formula $C_9H_{13}BrO_2$, infrared analysis, and NMR analysis of samples purified by gas chromatography.

The infrared spectrum (IR-5) included a strong absorption at 1740 cm.$^{-1}$ (ν C=O of an ester carbonyl) a weak absorption band at 1625 cm.$^{-1}$(νC = C), an absorption of medium intensity at 1445 cm.$^{-1}$ (allylic CH bending), a strong absorption at 1365 cm.$^{-1}$ (CH bending of acetate methyl), and a strong, broad absorption at 1245 cm.$^{-1}$ (ν_{as}C--O--C of an ester) (86, p. 20-48).

The NMR spectrum (NMR-2) is also consistent with the proposed structure. The spectrum shows a quartet (J = 6.7 cps.) centered at 3.72τ(1.02) which is the correct position for a vinyl proton (87, p. 60-62). The quartet is explained by a splitting of the vinyl proton by two nonequivalent methylene protons. The position of the vinyl-proton absorption may be compared with the proton (c) (τ = 3.98) (88) of 2,3-dibromopropane, which is cis to the vinyl bromine atom as is the vinyl proton







cis to the bromine atom in 2-bromo-2-cyclohepten-1-yl acetate (because of the size of the cycloheptene ring, the carbon atoms attached to the double bond must be cis to each other). The position of the vinyl absorption of 2-bromo-cyclohepten-1-yl acetate is also comparable to that of the vinyl proton of 2,3-dibromocyclohexene (3.84τ).

2-Bromo-2-cyclohepten-1-yl acetate has an absorption at 4.58τ(1.02), which is consistent with that expected for the allylic methine proton at the 1-position. This absorption appears to be a poorly resolved and broadened doublet (J = 4.9 cps.). The splitting pattern may be rationalized by considering that the two adjacent methylene protons are nonequivalent at the temperature of the determination. One proton has a very small coupling constant, perhaps 0.1 cps., while the other proton has a coupling constant of about 4.9 cps. The methine proton of a secondary alkyl acetate ($>$C$\underline{H}$—OAc) absorbs at about 5.0τ(89, p. 86-88). The inductive effect of the vinyl bromide group ($>$C = C$<^{Br}$) would be expected to shift the absorption to lower field.

The total relative area between 7.60τ and 7.96τ was 5.0. The sharp peak at 7.96τ is assigned to the methyl of the acetoxy group (89, p. 86). The absorption of the allylic methylene protons at C-4 would be expected to be shifted to lower field than the other methylenes and account for the absorption in this region. The relative area of the poorly resolved multiplet at 8.22τ was 6.0 and is assigned to the remaining six methylene protons. The methylene protons of cycloheptane absorb at 8.47τ(89, p. 86).

IV. PREPARATION OF AND ASSIGNMENT OF STRUCTURE TO 2,3-DIBROMOCYCLONONENE

2,3-Dibromocyclononene was prepared in 30% yield by brominating 1,2-cyclononadiene in carbon tetrachloride solution at -20°C. The 1,2-cyclononadiene was prepared by two different methods. In the first method, that of Untch, et al. (36), 1,2-cyclononadiene was prepared in one step from cyclooctene. A four-fold excess of cyclooctene and one equivalent of carbon tetrabromide at -65°C was treated with two equivalents of methyllithium in ether. The yield of 1,2-cyclononadiene by this method has been estimated by Untch, et al., by gas chromatography to be about 74%. This method is convenient as the yields are good and the 1,2-cyclononadiene is prepared in one step instead of two. However, this author was never able to achieve a satisfactory separation of the excess cyclooctene from the 1,2-cyclononadiene with the available equipment.

1,2-Cyclononadiene was also prepared from 9,9-dibromobicyclo [6.1.0]-nonane (33). The 9,9-dibromobicyclo [6.1.0] nonane was prepared by the method of von Doering and Hoffmann (31) in which a solution of bromoform in pentane* was added to a stirred slurry of potassium _t_-butoxide in cyclooctene and pentane*. This particular method is much more convenient than the method used to prepare 6,6-dibromobicyclo [3.1.0] hexane and 7,7-dibromobicyclo [4.1.0] heptane. Larger yields (up to 72%) are obtained by this method. The total reaction time is less than half the reaction time needed by the other method. The reaction of the potassium _t_-butoxide with _t_-butyl alcohol is minimized (the only _t_-butyl alcohol in the reaction mixture is that formed during the reaction), and the problem of removing all of the _t_-butyl alcohol from the reaction mixture is minimized since the amount of _t_-butyl alcohol involved is only that which is formed during the reaction and is a much smaller amount than that used when a _t_-butyl alcohol solution of potassium _t_-butoxide is employed. Addition of an ether solution of methyllithium to an ether solution of 9,9-dibromobicyclo [6.1.0]-nonane at -65°C yields 1,2-cyclononadiene. While the two-step method is not as convenient, time-wise, as the one-step method for preparing 1,2-cyclononadiene, this author was able to obtain good yields (51% over-all) of pure 1,2-cyclononadiene by the two-step method with the available equipment.

The yields of 2,3-dibromocyclononene from the bromination of 1,2-cyclononadiene were only fair (about 30%) and the twice distilled product was still impure. However, samples for elemental analysis, infrared analysis, and NMR analysis were obtained by preparative gas chromatography.

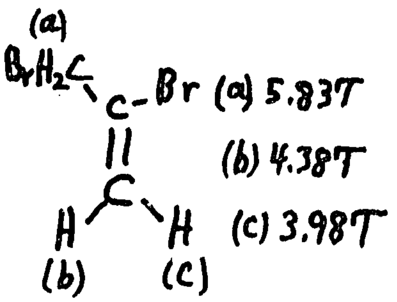
Apparently, the addition of bromine to 1,2-cyclononadiene under the conditions employed during this investigation leads to an unstable side-product in addition to 2,3-dibromocyclononene, or 2,3-dibromocyclononene undergoes partial decomposition during the work up of the reaction mixture. In any event, a large amount of a smelly black liquid is obtained as the forerun. 2,3-Dibromocyclononene is somewhat unstable. Freshly distilled samples turn yellow on standing for a few days even when stored under nitrogen and in a refrigerator. The elemental analysis was consistent with the empirical formula, $C_9H_{14}Br_2$. The infrared spectrum (IR-8) showed an absorption band of medium intensity at 1635 cm.$^{-1}$ (νC = C) (86, p. 24). Debromination of the product with magnesium and zinc in tetrahydrofuran to 1,2-cyclononadiene was additional evidence for the structure, 2,3-dibromocyclononene.

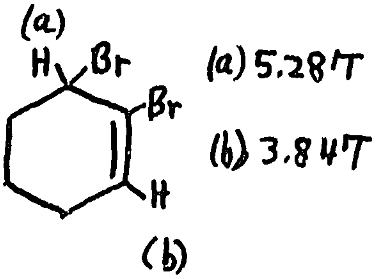
Both *cis*- and *trans*-cyclononene have been prepared (87). It was possible by the use of Fisher-Hirshfelder-Taylor models to construct molecular models for both the *cis*- and *trans*-isomers of 2,3-dibromocyclononene.

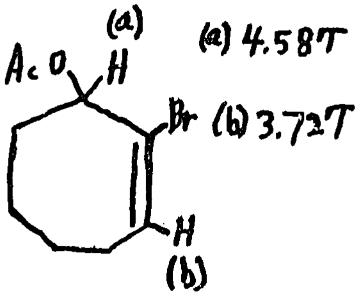
The NMR spectrum (NMR-3) showed two overlapped triplets at 3.89 τ (J = 8.8 cps.) and 4.11 τ (J = 8.8 cps.) which are in the expected position (87, p. 60-62) for vinyl protons and whose total relative area was 1.03. A quartet at 4.86 τ (J = 5.3 cps.) and a quintet (J = 5.8 cps.) at 5.84 τ, whose total relative area was 1.03, were in the position expected for an allylic methine proton. A multiplet at 7.28 τ, a broad, poorly resolved multiplet at 7.90 τ, and broad, poorly resolved singlets at 8.38 τ and 8.47 τ, whose total relative area was 11.95, were in the expected position for methylene protons of cyclic compounds (89, p. 86). The absorption of the allylic methylene protons at C-9 would be expected to be at lower field, as compared with the other methylene protons, because of its being adjacent to the carbon-carbon double bond. This would account for the absorption at 7.28τ. The simplest explanation which would account for this NMR data is that the 2,3-dibromocyclononene is a mixture of cis- and trans-2,3-dibromocyclononene. This assumption was verified by gas chromatography of the 2,3-dibromocyclononene. Two partially resolved peaks (see Fig. 1) were observed. Assuming that the height of the central peak of each of the two vinyl triplets was proportional to the amount of that isomer present in the mixture, the amount of the isomer with the triplet at 3.89τ was estimated to be 40% of the mixture and the isomer with the triplet at 4.11τ was estimated to be 60% of the mixture. A separation of the material (Fraction B), corresponding to the peak with the longest retention time (Peak B), from the mixture was achieved. The minimum purity of Fraction B was estimated from its NMR spectrum (NMR-4) by comparing the area under the strongest absorption in the vinyl proton triplet (4.11τ) of Fraction B with the area under the trace in the vicinity of the highest peak of the 3.89τ triplet found in the mixture. This method assumes that the area of the central peak of the triplet is proportional to the amount of that isomer present. The minimum purity of Fraction B was estimated to be 85%. The NMR spectrum of Fraction B (NMR-4) showed a triplet ($J = 8.8$ cps.) at 4.11τ (0.98), a quintet ($J = 5.8$ cps.) at 5.89τ (0.98), a multiplet at 7.28τ, a poorly resolved multiplet at 8.00τ, and a singlet at 8.37τ whose total relative area was 12.06. The triplet at 4.11τ is in the position expected for a vinyl proton. The triplet is explained by a splitting of the vinyl proton by two equivalent protons. While the quintet at 5.89τ is in the expected position for an allylic proton, the splitting pattern is not explainable by simple analysis.

Simple analysis predicts that the minimum number of peaks would be three if the allylic proton is split by two equivalent protons and would be four peaks if the allylic proton is split by two nonequivalent protons. The multiplet at 7.28τ is expected because the allylic methylene protons at C-9 are expected to be shifted to a lower field than ordinary ring methylene protons because these allylic protons are adjacent to the carbon-carbon double bond. The multiplet at 8.00τ and the singlet at 8.37τ are in the position expected for methylene protons of cycloalkenes (cyclooctane methylene protons absorb at 8.47τ (89, p. 86).

If vinyl and allyl absorptions of Fraction B (NMR-4) are "substracted" from the spectrum of the mixture (NMR-3) and only the remaining vinyl and allyl absorptions are considered, a triplet (J = 8.8 cps.) at 3.89τ and a quartet (J = 5.3 cps.) at 4.86τ remain. The absorption at 3.89τ corresponds closely to the position of the absorption of proton (c) of 2,3-dibromopropene (88), the vinyl proton of 2,3-dibromocyclohexene, and the vinyl proton of 2-bromo-2-cyclohepten-1-yl acetate, all of which must have vinyl protons which are cis to the vinyl bromine atom (the ring size of the cyclic compounds prohibits a trans-configuration of the carbon atoms attached to the double bond). Proton (b) of the 2,3-dibromopropene, which is trans to the vinyl bromine atom absorbs







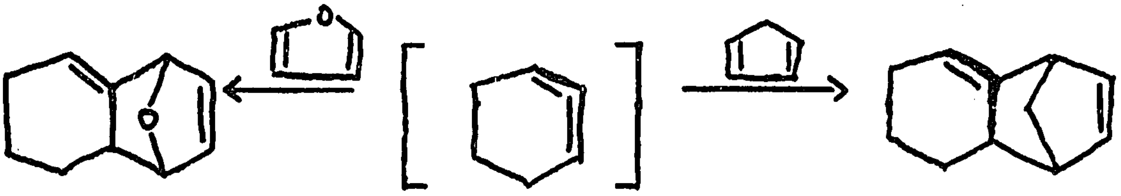
at higher field than proton (c) which is cis to the vinyl bromine atom. The high field triplet (4.11τ) of 2,3-dibromocyclononene corresponds closely to the position of proton (b). On this basis, cis-2,3-dibromocyclononene is the material designated Fraction A, which has the vinyl absorption at 3.89τ, and trans-2,3-dibromocyclononene is assigned as the structure of the material in Fraction B, whose vinyl proton absorbs at 4.11τ.

V. DEBROMINATION OF 2,3-DIBROMOCYCLONONENE

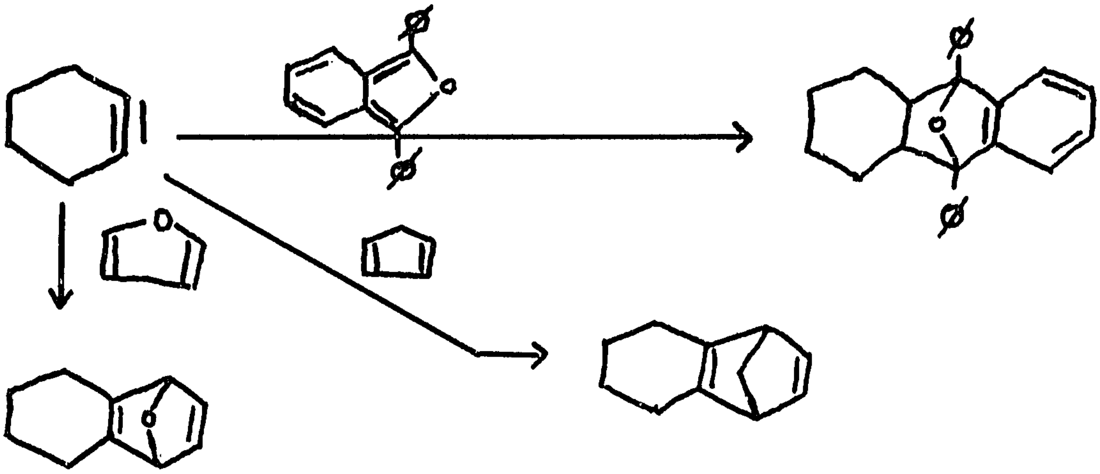
2,3-Dibromocyclononene was debrominated with magnesium in tetrahydrofuran and with magnesium in ether. 2,3-Dibromocyclononene was also debrominated with zinc dust in tetrahydrofuran. In each case, the product of the debromination was shown to be 1,2-cyclononadiene. This was established by the identity of the gas chromatography retention times with that of authentic samples and, in one case, the identity of the infrared spectrum with that of the authentic material. The debromination of 2,3-dibromocyclononene with metals to 1,2-cyclononadiene confirms the structure of 2,3-dibromocyclononene. An attempt was made to prepare a Diels-Alder adduct of 1,2-cyclononadiene, produced in one of the debromination reactions, with furan; this attempt was unsuccessful.

VI. DEBROMINATION OF 2,3-DIBROMOCYCLOHEXENE

A number of reports of the attempted preparation of 1,2-cyclohexadiene have been published (42-44); all of these attempts ended in failure. Models show that 1,2-cyclohexadiene would be a highly strained and, therefore, a very reactive molecule. It would be expected to isomerize or polymerize very quickly at room temperature. No previous attempts have been made to trap 1,2-cyclohexadiene as an unstable intermediate. With such reagents as furan or cyclopentadiene, 1,2-cyclohexadiene would be expected to react as in the equations below (50, 51), while



the isomeric cyclohexyne intermediate has been shown to add to 1,3-diphenylisobenzofuran to give 9,10-oxido-9,10-diphenyl-1,2,3,4,9,10-hexahydroanthracene (91-93) and could be expected to react analogously with furan or cyclopentadiene as in the equations below.



Accordingly, 2,3-dibromocyclohexene was debrominated in the presence of several trapping agents in hopes that any 1,2-cyclohexadiene which might be produced during a reaction would react in the predicted manner with the trapping agent.

Debromination of 2,3-dibromocyclohexene with magnesium in tetrahydrofuran at room temperature gave only a small amount of tar.

The debromination was also carried out in the presence of cyclohexene. The product of this reaction was a tar. No evidence for a 1:1 adduct was found.

The next series of experiments involved the debromination of 2,3-dibromocyclohexene by magnesium in tetrahydrofuran in the presence of tetraphenylcyclopentadienone, furan, and cyclopentadiene. All of the experiments were performed at room temperature.

The tetraphenylcyclopentadienone appeared to undergo some sort of reduction during the debromination. A small amount of a brown solid of indefinite composition was the only product isolated from the reaction.

Undistillable tars were the only products isolated when the debromination of 2,3-dibromocyclohexene with magnesium was performed in the presence of furan and in the presence of cyclopentadiene.

From the results of the debromination of 2,3-dibromocyclohexene with magnesium in tetrahydrofuran at room temperature, it appears that the rate of polymerization of 1,2-cyclohexadiene (if it is formed) is much greater than the rate of addition to a trapping agent. Lower temperatures and lower concentrations should lead to a lower rate of polymerization and the chance of intercepting 1,2-cyclohexadiene should be enhanced. Perhaps the conditions under which cyclobutadiene was prepared and trapped will be the proper conditions (94).

CHAPTER IV

EXPERIMENTAL

I. INTRODUCTION

The liquids used in this investigation were bromoform, pentane* t-butyl alcohol, cyclopentene, ether, phosphorous tribromide, pyridine, cyclohexene, glacial acetic acid, cyclooctene, methyl, iodide, bromine, 1,2-dibromoethane, tetrahydrofuran (THF), and cyclopentadiene. The details regarding source, purity, and special treatment have been given for each substance.

Bromoform (Eastman Kodak practical grade) was first dried over anhydrous magnesium sulfate and then twice distilled; the liquid boiling in the range of 147-8°C was collected and considered pure.

The pentane* was prepared from petroleum ether (30-60°). About 4.6.1. of petroleum ether was treated with 800 ml. of concentrated sulfuric acid. The mixture was kept on an ice bath at 0°C and stirred for 2½ hours. The acid layer was removed; and the pentane* was washed with 1 l. of water, 1 l. of 10% sodium bicarbonate, and 1 l. of water, Excess water was removed from the pentane* with calcium chloride. Further removal of water was accomplished with calcium hydride. The pentane* was distilled (boiling range = 36-56°C) from several grams of fresh calcium hydride. The pentane* was examined for "unsaturates" with bromine and basic aqueous potassium permanganate. No indication of "unsaturates" in the sulfuric acid-treated petroleum ether was found. Hereafter, petroleum ether treated as above is simply called pentane*.

J. T. Baker reagent grade t-butyl alcohol was used after being dried. To 4.5 l of the t-butyl alcohol was added 5 g. of sodium metal, from which all the oxide coating had been scraped with a knife. When all the sodium had dissolved, the mixture was distilled. The procedure was repeated with an additional 5 g. of sodium. Liquid boiling in the range of 82.5-83.0°C was collected and stored in tightly stoppered jugs until needed.

Cyclopentene was obtained from Aldrich Chemical Company and was used without additional treatment.

J. T. Baker "anhydrous" ether was used after being dried over sodium-lead alloy for at least 24 hours before use.

Phosphorus tribromide was obtained from a tightly stoppered bottle on which the manufacturer's name and statement of purity had been obliterated by action of the acid. However, this phosphorus tribromide gave quite satisfactory results when used.

The pyridine was 'Baker Analyzed' Reagent and was used without additional treatment.

The cyclohexene was carefully redistilled (b.p. = 82-3°C) and stored in a tightly stoppered bottle in a refrigerator until needed.

Dupont reagent grade glacial acetic acid was used without additional treatment.

Cyclooctene was taken from a bottle of Aldrich Chemical Company reagent grade cyclooctene and used without additional treatment. When the cyclooctene was analyzed by gas chromatography (5' x ¼" pyrex glass column packed with 20% Apiezon L and 30/60 mesh Chromosorb P, helium flow =

120 ml./min., injector = 155°C, detector = 157°C, and column = 100°C), the chromatograms showed a peak (retention time = 13.5 minutes) which corresponded to about 99% of the total peak area.

Fischer Certified reagent grade methyl iodide was used without additional treatment. However, methyl iodide from a bottle of 'Baker Analyzed' reagent was noted to be badly discolored, and it was necessary to distill the contents of this particular bottle of methyl iodide. The methyl iodide was distilled from a small amount of pure copper wire through a 6" column packed with ¼" sections of glass tubing. The purified reagent boiling in the range 42.0-42.2°C had n_D^{22} = 1.5302 (literature value (95): n_D^{25} = 1.5317) and was stored over several pieces of pure copper wire in a tightly stoppered brown bottle. Before storage and after each use, the bottle was flushed with nitrogen.

'Baker Analyzed' reagent bromine was used without further treatment.

1,2-Dibromoethane from a bottle of Eastman Kodak reagent was used without additional treatment.

Furan (Aldrich Chemical Company) was used without additional treatment. Analysis of the furan by gas chromatography (5' x ¼" pyrex glass column packed with 10% Carbowax 20M in hexamethyldisilane (HMDS) treated 80/100 mesh Chromosorb P, helium flow = 120 ml./min., injector = 112°C, detector = 115°C, and column = 53°C) showed a peak (retention time = 0.9 minutes) which corresponded to about 98% of the total peak area.

Tetrahydrofuran (THF) from a bottle of 'Baker Analyzed' reagent was first treated with potassium hydroxide pellets. The mixture was allowed to stand for several hours with occasional shaking. The potassium hydroxide was removed by filtration and the THF was dried by refluxing it over calcium hydride for 4 hours. The dry THF was then distilled from lithium aluminum hydridge; the fraction boiling in the range of 65.0-65.5°C was collected and stored over sodium-lead alloy in a tightly stoppered bottle which was kept in a refrigerator until needed.

Cyclopentadiene was prepared by heating Eastman Kodak technical grade cicyclopentadiene to the boiling point. The cyclopentadiene was collected after distillation through a 6" column packed with ¼" sections of glass tubing (b.p. = 41°C).

Both the hexane and the heptane used were of "Chromatoquality" (99 + mole per cent) from Matheson, Coleman, and Bell. Both were used without additional treatment.

Chloroform, stabilized with 0.75% ethanol, from Matheson, Coleman, and Bell was used without additional treatment.

Because the carbon tetrachloride was from a five-gallon can of "uncertain ancestory," the method listed by Fieser (96) was used to purify it. About 1500 ml. of carbon tetrachloride was shaken with 1/10 its volume of concentrated KOH solution and alcohol while being maintained at about 60°C. After three repetitions of that treatment, the carbon tetrachloride was stirred at 25°C with small portions of concentrated sulfuric acid until there was no further coloration of the acid layer. The carbon tetrachloride was then washed with water, dried over calcium chloride, and distilled. The fraction boiling in the range of 76.7-77.0°C was retained and stored in a tightly stoppered bottle until needed.

The solids used during this investigation were potassium metal, silver nitrate, anhydrous aluminum bromide, silver acetate, potassium t-butoxide, lithium metal, carbon tetrabromide, magnesium powder, zinc dust, hydroquinone, tetraphenylcyclopentadienone, silica gel G, and alumina G.

Potassium metal, reagent grade from Baker and Adamson Company (B & A), was prepared for use by trimming off the outer layer of oxide with a knife, while being careful to keep the fresh metal surface covered with mineral oil. The metal was then rinsed in petroleum ether to remove the mineral oil, dried by briefly shaking small pieces of the metal in the air, and weighed by placing the necessary amount of clean metal into a previously weighed beaker of petroleum ether. The weighed potassium was then transferred piece by piece after being briefly air dried to a flask filled to about 2/3 of its capacity with dry t-butyl alcohol. A drying tube filled with calcium chloride and soda lime was fitted to the flask while the potassium was in the process of dissolving in the t-butyl alcohol.

The Fischer Certified reagent grade silver nitrate was used without further treatment.

The anhydrous aluminum bromide also was Fischer Certified reagent and was used without further treatment. However, the opened container was flushed with nitrogen and tightly capped after each use. The container was then stored in a desiccator.

The purified silver acetate was from the J. T. Baker Chemical Company and was used without additional treatment.

Dry potassium t-butoxide was obtained from K and K Laboratories and was of reagent grade; the potassium t-butoxide came in bottles containing 100 g. of the reagent. Each bottle was sealed against atmospheric moisture with wax. Since potassium t-butoxide is extremely hygroscopic, it was found to be most convenient to use the entire contents of two such bottles (200 g. total) and to adjust the proportions of the other reagents to the amount of potassium t-butoxide during preparations involving this reagent. The reaction flask was charged with potassium t-butoxide and pentane* through a powder funnel while the reagents, the reaction flask, etc., more contained within a "glove-bag" which had been purged of air with nitrogen.

High purity lithium ribbon from Foote Mineral Company came covered with petrolatum and was wound on a reel. The lithium ribbon was quite uniform in the amount of lithium per centimeter of length (0.089 g. per centimeter) and was "weighed" by cutting off the calculated length as 10 centimeter strips plus any necessary fraction thereof. The strips of lithium were placed in a large beaker of petroleum ether in order to remove the petrolatum. Meanwhile, the 3-neck reaction flask was fitted with a stirrer, a reflux condenser to which had been attached a nitrogen inlet, and glass stopper. The necessary amount of ether was placed in the reaction flask. The reaction flask was purged with nitrogen and then fitted with a powder funnel through which nitrogen continuously flowed via the condenser and the reaction flask. The strips of lithium ribbon were thus continuously bathed in nitrogen as they were cut into small pieces and fell into the ether in the reaction flask through the powder funnel.

The zinc dust was of uncertain origin. The method of Fieser and Johnson (97) was used to remove sulfide and oxide from the surface of the particles of zinc. To about 25 g. of zinc dust was added 25 ml. of concentrated sulfuric acid to which a few drops of concentrated nitric acid had been added. The concentrated acid was allowed to act on the zinc dust for 10 minutes; then the excess acid was decanted. The remaining acid was diluted with water, and the dilute solution was allowed to react with the zinc dust for an additional 10 minutes. Filtration removed the zinc dust from the acid. Then the zinc dust was washed with water, acetone, and ether. The required amount of the purified zinc dust was weighed out and placed in the reaction flask, which had previously been thoroughly flushed with nitrogen. Then the zinc dust was thoroughly dried by heating the bottom and sides of the reaction flask with a bunsen burner. The reaction flask and its contents were allowed to cool before the other reagents were added.

Eastman Kodak reagent grade carbon tetrabromide was used without additional treatment.

'Baker Analyzed' reagent grade magnesium powder was used without additional treatment.

Photographic grade hydroquinone from Braun-Knecht-Heiman Company was used without further treatment.

The author is deeply indebted to Mr. William Gritz for the sample of tetraphenylcyclopentadienone which was prepared and purified according to the directions in Organic Syntheses (98).

Thin-layer chromatograms were made up from silica gel G (according to Sta hl) from the E. Merck A. G. Other thin-layer chromatography plates were made with aluminum oxide G also from E. Merck A. G.

All melting points were determined with a Thomas-Hoover Uni-Melt capillary melting point apparatus, are reported in degrees centigrade and are corrected. The melting point device was calibrated with melting point standards provided with the apparatus. Sublimed catechol was also used as a standard.

All boiling points are reported in degrees centigrade and are uncorrected. The pressure inside the distillation system at the time of distillation was determined by a McLeod gauge.

The gas chromatograph used during this investigation was an Aerograph P-90 (Wilkens Instrument and Research Company). Since the compounds prepared during this investigation proved to be unstable in the presence of hot metals, a glass column and glass injector inserts were used at all times. Unless otherwise noted, a 5' x $\frac{1}{4}$" pyrex glass column packed with 10% Carbowax 20M on hexamethyldisilane (HMDS) treated 80/100 mesh Chromosorb P was used for analyses and for purification of analytical samples by gas chromatography. Isothermal conditions were used during all analyses.

Infrared spectra were obtained using a double-beam Parkin-Elmer grating infrared spectrophotometer, model #337. All liquid samples were run "neat" between KBr plates; the solid samples were run as KBr pellets.

The author is deeply indebted to Shell Development Company in Modesto, California, for determining the nuclear magnetic resonance (NMR) spectra. A Varian A-60 (60 megacycle) instrument was used for all determinations. In each case, carbon tetrachloride, containing 1% tetramethylsilane (TMS) as the internal standard, was used as the solvent. A sweep width of 500 cycles per second (cps.) was used in each case. Chemical shifts are reported in τ-units (87, p. 47) relative to TMS. The numbers in parentheses after the τ-values correspond to the relative areas.

Carbon, hydrogen, bromine and oxygen analyses were carried out by Alfred Bernhardt at Mikroanalytisches Laboratorium in Max-Planck-Institute für Kohlenforshung, Hohenweg 17, Mulhein (Ruhr), Germany.

II. 6,6-DIBROMOBICYCLO 3.1.0 HEXANE

6,6-Dibromobicyclo [3.1.0] hexane was prepared by the method of von Doering and Hoffmann (31). In a typical preparation, a stirred solution of 200 ml. of pentane*, 160 g. (0.632 moles) of bromoform, 100 ml. of dry _t_-butyl alcohol, and 41.06 g. (0.602 moles) of cyclopentene was maintained at 0°C while 900 ml. of 1.02 _M_ potassium _t_-butoxide in _t_-butyl alcohol (made from 40.0 g. of potassium and 1 l. of dry _t_-butyl alcohol) was added at a rate of 50 ml. per hour. When the addition was complete, the mixture was stirred for one additional hour at 0°C. Then 500 ml. of water and 500 ml. of pentane* were added. The pentane layer was separated, washed with water (6 x 1000 ml.) and dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration, and the pentane* was removed under reduced pressure leaving 117 g. of crude product. The crude product was distilled through a 6" column packed with ¼" sections of glass tubing. A yield of 80.85 g. (56.0%) of 6,6-dibromobicyclo [3.1.0] hexane (b.p. = 45.7°C at 0.5 mm., n_D^{23} = 1.5562; literature values (80): b.p. = 63°C at 2.9 mm., n_D^{25} = 1.5562 was obtained. The infrared spectrum (IR-1) showed no absorption in the 1650 cm.$^{-1}$ region. Under the conditions employed (5' x ¼" pyrex glass column packed with 10% Carbowax 20M in HMDS treated 80/100 mesh Chromosorb P, helium flow = 300 ml./min., injector = 210°C, column = 155°C, and detector = 210°C), samples of 6,6-dibromobicyclo [3.1.0] hexane underwent extensive decomposition when injected into the gas chromatograph. Thus, it was not possible to obtain an accurate estimate of the purity of the 6,6-dibromobicyclo [3.1.0] hexane by gas chromatography.

III. 2-BROMO-3-HYDROXYCYCLOHEXENE

The method of Sonnenberg and Winstein (80) was used to prepare 2-bromo-3-hydroxycyclohexene. In a typical experiment, a mixture of 79.04 g. (0.329 moles) of 6,6-dibromobicyclo [3.1.0] hexane and 660 ml. of 1 M aqueous silver nitrate was stirred vigorously at 0°C for 7½ hours. The precipitated silver bromide was removed by filtration and washed with 100 ml. of water and 100 ml. of ether. The aqueous layer was extracted with ether (3 x 250 ml.). The combined ether extract was washed with 200 ml. of water, 200 ml. of 10% sodium bicarbonate, and 200 ml. of water. The ether solution was then dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and the ether was removed under reduced pressure, leaving 61.85 g. of crude product. The crude product was fractionally distillate was cooled on a dry ice-acetone bath and the bottom of the container was scratched with a stirring rod until the liquid solidified. Then about four volumes of petroleum ether were added. This mixture was warmed and stirred until the solid melted and dissolved in the petroleum ether. The solution was cooled in a refrigerator until crystallization occurred. The solid was removed by filtration, and the mother liquor was concentrated and cooled on a dry ice-acetone bath, whereupon a small further portion of solid was obtained. The combined solid was twice recrystallized from petroleum ether. A yield of 30.28 g. (52.0%) of the purified 2-bromo-3-hydroxycyclohexene was obtained. The observed melting point was 38-40°C (n_D^{20} = 1.5424--melted sample). The literature values (80) were: m.p. =

38.2-40.2°C; $n_D^{25} = 1.5404$. Analysis by gas chromatography (5' x ¼" pyrex glass column packed with 20% Apiezon L on 30/60 mesh Chromosorb P, helium flow = 120 ml./min., injector = 210°C, detector = 210°C, column = 150°C) showed a peak (retention time was 12.6 minutes) which corresponded to about 98% of the total peak area. An infrared spectrum (IR-2) of the pure product was obtained.

The excess petroleum ether was removed from the mother liquor under reduced pressure. A sample of this material gave positive tests for both nitrogen and bromine after fusion with sodium. Analysis by gas chromatography under the above conditions showed a peak (apparently the nitrate ester of 2-bromo-3-hydroxycyclohexene) which corresponded to about 20% of the total peak area and whose retention time (10.8 minutes) was considerably different from the retention time (12.6 minutes)of an authentic sample of 2-bromo-3-hydroxycyclohexene. In addition, the infrared spectrum of the mother liquor showed absorption bands at 1620 cm.$^{-1}$ (ν_{as} NO_2), 1270 cm.$^{-1}$ (ν_s NO_2), 845 cm.$^{-1}$ (O—N stretching), 755 cm.$^{-1}$ (out of plane bending), and 695 cm.$^{-1}$ (NO_2 bending) (86, p. 50).

IV. 2,3-DIBROMOCYCLOHEXENE

A mixture of 35.42 g. (0.200 moles) of 2-bromo-3-hydroxycyclohexene and 9.0 ml. of dry pyridine in 85 ml. of dry ether was placed in a 250 ml. 3-neck flask equipped with a reflux condenser with a calcium chloride guard tube, a stirrer, and a dropping funnel. The mixture was kept at 0°C on an ice bath while 27 g. (0.10 moles) of phosphorous tribromide was added dropwise with stirring over a period of 40 minutes. The reaction mixture was stirred an additional 5 minutes at 0°C. The cooling bath was removed and the mixture was refluxed for five hours. After being cooled to $0^{\circ}C$, the mixture was poured into about 100 ml. of ice-water. The ether layer was removed and washed with water. The reaction flask was rinsed with water and with ether; the combined washings and the aqueous layer were washed with ether (3 x 100 ml.). The combined ether extract was washed with 100 ml. of water, 100 ml. of 10% sodium bicarbonate, and 100 ml. of water and dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and the ether was removed under reduced pressure leaving 43.42 g. of crude product. The crude product was fractionally distilled through a 6" column packed with ¼" sections of glass tubing. A yield of 34.72 g. (72.3%) of 2,3-dibromocyclohexene (b.p. = 50-52°C at 0.4 mm., and n_D^{24} = 1.5770; literature values (80): b.p. = 94-95°C at 4.5 mm., and n_D^{25} = 1.5764) was obtained. Analysis by gas chromatography (1μl. injections onto a 5' x ¼" pyrex glass column packed with 10% Carbowax 20M on HMDS treated 80/100 mesh Chromosorb P, helium flow = 300 ml./min., injector = 210°C, detector = 210°C, column = 155°C) showed a peak (retention time = 8.7 minutes) whose area corresponded to about 90% of the total peak area and a peak whose retention time (0.9 minutes) corresponded to about 10% of the total peak area. However, 90% appeared to be a minimum purity and the purity may have been much higher. First, the refractive index of the product was in excellent agreement with that reported in the literature. Second, the liquid appeared to remain colorless on standing. And third, some of the other compounds showed similar tendencies toward partial decomposition upon injection into the gas chromatograph under the conditions employed. For example, samples of 2,3-dibromocyclononene and 2-bromo-2-cyclohepten-1-yl acetate, which had been collected by preparative gas chromatography, showed several small peaks (equivalent to about 1% of the total peak area) with short retention times which were due either to slight decomposition of the sample as it passed through the detector before collection or to decomposition of the reinjected sample. The infrared spectrum (IR-3) showed an absorption of medium intensity at 1625 $cm.^{-1}$ The NMR spectrum (NMR-1) showed a poorly resolved multiplet centered at 3.84τ(0.92), a poorly resolved multiplet at 5.28τ(0.94), and a singlet with some fine structure at 7.80τ and a poorly resolved multiplet at 8.03τ whose combined relative area was 6.14.

V. 7,7-DIBROMOBICYCLO[4.1.0]HEPTANE

The method of von Doering and Hoffmann (31) was also used to prepare 7,7-dibromobicyclo[4.1.0]heptane.

A stirred solution of 24.63 g. (0.300 moles) of cyclohexene and 75.5 g. (0.300 moles) of bromoform in 50 ml. of dry t-butyl alcohol was maintained at 0°C while a solution of 450 ml. of 1.03 M potassium t-butoxide in t-butyl alcohol (from 20.6 g., 0.515 moles, of potassium and 500 ml. of t-butyl alcohol) was added at a rate of 50 ml. per hour.

When the addition was complete, the mixture was stirred at 0°C for one additional hour. Then 250 ml. of water and 250 ml. of petroleum ether were added to the reaction mixture. The petroleum ether layer was removed and washed with water (6 x 500 ml.) until the water layer was no longer colored and all water-soluble material had apparently been removed from the petroleum ether solution. The first 500 ml. portions of water added resulted in the removal of an aqueous layer whose total volume was more than 500 ml. The petroleum ether solution was then dried over anhydrous magnesium sulfate.

The magnesium sulfate was removed by filtration and the petroleum ether was removed under reduced pressure leaving 50.78 g. of crude product. The crude product was then fractionally distilled twice. The boiling point at 0.5 mm. was 56-58°C with n_D^{29} = 1.5540. The literature (99) gives the values: b.p. = 79.80°C at 2 mm. and n_D^{25} = 1.5560. A yield of 31.14 g. (40.9%) of the purified product was obtained. Analysis of the 7,7-dibromobicyclo [4.1.0] heptane by gas chromatography (5' x ¼" pyrex glass column packed with 10% Carbowax 20M in HMDS treated 80/100 mesh Chromosorb P) showed a peak (retention time = 5.9 minutes) which corresponded to about 99% of the total peak area. The infrared spectrum (IR-4) showed no absorption in the 1650 cm.$^{-1}$ region.

VI. ATTEMPTED SYNTHESIS OF 2,3-DIBROMOCYCLOHEPTENE

7,7-Dibromobicyclo [4.1.0] heptane with aqueous silver nitrate. The first experiments in the attempt to synthesize 2,3-dibromocycloheptene involved treating 7,7-dibromobicyclo [4.1.0] heptane with aqueous silver nitrate in the hopes that 2-bromo-3-hydroxycycloheptene, which could subsequently be brominated with PBr_3 to yield 2,3-dibromocycloheptene, would be the product.

A mixture of 100 ml. of 1 _M_ aqueous silver nitrate and 12.70 g. (0.500 moles) of 7,7-dibromobicyclo [4.1.0] heptane was stirred vigorously in a 250 ml. 3-neck flask at room temperature and kept under a nitrogen atmosphere. Stirring was continued for 6 days during which time the reaction vessel was kept surrounded by aluminum foil to keep out light.

At the end of the 6 day reaction period, 100 ml. of ether was added to the reaction flask and a small amount of a black precipitate was removed by filtration. The reaction flask was rinsed with small amounts of water and ether. The washings were combined with the mixture that had been removed from the reaction flask. The water layer was removed and extracted with ether (3 x 100 ml.). The combined ether extract was washed with 100 ml. of water, 100 ml. of 10% sodium bicarbonate solution, and 100 ml. of water and then dried over anhydrous magnesium sulfate.

The magnesium sulfate was removed by filtration. The ether was removed under reduced pressure leaving 12.48 g. of crude product. The crude product was then distilled through a small Vigreux column at 0.5 mm. The refractive index of the distilled material was n_D^{24} = 1.5542 and the infrared spectrum was identical to that of an authentic sample of 7,7-dibromobicyclo [4.1.0] heptane. A sample injected into the gas chromatograph showed a peak whose retention time(9.5 minutes) was identical to that of an authentic sample of 7,7-dibromobicyclo [4.1.0] heptane and which corresponded to about 95% of the total peak area. The conditions for the analysis by gas chromatography were: 5' x ¼" pyrex glass column packed with 10% SE-30 on HMDS treated 80/100 mesh Chromosorb P, helium flow = 120 ml./min., injector = 215°C, detector = 214°C, and column = 150°C.

7,7-Dibromobicyclo [4.1.0] heptane with refluxing aqueous silver nitrate. In another experiment, 12.70 g. (0.0500 moles) of 7,7-dibromobicyclo [4.1.0] heptane was added to 100 ml. of 1 $\underline{N}$ aqueous silver nitrate in a 250 ml. 3-neck flask. The reaction mixture was vigorously stirred under a nitrogen atmosphere and heated to 80°C for 62 hours. During this time, the reaction vessel was surrounded by aluminum foil to keep out light. Then the reaction mixture was allowed to cool to room temperature and 100 ml. of ether was added. The small amount of black precipitate was removed by filtration and the reaction flask was washed with water and with ether. The washings were combined with the material removed from the reaction flask. The aqueous layer was removed and extracted with ether (3 x 100 ml.). The combined ether extract was washed with 100 ml. of water, 100 ml. of 10% sodium bicarbonate solution, and 100 ml. of water and dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration. The ether was removed under reduced pressure leaving 5.26 g. of crude product. The crude product was distilled at 0.5 mm. through a small Vigreux column. About 5 g. of a smelly yellow liquid, which turned black before the distillation was completed, was obtained; the rest of the material remained in the distillation flask as a black, smelly syrup.

7,7-Dibromobicyclo[4.1.0]heptane with anhydrous aluminum bromide (equimolar amounts) in pentane*. Anhydrous aluminum bromide was used as a Lewis acid in hopes that it would cause 7,7-dibromobicyclo[4.1.0]heptane to rearrange to 2,3-dibromocycloheptene.

To a stirred slurry of 27.0 g. (0.101 moles) of anhydrous aluminum bromide in 25 ml. of pentane* under nitrogen atmosphere was added dropwise a solution of 25.4 g. (0.100 moles) of 7,7-dibromobicyclo[4.1.0]-heptane in 75 ml. of pentane*. When, a short time after the addition was started, a colorless, acidic gas began to be evolved, the reaction mixture was cooled to 0^{o}C on an ice bath. The addition took 30 minutes; the reaction mixture was stirred an additional 5 minutes, then poured into 100 ml. of ice water, and stirred thoroughly. The tarry mixture was poured into a separatory funnel, and 100 ml. of pentane* was added. Three layers formed in the separatory funnel. The bottom tarry layer was drawn off, dissolved in benzene, and washed with 50 ml. of water, 50 ml. of 10% sodium bicarbonate solution, and 50 ml. of water. The benzene solution was then dried over anhydrous magnesium sulfate. The aqueous layer in the separatory funnel was drawn off and extracted with ether (2 x 100 ml.). The combined ether-pentane* extract was washed with 100 ml. of water, 100 ml. of 10% sodium bicarbonate solution, and 100 ml. of water and dried over anhydrous magnesium sulfate. Thin layer chromatograms of benzene solution and the ether-pentane solution were run on an Eastman Kodak Chromagram sheet, type K 301R (silica gel). The chromatograms were developed with carbon tetrachloride and visualized with iodine vapor. The thin layer chromatogram of the benzene solution and the ether-pentane solution showed only one spot each; all the spots had an identical R_f value (0.70). Therefore, the two solutions were combined after the magnesium sulfate had been removed by filtration. The solvents were then removed under reduced pressure. The crude product was then distilled through a small Vigreux column at 0.5 mm. About 2 ml. of a very smelly liquid, which was originally colorless but which quickly turned black was obtained. The liquid gave a positive test for bromine after sodium fusion and gave an immediate precipitate of silver bromide with alcoholic silver nitrate.

7,7-Dibromobicyclo [4.1.0] heptane with anhydrous aluminum bromide (catalytic amount) in pentane*. In another experiment, a solution of 24.5 g. (96.5 mmoles) of 7,7-dibromobicyclo [4.1.0] heptane in 100 ml. of pentane* was added dropwise over a period of 70 minutes to a well-stirred slurry of 2.58 g. (9.65 mmoles) of aluminum bromide in 100 ml. of pentane*.

The contents of the reaction flask were maintained at -20°C and under a nitrogen atmosphere. When the addition was complete, the reaction mixture was stirred an additional 10 minutes. At the end of two hours from the beginning of the addition and thereafter at intervals, small samples of the reaction mixture were removed for analysis by thin layer chromatography. Known samples of 7,7-dibromobicyclo[4.1.0]heptane (1% in CCl_4) were run against approximately 1% solutions of samples of the reaction mixture (0.5 ml. of the pentane solution was removed from the reaction flask, washed with water to remove $AlBr_3$, and diluted with 4.5 ml. of CCl_4). The chromatograms were run on glass plates coated with silica gel which had been activated by heating them at 250°C for one hour, developed with carbon tetrachloride, and visualized with concentrated sulfuric acid-potassium dichromate solution, which was prepared by adding about 5 g. of potassium dichromate to 100 ml. of hot concentrated sulfuric acid. The R_f value of the 7,7-dibromobicyclo[4.1.0]heptane was 0.72. Only 7,7-dibromobicyclo[4.1.0]heptane was detected even 20 hours after the start of the reaction. Therefore, the reaction mixture was warmed to 0°C. Further samples were removed from the reaction flask at various intervals beginning 24 hours after the start of the reaction. They were analyzed by thin layer chromatography as above. Forty-four hours after the start of the reaction, evidence of a reaction product (R_f value = 0.770) appeared, but the starting material obviously predominated in the reaction mixture. When at the end of 63 hours after the beginning of the reaction the amount of product appeared to be unchanged, the reaction mixture was allowed to warm to room temperature for 3 hours and then refluxed for 2 hours. Then the reaction mixture was allowed to cool and was poured into 200 ml. of water. The water layer was removed and extracted with ether (3 x 100 ml).

The combined ether-pentane* extract was washed with 100 ml. of water, 100 ml. of 10% sodium bicarbonate solution, and 100 ml. of water. The ether-pentane* solution was then dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and the solvents were removed under reduced pressure leaving 24.35 g. of crude product. The crude product was distilled through a small Vigreux column at 0.8 mm. About 18 g. of a greenish-black liquid were obtained. The product was again distilled through a small Vigreux column at 0.5 mm.; this time the product was colorless initially but soon turned black. The product was then distilled through a 6" column of ¼" sections of glass tubing at 0.3 mm. Again the material was colorless initially but quickly turned black. A total of 10.13 g. of the liquid was collected. Analysis by gas chromatography (5' x ¼" pyrex glass column packed with 10% SE-30 on HMDS treated 80/100 mesh Chromosorb P, helium flow = 120 ml./min., injector = 215°C, detector = 214°C and column = 150°C) showed a peak whose retention time (9.5 minutes was identical with that of an authentic sample of 7,7-dibromobicyclo[4.1.0]heptane and which represented about 95% of the total peak area. The refractive index of the liquid was n_D^{23} = 1.5549.

<u>7,7-Dibromobicyclo[4.1.0]heptane with anhydrous aluminum bromide (catalytic amount) in ether</u>. In another series of experiments, ether was used as the solvent instead of pentane*. To a well-stirred slurry of 2.70 g. (10.0 mmoles of anhydrous aluminum bromide in 100 ml. of dry ether at -20°C under nitrogen was added dropwise a solution of 25.4 g. (100 mmoles) of 7,7-dibromobicyclo[4.1.0]heptane in 100 ml. of ether. The addition took place over a period of 90 minutes. The mixture was then stirred an additional 130 minutes. Then samples were removed at various intervals

from the reaction flask and diluted with carbon tetrachloride until the concentration of 7,7-dibromo [4.1.0] heptane (assuming no reaction had taken place) was about 1%. The samples were run against a 1% CCI solution of a genuine sample of 7,7-dibromobicyclo [4.1.0] heptane on glass plates coated with silica gel, which had been activated by heating them to 250°C for one hour, developed with CCl_4, and visualized with concentrated sulfuric acid-potassium dichromate solution. When at the end of 7 hours after the start of the addition, no reaction appeared to have occurred, the mixture was worked up by pouring it onto 100 ml. of crushed ice and water. The aqueous layer was removed and extracted with ether (3 x 100 ml.). The combined ether extract was washed with 100 ml. of water, 100 ml. of sodium bicarbonate solution, and 100 ml. of water and dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration; and the ether was removed under reduced pressure leaving 25.50 g. of crude product. The crude product was fractionally distilled through a small Vigreux column at 2.0 mm. Unreacted starting material in the amount of 21.92 g. was recovered. Its refractive index was n_D^{24} = 1.5576. Its infrared spectrum was identical with that of an authentic sample of 7,7-dibromobicyclo [4.1.0] heptane. Analysis by gas chromatography (5' x ¼" pyrex glass column packed with 10% SE-30 on HMDS treated 80/100 mesh Chromosorb P, injector = 215°C, detector = 214°C, and column = 150°C) showed a peak whose retention time (9.5 minutes) was identical with that of an authentic sample of 7,7-dibromobicyclo [4.1.0] heptane.

7,7-Dibromobicyclo [4.1.0] heptane with anhydrous aluminum bromide (equimolar amounts) in ether. In a second experiment using ether as the solvent, a solution of 22.0 g. (86 mmoles) of 7,7-dibromobicyclo [4.1.0] -

heptane in 25 ml. of dry ether was added dropwise to a stirred slurry of 2.44 g. (91.5 mmoles) of anhydrous aluminum bromide in 25 ml. of dry ether at 0°C under a nitrogen atmosphere. The addition took 30 minutes. When after being stirred for 7 days at 0°C there was no sign of a reaction having occurred, the reaction mixture was stirred at room temperature for 8 hours and then refluxed for 30 hours. At the end of this time, a sample was injected into the gas chromatograph (5' x ¼" pyrex glass column packed with 10% SE-30 on HMDS treated 80/100 mesh Chromosorb P, helium flow = 120 ml./min., injector = 215°C, detector = 214°C, column = 150°C) and showed, in addition to a peak due to the solvent, a peak whose retention time (9.5 minutes) was identical to that of an authentic sample of 7,7-dibromobicyclo[4.1.0]heptane. Since no reaction had occurred, the reaction mixture was allowed to cool and was added to 100 ml. of water and 100 ml. of ether. The mixture was stirred vigorously. The aqueous layer was removed and extracted with ether (3 x 5 ml.). The combined ether extract was washed with 100 ml. of water, 100 ml. of 10% sodium bicarbonate solution, and 100 ml. of water and then dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration; and the ether was removed under reduced pressure leaving 21.51 g. of crude product. The crude product was then fractionally distilled at 0.5 mm. through a small Vigreux column. Gas chromatography (5' x ¼" pyrex glass column packed with 10% SE-30 on HMDS treated 80/100 mesh Chromosorb P, helium flow = 120 ml./min., injector = 215°C, detector = 214°C, and column = 150°C) showed a peak whose retention time (9.5 minutes) was identical to that of an authentic sample of 7,7-dibromobicyclo[4.1.0]heptane and corresponded to about 99% of the total peak area. The refractive index was n_D^{25} = 1.5570. The infrared spectrum of the material (16.78 g.) was identical to that of 7,7-dibromobicyclo [4.1.0] heptane.

VII. 2-BROMO-2-CYCLOHEPTEN-1-YL ACETATE

Because all of the pure 7,7-dibromobicyclo [4.1.0] heptane had been used in the previously described experiments, the 7,7-dibromobicyclo [4.1.0]-heptane recovered from some of those experiments (see p. 41) was used in the following experiment. Thus, the starting material was in this case not of the highest quality.

A mixture of 19.5 g. (76.8 mmoles) of 7,7-dibromobicyclo [4.1.0]-heptane and 25.4 g. (0.15 moles) of silver acetate in 150 ml. of glacial acetic acid was stirred vigorously under a nitrogen atmosphere for 4 days. Thin layer chromatography was used to follow the progress of the reaction. Samples of the reaction mixture were diluted to about 1% concentration with n-hexane, were spotted on glass plates coated with alumina G, which had been activated by heating them to 250°C for one hour, and were run against authentic samples of 7,7-dibromobicyclo [4.1.0] heptane (1% in hexane). n-Hexane was used to develop the chromatograms which were then visualized with concentrated sulfuric acid-potassium dichromate solution. By the end of four days, the thin layer chromatograms showed that some reaction had occurred (spots with the following R_f values were noted: 0.053, 0.185, and 0.900). The latter R_f value was identical to the R_f value for authentic 7,7-dibromobicyclo [4.1.0] heptane, but the reaction was still far from being complete. Therefore, the mixture was refluxed for 24 hours. The reaction mixture was then allowed to cool and 100 ml. of ether and 100 ml. of water was added. The acetic acid was carefully neutralized with solid sodium bicarbonate. The ether layer was separated and the aqueous layer was extracted with 250 ml. of ether. The combined ether extract was washed with 100 ml. of water, 100 ml. of 10% sodium bicarbonate solution, and 100 ml. of water and then dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure leaving 11.60 g. of crude product. The crude product was distilled through a small Vigreux column at 0.3 mm. The forerun was rejected, but the other fractions of distillate were combined and distilled at 0.3 mm. through a 6" column packed with ¼" sections of glass tubing. A yield of 3.54 g. (21.2%) of the purified product (b.p. = 60°C at 0.3 mm.) was obtained. Analysis of the distillate by gas chromatography (5' x ¼" pyrex glass column packed with 10% carbowax 20M in HMDS treated 80/100 mesh Chromosorb P, helium flow = 300 ml./min., injector = 210°C, detector = 210°C, column = 155°C) showed a peak (retention time = 12.0 minutes) corresponding to about 90% of the total peak area. Another peak corresponding to about 7% of the sample injected, had an identical retention time (4.6 minutes) with that of an authentic sample of 7,7-dibromobicyclo[4.1.0]-heptane. Therefore, pure samples for the refractive index determination, infrared analysis, NMR analysis, and elemental analysis were obtained by preparative gas chromatography. The refractive index of the gas chromatograph purified 2-bromo-2-cyclohepten-1-yl acetate was found to be: n_D^{23} = 1.5090. The infrared spectrum (IR-5) included absorptions at 1740 cm.$^{-1}$, 1625 cm.$^{-1}$, 1445 cm.$^{-1}$, 1365 cm.$^{-1}$, and 1245 cm.$^{-1}$ The NMR spectrum (NMR-2) showed a quartet (J = 6.7 cps.) at 3.72τ (1.02), a doublet (J = 4.9 cps.) at 4.58τ (1.02), a singlet at 7.96τ (the relative area between 7.60τ and 7.96τ corresponded to 5 protons) and a broad, poorly resolved multiplet at 8.22τ (5.99). Elemental analysis gave the following values for $C_9H_{13}BrO_2$,

calculated: C, 46.37%; H, 5.66%; Br. 34.38%; O, 13.73%;
found: C, 46.24%; H, 5.45%; Br. 34.35%; O, 13.76%.

1,2-Cyclononadiene in One Step from Cyclooctene. The method of Untch, *et al.* (36), was used to prepare 1,2-cyclononadiene in one step from cyclooctene.

First, methyllithium was prepared by the method of Gilman, *et. al.* (100). A typical experiment is as follows. Lithium ribbon (97.5 cm., 8.68 g., 1.25 g.-atoms) was cut into small pieces and added to 150 ml. of dry ether in the reaction flask to which had been fitted a reflux condenser with a nitrogen inlet and a stirrer. About 2 ml. of methyl iodide was added to start the reaction; the rest of the methyl iodide (total methyl iodide added was 71.0 g., 0.500 moles) was dissolved in 150 ml. of ether and placed in a dropping funnel, which was then connected to the reaction flask. The methyl iodide-ether solution was added dropwise over a period of 65 minutes. The mixture was refluxed for one additional hour and then allowed to stand for 30 minutes, after which two 5 ml. aliquots were removed, hydrolized with water, and titrated with 0.252 *N* HCI using phenolphthalein as the indicator. The average volume needed to titrate 5 ml. of the ethereal methyllithium was 27.45 ml. of the standard HCI. Therefore, the methyllithium concentration was 1.39 moles per liter. The yield of methyllithium was in this case about 83%.

The 1,2-cyclononadiene was prepared as follows: To a stirred mixture of 55.0 g. (0.500 moles) of cyclooctene and 41.5 g. (0.135 moles) of carbon tetrabromide at -62°C under a nitrogen atmosphere were added 90 ml. (0.125 moles) of freshly prepared methyllithium in ether over a period of

45 minutes. The stirred mixture was kept at -62°C for an additional 30 minutes. Then 97.5 ml. (0.135 moles) of the ethereal methyllithium was added during a 30 minute period. The reaction mixture was stirred for an additional 30 minutes at -62° and then allowed to warm to 0°C. Then 100 ml. of water was added, and the water layer was removed. The ether layer was washed with water (4 x 100 ml.) and dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and the excess ether was removed under reduced pressure. The bulk of the cyclooctene was removed by distillation through a 6" column packed with ¼" sections of glass tubing at about 28 mm. When most of the cyclooctene had been removed, the distillation was interrupted and the fractionating column was removed in favor of a simple Claisen head. The remaining liquid was then distilled through the Claisen head at 28 mm. The product (7.39 g., 45% yield) boiled at 73-75°C at 28 mm. (n_D^{25} = 1.5000); literature values (35): b.p. = 62°C at 16 mm., n_D^{20} = 1.5060. Analysis by gas chromatography (5' x ¼" pyrex glass column packed with 20% Apiezon L on 30/60 mesh Chromosorb P, helium flow = 120 ml./min., injector = 155°C, detector = 157°C, column = 100°C) showed a peak, whose retention time (12.6 minutes was identical to that of an authentic sample of cyclooctene, and a peak, whose retention time was 45.7 minutes and which corresponded to about 85% of the total peak area. A pure sample (n_D^{23} = 1.5053) was collected via preparative gas chromatography; an infrared spectrum (see IR-7) was obtained. This method for preparing 1,2-cyclononadiene proved to be unsatisfactory for the purpose of this investigation as this investigator was never able to obtain pure 1,2-cyclononadiene (except tiny amounts by gas chromatography) with the equipment available. However, small amounts of the above described product were

used to help establish conditions for brominating 1,2-cyclononadiene to 2,3-dibromocyclononene.

IX. 9,9-DIBROMOBICYCLO [6.1.0] NONANE

The method employed for preparing 9,9-dibromobicyclo [6.1.0] nonane was essentially that described by von Doering and Hoffmann (31). To a stirred slurry of 200 g. (1.79 moles) of dry potassium t-butoxide in 700 ml. of dry pentane* and 118 g. (1.07 moles) of cyclooctene at 0°C under a nitrogen atmosphere was added dropwise a solution of 313 g. (1.20 moles) of bromoform in 100 ml. of pentane over a period of 9 hours. After the addition was complete, the mixture was stirred at 0°C for an additional 12 hours. To the reaction mixture was added 500 ml. of water and the aqueous layer was removed. The reaction flask was washed with 500 ml. of pentane and 500 ml. of water. The combined pentane extract was washed with water (3 x 1 l.) and dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and the pentane* was removed under reduced pressure leaving 342.8 g. of crude product. The crude product was then fractionally distilled through a small Vigreux column at 1.0 mm. The low-boiling forerun was rejected (8.80 g., boiling range at 1.0 mm. = 40-100°C) but the other fractions (228.28 g., boiling range at 1.0 mm. = 100-112°C) were combined and fractionally distilled at 0.2 mm. The pure product distilled at 77-79°C at 0.15 mm. and had n_D^{24} = 1.5510; literature values (16) are b.p. = 80-82°C at 0.1 mm., n_D^{20} = 1.5520. A yield of 217 g. (71.8%) of the 9,9-dibromobicyclo [6.1.0] nonane was obtained. Analysis of the liquid by gas chromatography (5' x ¼" pyrex glass column packed with 10% Carbowax 20M in HMDS treated 80/100 mesh Chromosorb P, helium flow = 300 ml./min., injector = 210°C, detector 210°C, column = 155°C) showed a peak with a retention time of 16.5 minutes which corresponded to about 99% of total peak area. The infrared spectrum (IR-6) showed no absorption in the 1650 cm.$^{-1}$ region.

X. 1,2-CYCLONONADIENE FROM 9,9-DIBROMOBICYCLO [6.1.0] NONANE

The method of Moore and Ward (33) was used to prepare 1,2-cyclononadiene from 9,9-dibromobicyclo [6.1.0] nonane.

Methyllithium was prepared in the same manner as on p. 50. To a stirred solution of 141.0 g. (0.500 moles) of 9,9-dibromobicyclo [6.1.0]-nonane in 125 ml. of ether at -65°C under a nitrogen atmosphere were added dropwise 460 ml. (0.600 moles) of an ether solution of methyllithium. The addition took place over a period of 2 hours. The mixture was stirred for an additional ½ hour at -65°C. Then the temperature was allowed to rise to 0°C. Then 250 ml. of water was added to the reaction mixture. The aqueous layer was drawn off and extracted with ether (3 x 100 ml.). The combined ether extract was washed with water until the water layer was no longer basic to phenolphthalein. The ether solution was then dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and the ether was removed by distillation under reduced pressure. The crude product was then fractionally distilled at 17 mm. through a 6" column packed with ¼" sections of glass tubing. A yield of 42.90 g. (70.3%) of pure 1,2-cyclononadiene (b.p. = 58°C at 6 mm., n_D^{22} = 1.5061; literature values (35): b.p. = 62°C at 16 mm., n_D^{20} = 1.5060) was obtained. Analysis by gas chromatography (5' x ¼" pyrex glass column packed with 10% Carbowax 20M on HMDS treated 80/100 mesh Chromosorb P, helium flow = 120 ml./min., injector = 156°C, detector = 153°C and column = 103°C) showed a peak (retention time = 6.9 minutes) which corresponded to about **99%** of the total peak area. The infrared spectrum (IR-7) showed an absorption at 1950 cm.$^{-1}$ (16) but no absorption in the 2300-2000 cm.$^{-1}$ range (cyclononyne (101) shows an absorption of medium intensity at 2203 cm.$^{-1}$).

XI. 2,3-DIBROMOCYCLONONENE

To a stirred solution of 12.22 g. (0.100 moles) of 1,2-cyclononadiene in 45 ml. of carbon tetrachloride at -20°C under a nitrogen atmosphere was added dropwise a solution of 16.22 g. (0.102 moles) of bromine in 45 ml. of carbon tetrachloride. The addition took place over a period of 40 minutes. The mixture was then stirred an additional 5 minutes at 20°C and 50 ml. of a 20% sodium thiosulfate solution was added. The aqueous layer was removed and the carbon tetrachloride solution was washed with water (2 x 50 ml.) and dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration; the carbon tetrachloride was removed under reduced pressure leaving 28.50 g. of crude product. The crude product was then distilled through a small Vigreux column at 2 mm. During the distillation, a considerable amount of forerun was obtained. This smelly liquid distilled over a range of 65-100°C; and although initially a pale yellow, it quickly turned black. The liquid, initially colorless but which slowly turned yellow on standing for several days, boiling in the range of 106-10°C was retained, while the forerun was rejected. A yield of 8.72 g. of the liquid (n_D^{23} = 1.5698), which was subsequently identified as 2,3-dibromocyclononene, was obtained. Before being used in other experiments, however, the combined yields of several preparations were redistilled through a small Vigreux column (b.p. = 84°C at 0.2 mm., n_D^{23} = 1.5671). The liquid gave a positive test for bromine after being fused with sodium; treatment with both alcoholic silver nitrate and aqueous silver nitrate resulted in an immediate precipitate of silver bromide indicating a rapidly ionized bromine atom. Analysis of the liquid by gas chromatography (5' x ¼" pyrex glass column packed with 10% Carbowax 20M on HMDS treated 80/100 mesh Chromosorb P, helium flow = 300 ml./min., injector = 210°C, detector = 210°C, column = 155°C) showed two poorly resolved peaks (retention times = 27.3 and 29.6 minutes, respectively) which corresponded to about 85% of the total peak area. The analytical data tabulated below were obtained from spectral and elemental analyses performed on samples which had been purified by gas chromatography (the experiments needed to establish a successful method for purification of samples of 2,3-dibromocyclononene by gas chromatography are described later). The infrared spectrum (IR-8) showed an absorption band of medium intensity at 1635 cm.$^{-1}$ The NMR spectrum (NMR-3) showed two overlapped triplets at 3.89τ (J = 8.8 cps.) and 4.11τ (J = 8.8 cps.) whose total relative area was 1.03, a quartet at 4.86τ (J = 5.3 cps.) and a quintet at 5.84τ (J = 5.8 cps.) whose total relative area was 1.03, a multiplet at 7.28τ, a broad poorly resolved multiplet centered at 7.90τ, and two broad, poorly resolved singlets at 8.38τ and 8.47τ, whose total relative area was 11.95. The most reasonable explanation of the NMR data was that the 2,3-dibromocyclononene was a mixture of <u>cis</u>-2,3-dibromocyclononene and <u>trans</u>-2,3-dibromocyclononene. From the NMR spectrum, the mixture was estimated to be a 2:3 ratio of one isomer to the other (see Chapter III for details). Elemental analysis gave the following values for $C_9H_{14}Br_2$.

calculated: C, 38.33%; H, 5.00%; Br, 56.67%.
found: C, 38.47%; H, 5.08%; Br, - - .
found: C, 38.56%; H, 5.05%; Br, 56.57%.

A number of attempts to demonstrate conclusively the presence of the cis- and trans-isomers of 2,3-dibromocyclononene involved the use of thin layer chromatography.

In the first experiment, 1% solutions of 9,9-dibromobicyclo[6.1.0]-nonane and 2,3-dibromocyclononene in carbon tetrachloride were prepared and spotted on glass plates coated with silica gel G which had been activated by heating them to 250°C for one hour. The amount of separation between the gem-dibromide and the 2,3-dibromide was an indication of the efficiency of separation. If the 2,3-dibromide and the gem-dibromide could not be cleanly separated, it would be unlikely that the cis- and trans-isomers of 2,3-dibromocyclononene could be separated. The chromatograms were developed with carbon tetrachloride and visualized with concentrated sulfuric acid-potassium dichromate solution (about 5 g. of the potassium dichromate in 100 ml. of hot concentrated sulfuric acid). The R_f values (average of several runs) for 9,9-dibromobicyclo[6.1.0]nonane and 2,3-dibromocyclononene were, respectivel y, 0.700 and 0.620. There was sufficient separation between the gem-dibromide and the 2,3-dibromide that they could easily be differentiated. However, no evidence for the cis-trans isomerism in the 2,3-dibromocyclononene could be seen under the conditions listed above.

In another series of experiments, thin layer chromatography plates coated with aluminum oxide G were prepared. The plates were activated by heating them in an oven at 250°C for one hour and were used immediately after they had cooled to room temperature. Longer heating gave less separation than the procedure listed above.

In other experiments, 1% solutions of 9,9-dibromobicyclo[6.1.0]-nonane and 2,3-dibromocyclononene in n-heptane were spotted on the thin layer chromatography plates coated with alumina G. The chromatograms were developed with n-heptane and visualized with concentrated sulfuric acid-potassium dichromate solution (from 5 g. of potassium dichromate and 100 ml. of hot concentrated sulfuric acid). The R_f values for 9,9-dibromobicyclo-[6.1.0] nonane and 2,3-dibromocyclononene were, respectively, 0.860 and 0.687. Obviously, the thin layer chromatography plates coated with alumina gave better separation than the plates coated with silica gel. Again, however, no evidence for the cis-trans isomerism in the 2,3-dibromocyclononene could be seen.

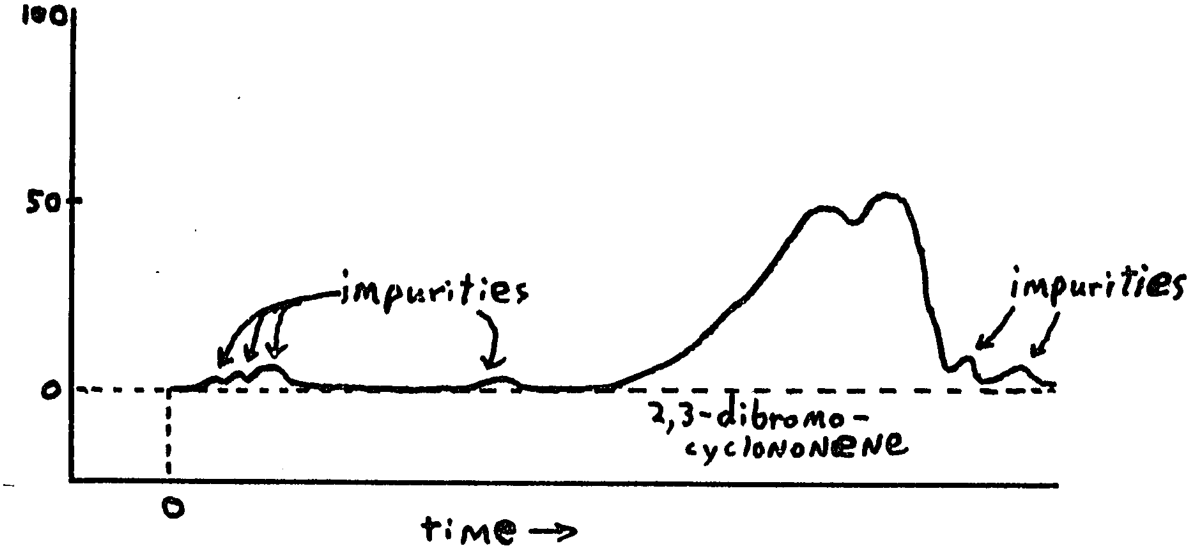
Since the author was unable to separate the cis- from the trans-2,3-dibromocyclononene by thin layer chromatography, it was necessary to turn to gas chromatography in an effort to affect the desired separation and purification.

The following columns were tried without success: 5' x $\frac{1}{4}$" pyrex glass column with 20% Apiezon L on 30/60 mesh Chromosorb P, 5' x $\frac{1}{4}$" pyrex glass column with 2% Apiezon L on Teflon 6, 5' x $\frac{1}{4}$" pyrex glass column with 10% SE-30 on HMDS treated 80/100 mesh Chromosorb P, and 5' x $\frac{1}{4}$" stainless steel column with 10% PDEAS on HMDS treated 60/30 mesh Chromosorb P. In each case, the conditions were as follows: helium flow = 120 ml./min., injector = 210°C, detector = 210°C, and column = 150°C. With all of the columns listed above, extensive decomposition of samples injected into the gas chromatograph was noted. The size of the samples injected ranged from 1 µl. to 25 µl. Glass injector inserts were used in all of the above trials.

Finally a 5' x $\frac{1}{4}$" pyrex glass column with 10% Carbowax 20 M on HMDS treated 80/100 mesh Chromosorb P (helium flow = 300 ml./min., injector = 210°C, column = 150°C) was tried and found to be the most effective of all the columns tried. Glass injector inserts were used at all times. The size of the samples injected ranged from 1µl. to 25µl. However, decomposition of the sample was minimized when samples injected were not larger than 10µl. Figure 1 shows a typical gas chromatogram of 2,3-dibromocyclononene using the carbowax column. As can be seen, complete separation of the cis- and trans-isomers was not achieved. However, this procedure was satisfactory for preparation of samples for infrared, NMR, and elemental analysis, the results of which are recorded on page 55.

FIGURE I

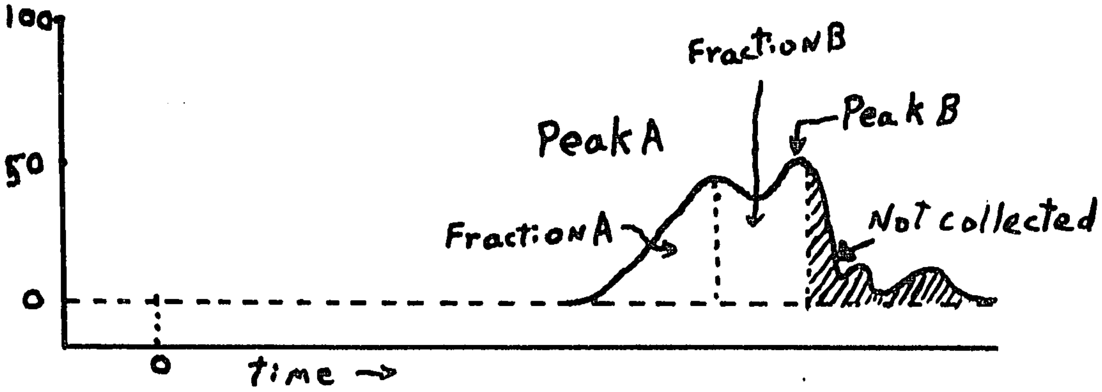
A TYPICAL GAS CHROMATOGRAM OF 2,3-DIBROMOCYCLONONENE



While complete separation of the cis- and trans-isomers of 2,3-dibromocyclononene was not achieved, a partial separation of one isomer from the mixture was achieved by collecting Fractions A and B as shown in Figure 2, reinjecting each fraction individually, and again collecting Fractions A and B. Analysis of Fraction A thus collected by gas chromatography showed

FIGURE 2

CHROMATOGRAM OF 2,3-DIBROMOCYCLONONENE SHOWING HOW PARTIAL SEPARATION OF THE CIS- AND TRANS-ISOMERS WAS ACHIEVED



that it was still largely a mixture, but analysis of Fraction B showed only one peak (retention time = 29.6 minutes). It is not likely under the circumstances that Fraction B was completely pure; however, the NMR spectrum (NMR-4) of Fraction B showed the presence of only one of the isomers. There were no absorption peaks due to the vinyl or allyl protons of Fraction A. The minimum purity of Fraction B was estimated from its NMR spectrum to be about 85% (see Chapter III for details). The NMR spectrum (NMR-4) showed a triplet ($J = 8.8$ cps.) at 4.11τ (0.98), a quintet ($J = 5.8$ cps.) at 5.89τ (0.98), a multiplet at 7.28τ, a poorly resolved multiplet at 8.00τ, and a singlet at 8.37τ, whose total relative area was 12.06.

XII. DEBROMINATION OF 2,3-DIBROMOCYCLONONENE

Debromination of 2,3-dibromocyclononene with magnesium in tetrahydrofuran. A solution of 1.00 g. (3.55 mmoles) of 2,3-dibromocyclononene in 15 ml. of tetrahydrofuran (THF) was added to 0.86 g. (35.5 mmoles) of magnesium powder. The mixture was stirred and kept under a nitrogen atmosphere at room temperature. An exothermic reaction began about three minutes after the reagents were mixed. About ninety minutes after the reaction had begun, a sample was removed and injected into the gas chromatograph (5' x $\frac{1}{4}$" pyrex glass column packed with 10% Carbowax 20M on HMDS treated 80/100 mesh Chromosorb P, helium flow = 120 ml./min., injector = 155°C, detector = 150°C, and column = 102°C). A peak, whose retention time (5.1 minutes) was identical with that of an authentic sample of 1,2-cyclononadiene, was found on the chromatogram. The reaction mixture was allowed to stand for 24 hours in order to see if the magnesium bromide produced in the reaction would cause acid-catalyzed dimerization, polymerization, or rearrangement of the 1,2-cyclononadiene. However, no product of isomerization was detected by gas chromatography. Since the amount of 1,2-cyclononadiene in the reaction mixture was very small (about 2% by weight of the mixture), the magnesium powder was removed by filtration and excess solvent was carefully removed under reduced pressure. Despite the care employed in removing the excess THF, much of the 1,2-cyclononadiene dimerized (102, 103) and precipitated to the bottom of the container. However, there was sufficient remaining 1,2-cyclononadiene that a sample was collected by gas chromatography (conditions as above) for an infrared spectrum. The infrared spectrum of the collected sample was identical with that of authentic 1,2-cyclononadiene prepared by the method of Moore and Ward (33) from 9,9-dibromobicyclo-[6.1.0] nonane.

<u>Debromination of 2,3-dibromocyclononene with zinc dust</u>. A mixture of 1.00 g. (3.55 mmoles) of 2,3-dibromocyclononene, 2.32 g. (35-5 mmoles) of zinc dust, and 15 ml. of THF was stirred at room temperature and under nitrogen atmosphere for 26 hours. A sample was then removed for analysis

by gas chromatography (conditions as listed on preceding page); the chromatogram showed a peak whose retention time (5.1 minutes was identical with that of an authentic sample of 1,2-cyclononadiene.

Debromination of 2,3-dibromocyclononene with magnesium in ether. A mixture of 4.52 g. (24.0 mmoles) of 1,2-dibromoethane, 6.77 g. (24.0 mmoles) of 2,3-dibromocyclononene and 5.84 g. (240 mmoles) of magnesium powder in 50 ml. of dry ether under a nitrogen atmosphere was stirred for three hours at room temperature. By this time, the peculiar odor of 1,2-cyclononadiene from the reaction mixture was quite evident. A sample was removed for analysis by gas chromatography (5' x ¼" pyrex glass column packed with 10% Carbowax 20M on HMDS treated 80/100 mesh Chromosorb P, helium flow = 120 ml./min., injector = 155°C, detector = 150°C, column = 102°C). The chromatogram showed a peak whose retention time (5.1 minutes) was identical with that of an authentic sample of 1,2-cyclononadiene.

The magnesium powder and any other solid material was removed by filtration; 50 ml. of furan was then added in hopes that furan would form a Diels-Alder adduct with the 1,2-cyclononadiene. The mixture was stirred at room temperature for 24 hours. At the end of the 24 hour period, a sample was removed for analysis by gas chromatography (conditions as above). The chromatogram showed only peaks whose retention times (0.45 minutes, 0.60 minutes, and 5.1 minutes) were identical with those of authentic samples of furan, tetrahydrofuran, and 1,2-cyclononadiene, respectively. There was a small amount of white precipitate in the bottom of the flask, presumably of a polymer of furan.

XIII. DEBROMINATION OF 2,3-DIBROMOCYCLOHEXENE

Debromination of 2,3-dibromocyclohexene in tetrahydrofuran. A mixture of 1.00 g. (4.17 mmoles) of 2,3-dibromocyclohexene, 1.01 g. (41.7 mmoles) of magnesium powder, and 18 ml. of tetrahydrofuran (THF) was stirred at room temperature under nitrogen atmosphere. About 3 minutes after the reagents had been mixed, a fairly vigorous reaction began. After 5 hours, a sample was removed for analysis by gas chromatography (5' x ¼" pyrex glass column packed with 10% Carbowax 20M on HMDS treated 80/100 mesh Chromosorb P, helium flow = 300 ml./min., injector = 210°C, detector = 210°C, and column = 155°C). The chromatograms showed no peak with a retention time of 8.7 minutes, the retention time of the 2,3-dibromocyclohexene, but showed only a peak whose retention time (0.2 minutes) was identical to that of tetrahydrofuran. The reaction mixture was filtered to remove the magnesium powder and the THF was carefully removed under reduced pressure. The remaining solid material was treated with 25 ml. of ether and 10 ml. of 3 *M* HCl. The ether solution was removed, washed with water, and dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and the ether was removed under reduced pressure leaving about 0.5 g. of a very sticky, yellow syrup. The syrup solidified only when cooled on a dry ice-acetone bath. The syrup gave a very small amount of silver bromide after being fused with sodium and treated with silver nitrate. Addition of one drop of the syrup to an aqueous solution of silver nitrate also gave a very small amount of silver bromide.

Debromination of 2,3-dibromocyclohexene in the presence of cyclohexene. A mixture of 1.00 g. (4.17 mmoles) of 2,3-dibromocyclohexene, 1.01 g. (41.7 mmoles) of magnesium powder, and 3 ml. of cyclohexene in 15 ml. of

THF was stirred under a nitrogen atmosphere and at room temperature for 6 hours. Then a sample was removed for analysis by gas chromatography (5' x ¼" pyrex glass column packed with 10% Carbowax 20M on HMDS treated 80/100 mesh Chromosorb P, helium flow = 120 ml./min., injector = 155°C, detector = 150°C, column = 102°C). The absence of a peak on the chromatogram with a retention time of about 8.7 minutes (the retention time of 2,3-dibromocyclohexene) showed that all of the 2,3-dibromocyclohexene had been consumed in the reaction. The reaction mixture was filtered to remove the magnesium powder and the THF was removed under reduced pressure. The solid material which remained was treated with 25 ml. of ether and 10 ml. of 3 M HCl. The ether solution was removed, washed with water (3 x 10 ml.), and dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and the ether was removed under reduced pressure leaving about 0.5 g. of a very sticky, brown tar.

After fusion with sodium, the tar yielded a very small amount of silver bromide indicating the presence of only a small amount of bromine. A very small amount of silver bromide was obtained when some of the tar was treated with aqueous silver nitrate.

Debromination of 2,3-dibromocyclohexene in the presence of tetraphenylcyclopentadienone. A mixture of 1.00 g. (4.17 mmoles) of 2,3-dibromocyclohexene, 1.01 g. (41.7 mmoles) of magnesium powder, and 1.60 g. (4.15 mmoles) of tetraphenylcyclopentadienone in 18 ml. of THF under a nitrogen atmosphere was stirred for a total of 30 minutes at room temperature. A fairly vigorous reaction began about 5 minutes after the reagents had been mixed; after 10 minutes, the deep purple color of tetraphenylcyclopentadienone had become a greenish color. An additional 82 ml.

of THF was added to the reaction mixture, 100 ml. of ether was also added. Sufficient 3 M HCl to acidify the reaction was added. The aqueous layer was removed and the ether layer was washed with 100 ml. of water, 100 ml. of 10% sodium bicarbonate solution, and 100 ml. of water. The ether solution was dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and the ether was removed under reduced pressure. The residue was extracted with 95% ethanol leaving about 0.5 g. of a brown solid. The alcohol solution appeared to be mostly tetraphenylcyclopentadienone. The solid appeared to be a tar which was heavily contaminated with tetraphenylcyclopentadienone. It was not possible to remove all of the tetraphenylcyclopentadienone from the tar.

Debromination of 1,2-dibromoethane in the presence of tetraphenylcyclopentadienone. A mixture of 0.78 g. (4.17 mmoles) of 1,2-dibromoethane, 1.01 g. (4.17 mmoles) of magnesium powder, and 1.60 g. (4.15 mmoles) of tetraphenylcyclopentadienone in 18 ml. of THF under a nitrogen atmosphere was stirred for a total of 2 hours. During this time, the purple color of the tetraphenylcyclopentadienone turned to a chrome yellow. At the end of the two-hour reaction period, 100 ml. of ether was added and the mixture was filtered in order to remove the magnesium. Upon the addition of 25 ml. of water to the reaction mixture, the yellow color disappeared and the ether layer became pink. The ether solution was removed, washed with water (3 x 50 ml.), and dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and the ether was removed under reduced pressure. The glassy solid which remained in the flask was extracted with 95% ethanol leaving about 0.2 g. of the pink solid. This solid decomposed over a range of 79°C to 105°C and appeared to be a substance with a high molecular might.

Debromination of 2,3-dibromocyclohexene in the presence of furan. A mixture of 1.00 g. (4.17 mmoles) of 2,3-dibromocyclohexene in 9 ml. of THF was added dropwise over a period of 15 minutes to a stirred mixture of 1.01 g. (41.7 mmoles) of magnesium powder in 6 ml. of THF and 3 ml. (2.8 g., 41 mmoles) of furan. The reaction mixture was kept under a nitrogen atmosphere and at room temperature. A moderately vigorous reaction began about 5 minutes after the addition was begun. At the end of 3 hours, a sample was removed for analysis by gas chromatography (5' x $\frac{1}{4}$" pyrex glass column packed with 10% Carbowax 20M on HMDS treated 80/100 mesh Chromosorb P, helium flow = 300 ml./min., injector = 210°C, detector = 210°C, column = 155°C). The chromatogram showed no peak with a retention time of 8.7 minutes (the retention time of 2,3-dibromocyclohexene) but showed only a peak whose retention time (about 0.2 min.) was identical with that of an authentic sample of furan and tetrahydrofuran. The peaks due to furan and tetrahydrofuran were not resolved under the above conditions and appeared as a single peak. Thus, the 2,3-dibromocyclohexene had been consumed in the reaction. Analysis of the reaction mixture by gas chromatography under a different set of conditions (5' x $\frac{1}{4}$" pyrex glass column packed with 10% Carbowax 20M on HMDS treated 80/100 mesh Chromosorb P, helium flow = 120 ml./min., injector = 112°C, detector = 115°C, and column = 58°C) showed only two peaks whose retention times (0.9 minutes and 1.8 minutes) were identical with those of authentic samples of furan and THF, respectively.
The magnesium was removed by filtration and the THF was removed under reduced pressure and the remaining solid was treated with 10 ml. of 3 M HCl and 15 ml. of ether. The aqueous layer was extracted with 10 ml. of ether.

The combined ether extract was washed with water (3 x 10 ml.) and dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and the ether was removed under reduced pressure leaving about 0.5 g. of a very sticky, brown tar. The tar gave a positive test for bromine after fusion with sodium but gave no precipitate of silver bromide when tested with either aqueous or alcoholic silver nitrate.

Debromination of 2,3-dibromocyclohexene in the presence of cyclopentadiene. A solution of 1.00 g. (4.17 mmoles) of 2,3-dibromocyclohexene in 9 ml. of THF was added dropwise to a well-stirred mixture of 1.01 g. (41.7 mmoles) of magnesium powder in 6 ml. of THF and 3 ml. (2.4 g., 36.3 mmoles) of cyclopentadiene under a nitrogen atmosphere. The addition took place over a period of 12 minutes. A moderately vigorous reaction began about 5 minutes after the addition was begun. The mixture was stirred for a total of 3 hours. At that time a sample was removed for analysis by gas chromatography (5' x ¼" pyrex glass column packed with 10% Carbowax 20M in HMDS treated 80/100 mesh Chromosorb P, helium flow = 300 ml./min., injector = 210°C, detector = 210°C, column = 155°C). The chromatogram showed no peak with a retention time of 8.7 minutes (the retention time of 2,3-dibromocyclohexene). Thus, it appeared that all the 2,3-dibromocyclohexene had been consumed in the reaction. Analysis of the reaction mixture by gas chromatography under a different set of conditions (column and packing as above, helium flow = 120 ml./min., injector = 112°C, detector = 115°C, and column = 58°C) showed three peaks whose retention times (0.75 minutes, 1.85 minutes, and 27.9 minutes) were identical with authentic samples of cyclopentadiene, THF, and dicyclopentadiene, respectively. The magnesium was removed by filtration. The tetrahydrofuran was removed under reduced pressure and the residual solid was treated with 10 ml. of 3 _M_ HCl and 15 ml. of ether. The aqueous layer was extracted with 10 ml. of ether. The combined ether extract was washed with water (3 x 10 ml.) and dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and the ether was removed under reduced pressure leaving about 0.5 g. of a very sticky tar. The tar gave a very faint test for bromine after fusion with sodium but gave no precipitate of silver bromide when treated directly with alcoholic or aqueous silver nitrate.

CHAPTER V

SUMMARY

The synthesis and characterization of 2-bromo-2-cyclohepten-1-yl acetate and 2,3-dibromocyclononene were accomplished. Structural assignments were based on satisfactory elemental analyses and analyses of their infrared and nuclear magnetic resonance spectra. In the case of 2,3-dibromocyclononene, chemical evidence supporting the assigned structure included debromination to 1,2-cyclononadiene and immediate formation of silver bromide upon treatment with aqueous silver nitrate and upon treatment with alcoholic silver nitrate.

Gas chromatography and analysis of the nuclear magnetic resonance spectrum of 2,3-dibromocyclononene showed that it was a mixture of cis- and trans-isomers. A separation of the isomer whibh had a slightly longer gas chromatography retention time in a carbowax liquid phase was achieved by preparative gas chromatography. On the basis of its nuclear magnetic resonance spectrum, the structure, trans- 2,3-dibromocyclononene, was assigned to this isomer. The isomer with the shorter retention time was, therefore, assigned the cis-structure.

A number of synthetic procedures were examined in an attempt to develop a general synthetic route to 2,3-dibromocycloalkenes.

2,3-Dibromocyclohexene was readily debrominated with magnesium yielding a substance with a high molecular weight. Experiments performed in an attempt to trap 1,2-cyclohexadiene as a reaction intermediate proved unsuccessful.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. G. Aarland, J. prakt. Chem., (2) 6, 260 (1873).

2. L. Henry, Ber., 8, 398 (1875).

3. A. A. Al'bitskii, Zhur. Russ. Fiz. -Khim. Obshch., 19, 364 (1887), Chem. Zentr., I, 1248 (1887).

4. Ya. M. Slobodin, Zhur. Obshch. Khim., 22, 1958 (1952), Chem. Abs., 47, 8630 g. (1953).

5. A. A. Petrov and A. V. Fedorova, Russ. Chem. Rev., 33, 1 (1964).

6. W. D. Celmer and Y.A. Solomons, J. Am. Chem. Soc., 74, 1870 (1952); ibid., 2245 (1952); ibid., 3838 (1952).

7. J. D. Bu'Lock, E.R. H. Jones, P. R. Leeming, and J. M. Thompson, J. Chem. Soc., 4270 (1955); ibid., 3767 (1956).

8. R. C. Cambie, A. Hirschberg, E. R. H. Jones, and G. Lowe, J. Chem. Soc., 4120 (1963).

9. F. Bohlman, H. Bornowski, and C. Arndt, Chem. Ber., 98, 2236 (1965).

10. H. W. Sprecher, R. Maier, M. Barber, and R. T. Holman, Biochemistry, 4, 1856 (1965).

11. M. O. Bagby, C. R. Smith, Jr., and I. A. Wolff, J. Org. Chem., 30, 4227 (1965).

12. R. E. Bew, J. R. Chapman, E. R. H. Jones, B. E. Lowe, and G. Lowe, J. Chem. Soc., Org., 129 (1966); R. E. Bew, R. C.Cambie, E. R. H. Jones, and G. Lowe, J. Chem. Soc., Org., 135 (1966).

13. E. R. H. Jones, L. Skattebol, and M. C. Whiting, J. Chem. Soc., 3483 (1960).

14. D. Rewicki, Chem. Ber., 99 392 (1966).

15. W. J. Ball and S. T. Landor, J. Chem. Soc., 2298 (1962).

16. L. Skattebol, Acta Chem. Scand., 17, 1683 (1963).

17. T. L. Jacobs and R. A. Meyers, J. Am. Chem. Soc., 86, 5244 (1964); J. C. Martin, U. S. Patent 3,131, 234, Chem. Abs., 61, 2969f (1964).

18. H. D. Hartzler, J. Org. Chem., 29, 1311 (1964).

19. H. Fischer and H. Fischer, Chem. Ber., 97, 2975 (1964).

20. R. Ya. Levina and E. A. Viktorova, Uspekhi Khim., 27, 162 (1958), Chem. Abs., 52, 10864f (1958).

21. G. G. Gustavson and N. Demjanov, Zhur. Russ. Khim. Obshch., 20, 615 (1888); J. prakt. Chem., 38, 201 (1888).

22. Ya. M. Slobodin and A. P. Khitrov, Zhur. Obshch. Khim., 31, 3945 (1961), Chem. Abs., 57, 3410e (1962).

23. A. T. Blomquist, R. E. Burge, and A. C. Sucsy, J. Am. Chem. Soc., 74, 3636 (1952).

24. Ya. I. Ginzburg, Zhur. Obshch. Khim., 10, 513 (1940), Chem. Abs., 34, 7843^9 (1940); Zhur. Obshch. Khim., 15, 442 (1945), Chem. Abs., 40, 4655^3 (1946).

25. W. J. Bailey and C. R. Pfeifer, J. Org. Chem., 20, 95 (1955).

26. G. F. Hennion and J. J. Sheehan, J. Am. Chem. Soc., 71, 1964 (1949).

27. T. L. Jacobs, E. G. Teach, and D. Weiss, J. Am. Chem. Soc., 77, 6254 (1955).

28. M. Bertrand, Bull. Soc. Chim. France, 461, (1956).

29. M. Gaudemar, Compt. Rend., 232, 1945 (1951); ibid., 243, 1216 (1956); Ann. Chim. (France), 1, 161 (1956).

30. W. von E. Doering and P. M. LaFlamme, Tetrahedron. 2, 75 (1958).

31. W. von E. Doering and A. K. Hoffmann, J. Am. Chem. Soc., 76, 6162 (1954).

32. T. J. Logan, Tetrahedron Letters, 173,(1961).

33. W. R. Moore and H. R. Ward, J. Org. Chem., 25, 2073 (1960).

34. W. R. Moore and H. R. Ward, J. Org. Chem., 27, 4179 (1962).

35. L. Skattebol, Tetrahedron Letters, 167 (1961).

36. K. G. Untch, D. J. Martin, and N. T. Castellucci, J. Org. Chem., 30, 3572 (1965).

37. E. U. Elan, R. D. Clark, and J. C. Martin, Brit. Patent 1,014,653, Chem. Abs., 64, 11092d (1966).

38. R. T. Conley and T. F. Rutledge, U. S. Patent 2,818,456, *Chem. Abs.*, *55*, 6391f (1958).

39. W. M. Jones and M. H. Grasley, *Tetrahedron Letters*, 927 (1962); W. M. Jones, M. H. Grasley, and D. G. Beards, *J. Am. Chem. Soc.*, *86*, 912 (1964).

40. W. M. Jones; I. W. Wilson, Jr., and F. B. Tutwiler, *J. Am. Chem. Soc.*, *85*, 3309 (1963).

41. A. E. Favorsky, *J. Gen. Chem.* (*USSR*), *6*, 720 (1936), *Chem. Abs.*, *30*, 6337 (1936).

42. D. V. Tishchenko, *J. Gen. Chem.* (*USSR*), *8*, 1326 (1938), *Chem. Abs.*, *33*, 4190^6 (1939).

43. N. A. Domnin, *J. Gen. Chem.* (*USSR*), *10*, 1939 (1940), *Chem. Abs.*, 35, 3979^5 (1941); *J. Gen. Chem.* (*USSR*), *15*, 461 (1945), *Chem. Abs.*, *40*, 4682^8 (1946); *J. Gen. Chem.* (*USSR*), *15*, 469 (1945), *Chem. Abs.*, *40*, 4683^1 (1946).

44. N. A. Domin, *Vestnik Leningrad University*, *1*, No. 3, 103 (1946), *Chem. Abs.*, *42*, 3337f (1948).

45. W. J. Ball and S. R. Landor, *J. Chem. Soc.*, 2298 (1962).

46. A. T. Blomquist, L. H. Liu, and J. C. Bohrer, *J. Am. Chem. Soc.*, *74*, 3643 (1952).

47. V. I. Pansevich-Kolyada, *Belorus*, *Politekh. Inst. im I. V. Stalina*, *Nauch. Trudov.*, No. 87, p. 3 (1959), Chem. Abs., 56, 297b (1962).

48. H. G. Peer, *Rec. Trav. Chim.*, *81*, 113 (1962).

49. A. V. Fedorova, *Zhur. Obshch. Khim.*, *33*, 3575 (1963), *Chem. Abs.*, *60*, 7905c (1964).

50. H. N. Cripps, U. S. Patent 3,214,483, *Chem. Abs.*, 64, 3380h (1966).

51. E. R. H. Jones, G. H. Mansfield and M. C. Whiting, *J. Chem. Soc.*, 4073 (1956).

52. H. Greenfield, I. Wender, and J. H. Wotiz, *J. Org. Chem.*, *21*, 875 (1956).

53. K. Schloegl and A. Mohar, *Monatsh*, *93*, 861 (1962).

54. R. G. Schultz, *Tetrahedron Letters*, 301 (1964); *Tetrahedron*, *20*, 2809 (1964).

55. A. Nakamura, Pu-Jun Kim, and N. Hagihara, *Bull. Chem. Soc. Japan*, *37*, 292 (1964), *Chem. Abs.*, *60*, 12049h (1964); *J. Organometal. Chem.*, *3*, 7 (1965); *ibid.*, 355 (1965).

56. M. S. Lupin and B. L. Shaw, *Tetrahedron Letters*, 883 (1964).

57. P. J. Ashworth, G. H. Whitman, and M. C. Whiting, *J. Chem. Soc.*, 4633 (1957).

58. R. W. Rosenthal and L. H. Swartzman, *J. Org. Chem.*, *24*, 836 (1959).

59. G. P. Chiusoli, *Chim. e ind.* (Milan), *41*, 513 (1959), *Chem. Abs.*, *54*, 513 (1959); *Angew. Chem.*, *72*, 74 (1960).

60. R. E. Benson and R. V. Lindsey, *J. Am. Chem. Soc.*, *81*, 4247 (1959); *ibid.*, 4250 (1959); E. I. Dupont de Nemours and Company, Brit. Patent 812,902, *Chem. Abs.*, *54*, 7591c (1960).

61. T. J. Kealey and R. E. Benson, *J. Org. Chem.*, 26, 3126 (1961).

62. J. Tsuji and T. S. Susuki, *Tetrahedron Letters*, 3027 (1965).

63. Pu-Jun Kim and N. Hagihara, *Bull. Chem. Soc. Japan*, *38*, 2022 (1965), *Chem. Abs.*, *64*, 6577c (1966).

64. L. N. Cherkasov and Kh. V. Bal'yan, *Zhur. Organ. Khim.*, *1*, 1811, (1965), *Chem. Abs.*, *64*, 3411c (1966).

65. E. Favre and M. Gaudemar, *Compt. Rend.*, Ser. C, *262*, 1332 (1966).

66. H. H. Lindner and T. Onak, *J. Am. Chem. Soc.*, *88*, 1386 (1966).

67. W. C. Agosta, *Tetrahedron*, *22*, 1195 (1966).

68. D. Rewicki, *Chem. Ber.*, *99*, 392 (1966).

69. D. K. Black and S. R. Landor, *Tetrahedron Letters*, 1065 (1963).

70. R. F. Merrit, *J. Org. Chem.*, *30*, 4367 (1965).

71. W. J. Linn, O. W. Webster, and R. E. Benson, *J. Am. Chem. Soc.* *87*, 3657 (1965).

72. M. Bertrand, *Comot. Rend.*, *245*, 2306 (1957).

73. M. Bertrand, R. Jacquier, and J. LeGras, *Compt*, *Rend.*, Ser. C, *262*, 782 (1966).

74. Eastman Kodak Company, Fr. Patent 1,414,456, *Chem. Abs.*, *64*, 6523f (1966).

75. G. S. D'Alcontres and G. L. Vecchio, Gazz. *Chim. Ital.*, *90*, 1239 (1960), *Chem. Abs.*, *56*, 5943g (1962).

76. I. A. D'yankanov, *Zhur. Obshch. Khim.*, *15*, 473 (1945), *Chem. Abs.*, *40*, 4718^4 (1946).

77. P. Dowd, *J. Am. Chem. Soc.*, *88*, 2587 (1966).

78. R. J. Crawford and D. M. Cameron, *J. Am. Chem. Soc.*, 88, 2589 (1966).

79. W. Ried and H. Mengler, *Ann. Chem.*, *678*, 95 (1964).

80. J. Sonnenberg and S. Winstein, *J. Org. Chem.*, *27*, 748 (1962).

81. G. R. Lucas and L. P. Hammett, *J. Am. Chem. Soc.*, *64*, 1928 (1942).

82. S. J. Cristol, B. Franzus, and A. S. Shadan, *J. Am. Chem. Soc.*,*77*, 2512 (1955).

83. C. L. Stevens and J. A. Valicenti, *J. Am. Chem. Soc.*, *87*, 838, (1965).

84. P. S. Skell and S. R. Sandler, *J. Am. Chem. Soc.*, *80*, 2024 (1958).

85. L. Skattebol and B. Boulette, *J. Org. Chem.*, *31*, 8 (1966).

86. K. Nakanishi, *Infrared Absorption Spectroscopy - Practical*, Holden-Day, Inc., San Francisco, 1962.

87. L. M. Jackman, *Applications of Nuclear Resonance Spectroscopy in Organic Chemistry*, The Mcmillan Company, New York, 1959.

88. N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, *High Resolution Nuclear Magnetic Resonance Spectra Catalog*, Varian Associates, 1962, Spectrum 17.

89. J. R. Dyer, *Applications of Absorption Spectroscopy of Organic Compounds*, Prentice-Hall, Englewood Cliffs, N. J., 1965.

90. A. C. Cope, P. T. Moore, and W. R. Moore, *J. Am. Chem. Soc.*, *82*, 1744 (1960).

91. G. Wittig, A. Krebs, and R. Pohlke, *Angew. Chem.* *72*, 324 (1960).

92. G. Wittig and A. Krebs, *Chem. Ber.*, *94*, 3260 (1961).

93. G. Wittig and R. Pohlke, *Chem. Ber.*, *94*, 3276 (1961).

94. L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Am. Chem. Soc.*, *87*, 3253 (1965).

95. A. I. Vogel, _J. Chem. Soc._, 636 (1943).

96. Louis F. Fieser, _Experiments in Organic Chemistry_, 3rd edition, D. C. Heath and Company, Boston, 1957, p. 283.

97. L. F. Fieser and W. S. Johnson, _J. Am. Chem. Soc._, _62_, 576 (1940).

98. E. C. Hornung (ed.), _Organic Syntheses_, Vol. III, John Wiley and Sons, Inc., New York, 1955, p. 806.

99. P. S. Skell and A. Y. Garner, _J. Am. Chem. Soc._, 78, 5430 (1956).

100. H. Gilman, E. A. Zoellner, and W. M. Selby, _J. Am. Chem. Soc._, _55_, 2152 (1933).

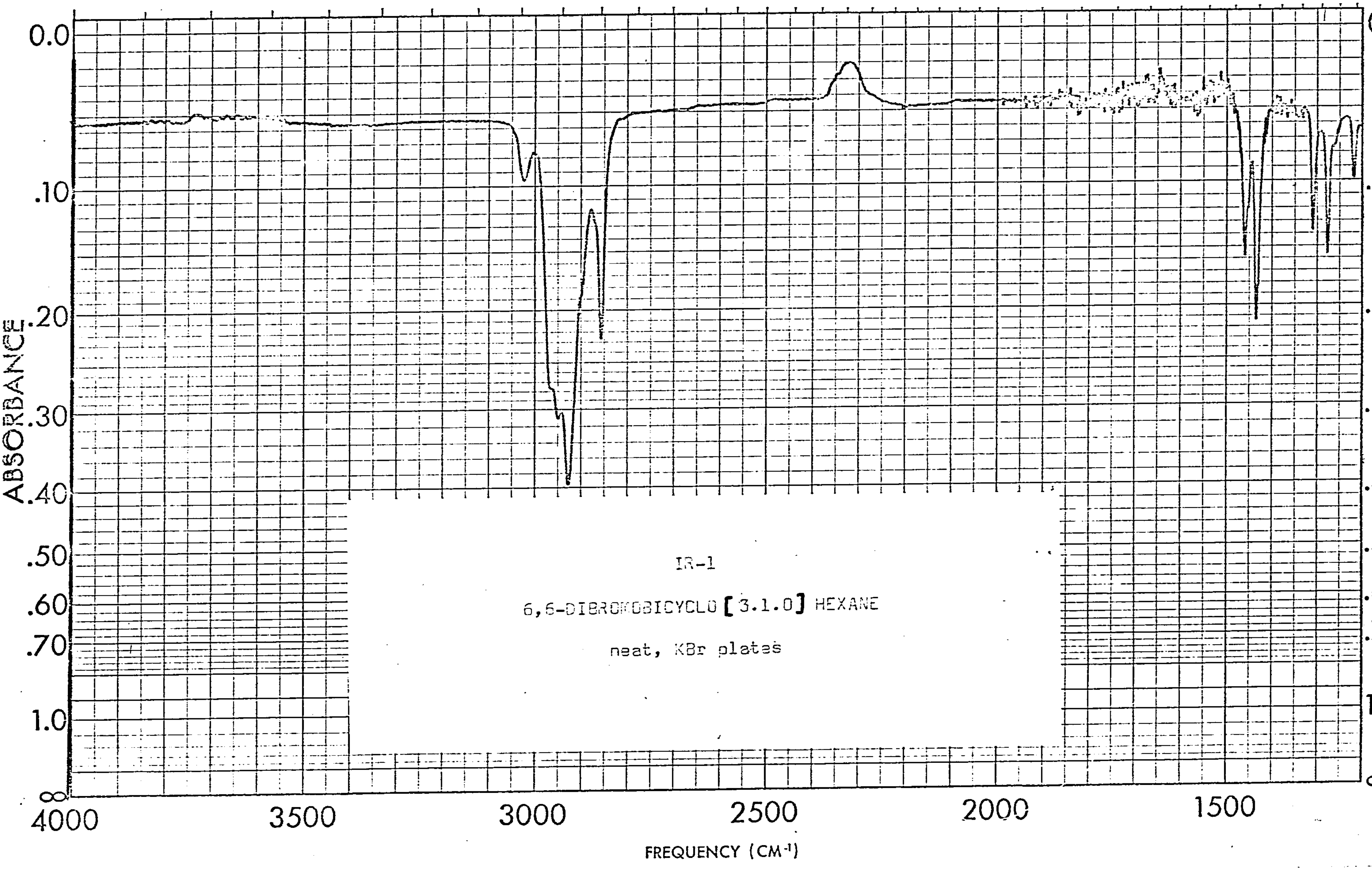
101. A. T. Blomquist, R. E. Burge, Jr., L. H. Liu, J. C. Bohrer, A. C. Sucsey, and J. Kleis, _J. Am. Chem. Soc._, _73_, 5510 (1951).

102. K. G. Untch and D. J. Martin, _J. Am. Chem. Soc._, _87_, 4501 (1965).

103. L. Skattebol and S. Soloman, _J. Am. Chem. Soc._, _87_, 4506 (1965).

104. W. C. Kray and C. E. Castro, _J. Am. Chem. Soc._, _86_, 4603 (1964).

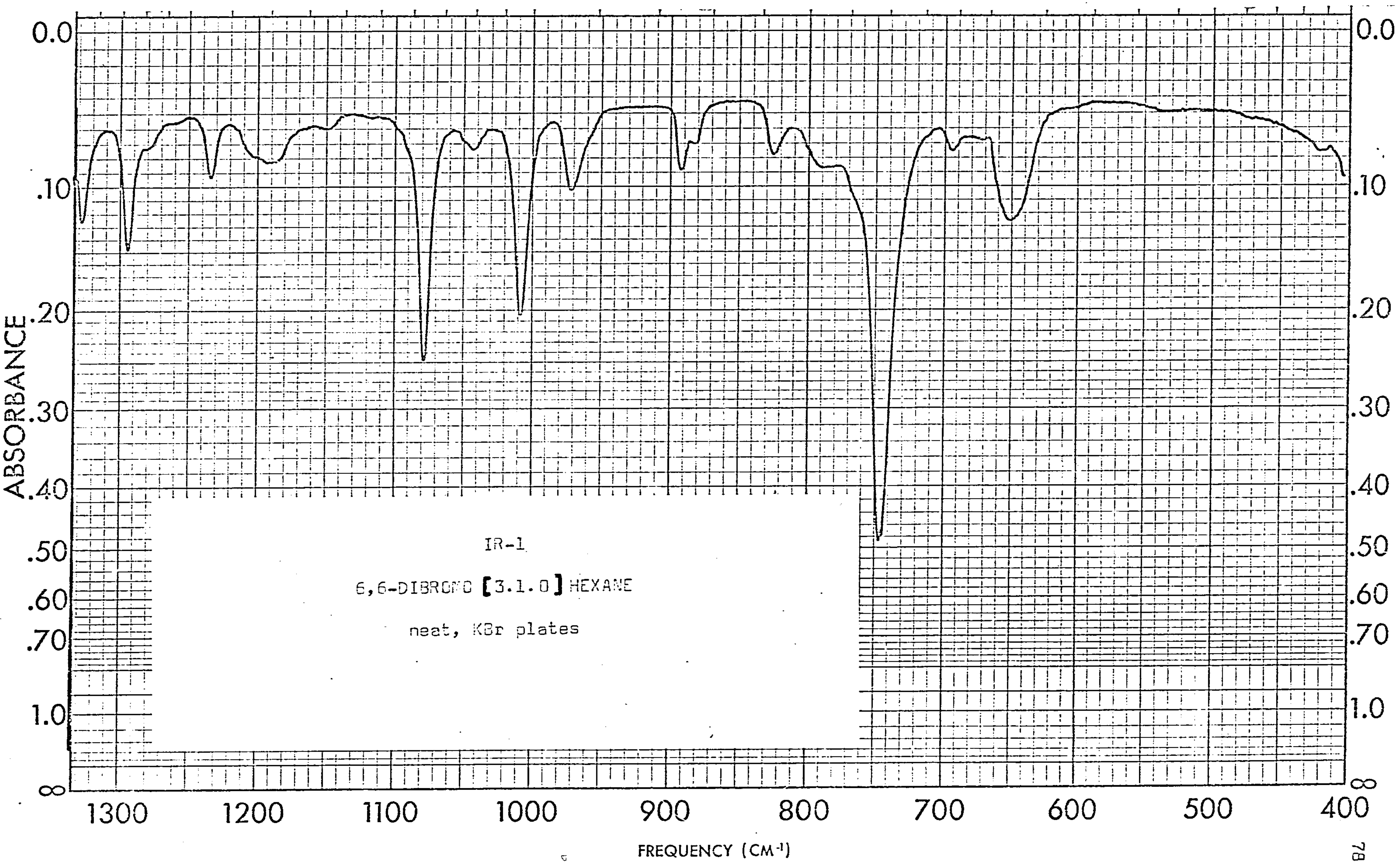
APPENDIX A



IR-1

6,6-DIBROMOBICYCLO [3.1.0] HEXANE

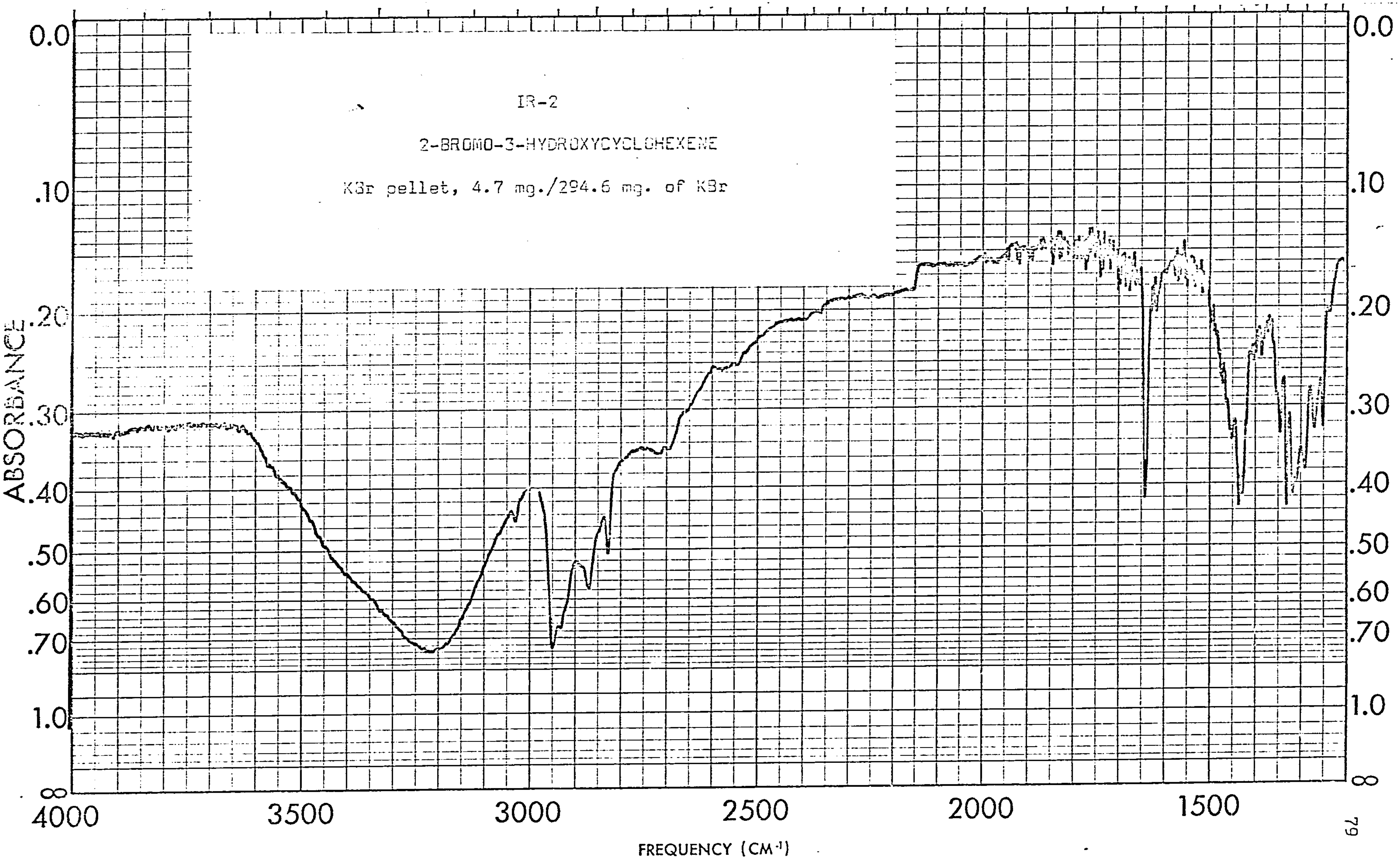
neat, KBr plates



IR-1

6,6-DIBROMO [3.1.0] HEXANE

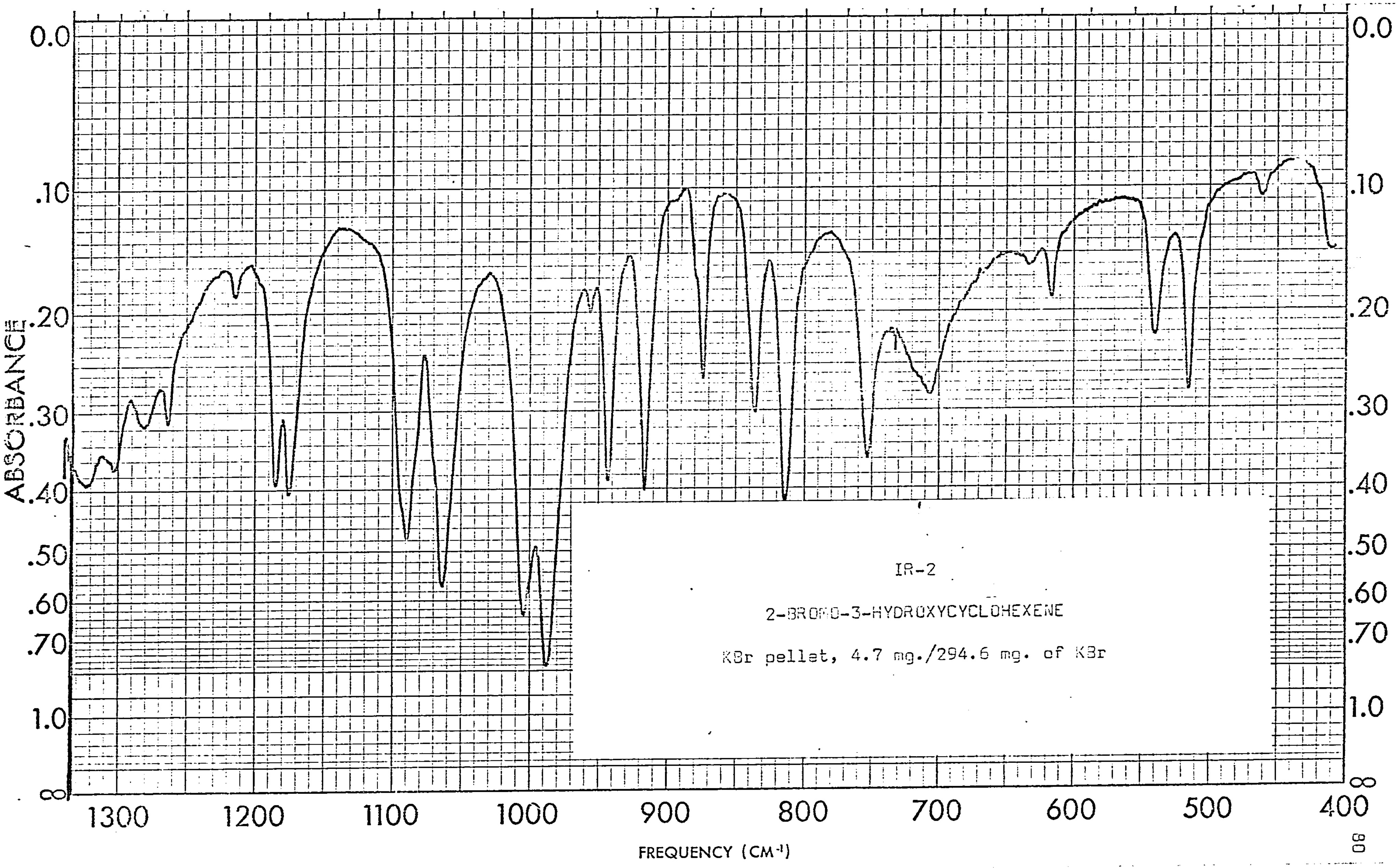
neat, KBr plates



IR-2

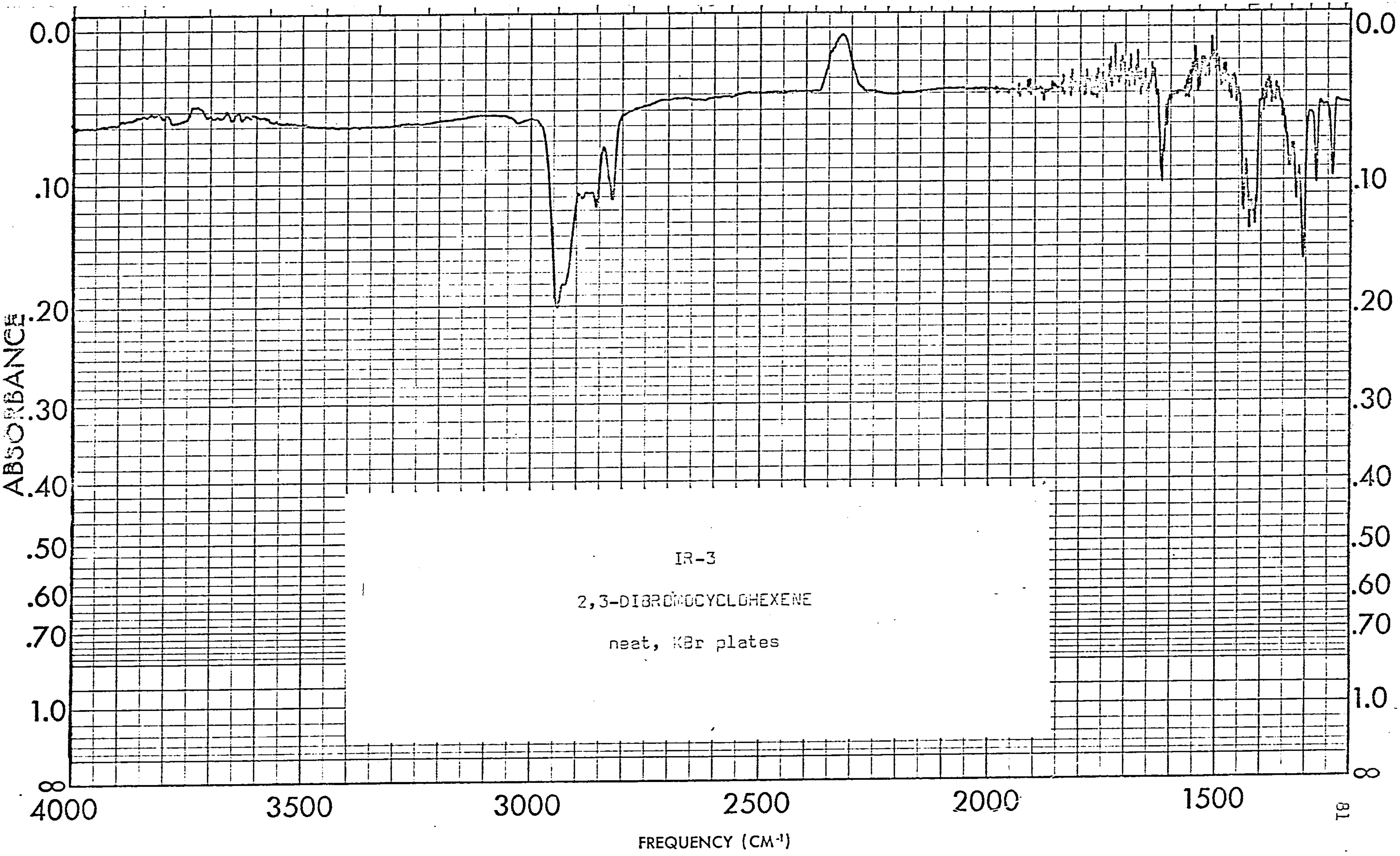
2-BROMO-3-HYDROXYCYCLOHEXENE

KBr pellet, 4.7 mg./294.6 mg. of KBr


IR-2

2-BROMO-3-HYDROXYCYCLOHEXENE

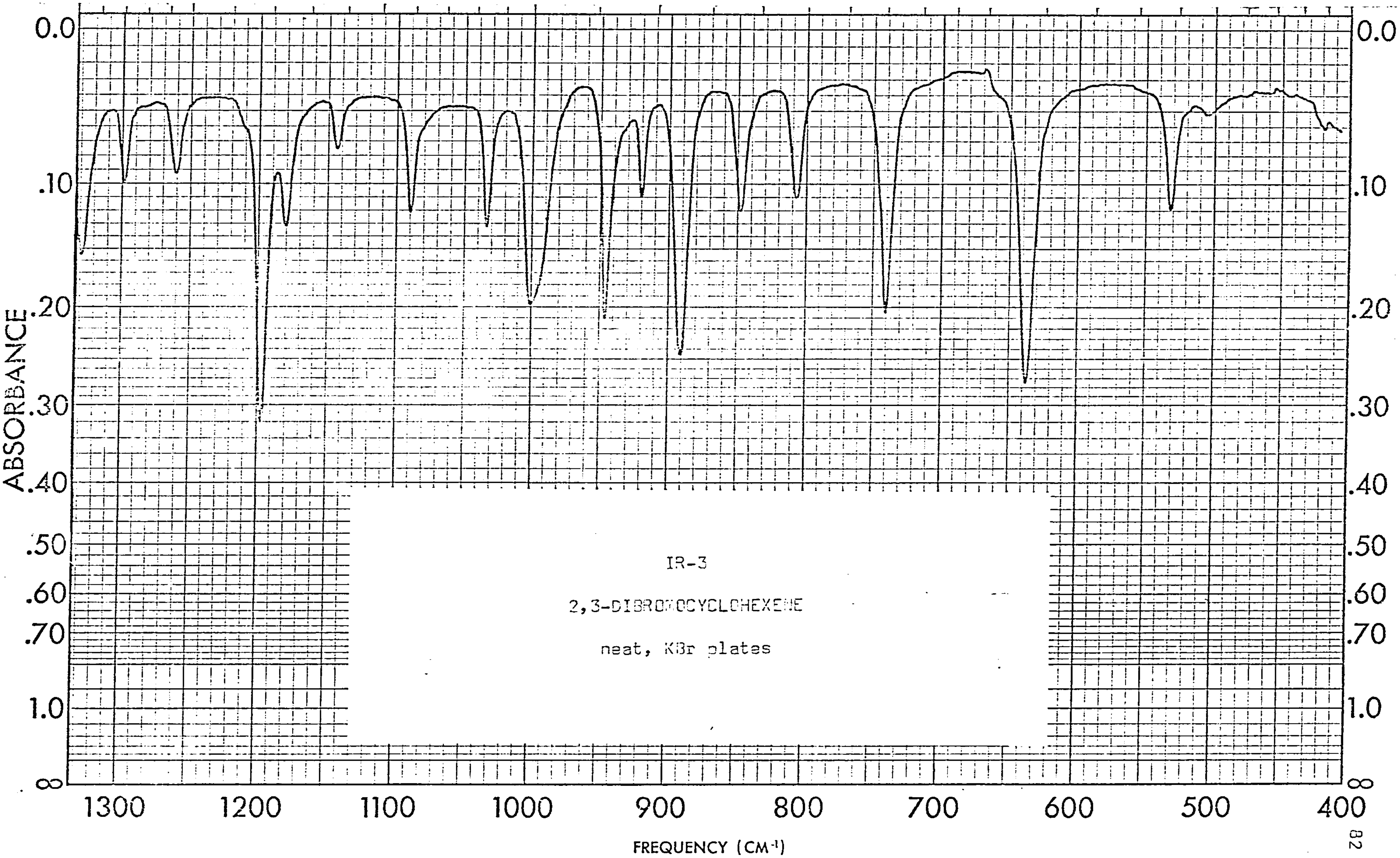
KBr pellet, 4.7 mg./294.6 mg. of KBr



IR-3

2,3-DIBROMOCYCLOHEXENE

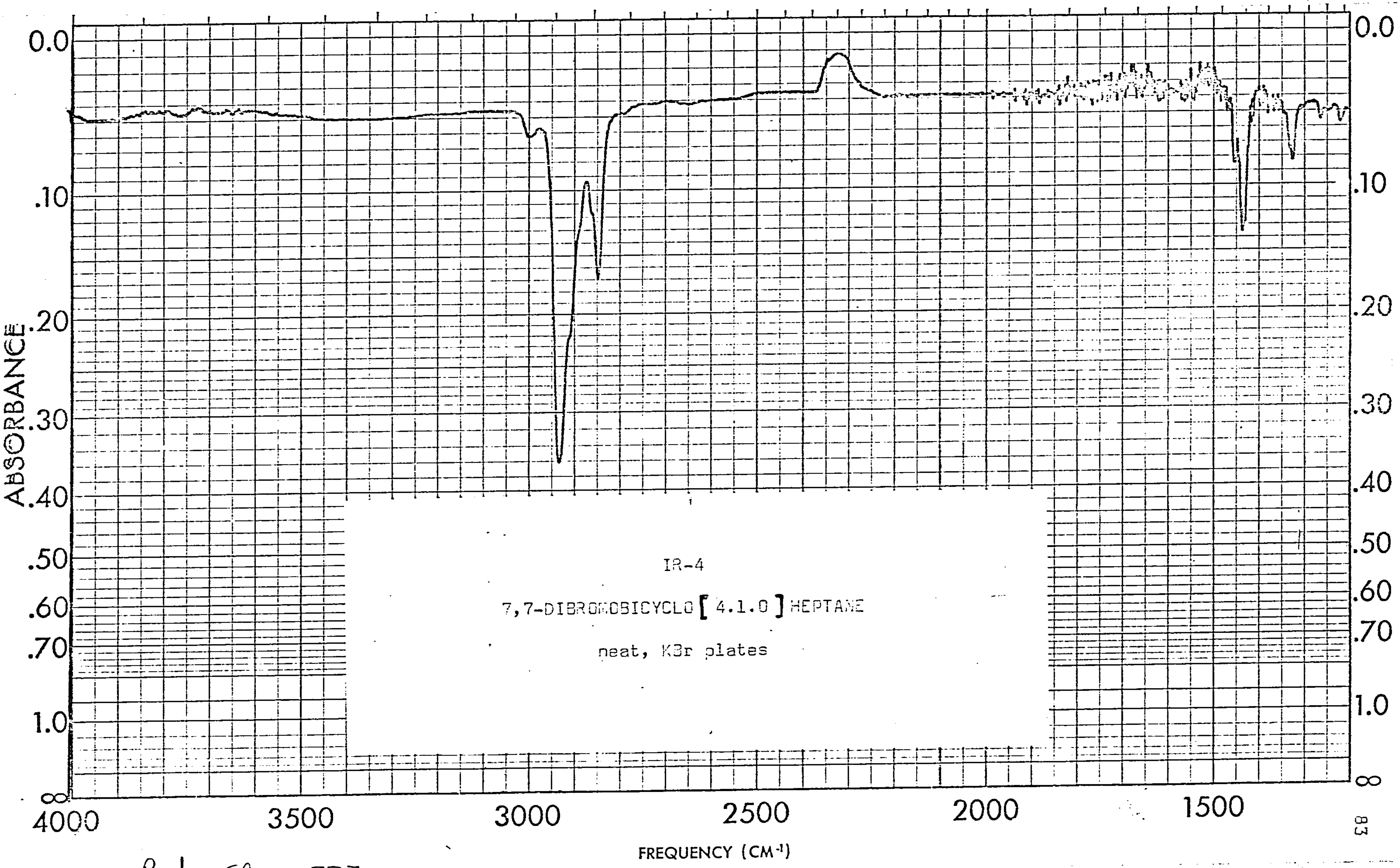
neat, KBr plates



IR-3

2,3-DIBROMOCYCLOHEXENE

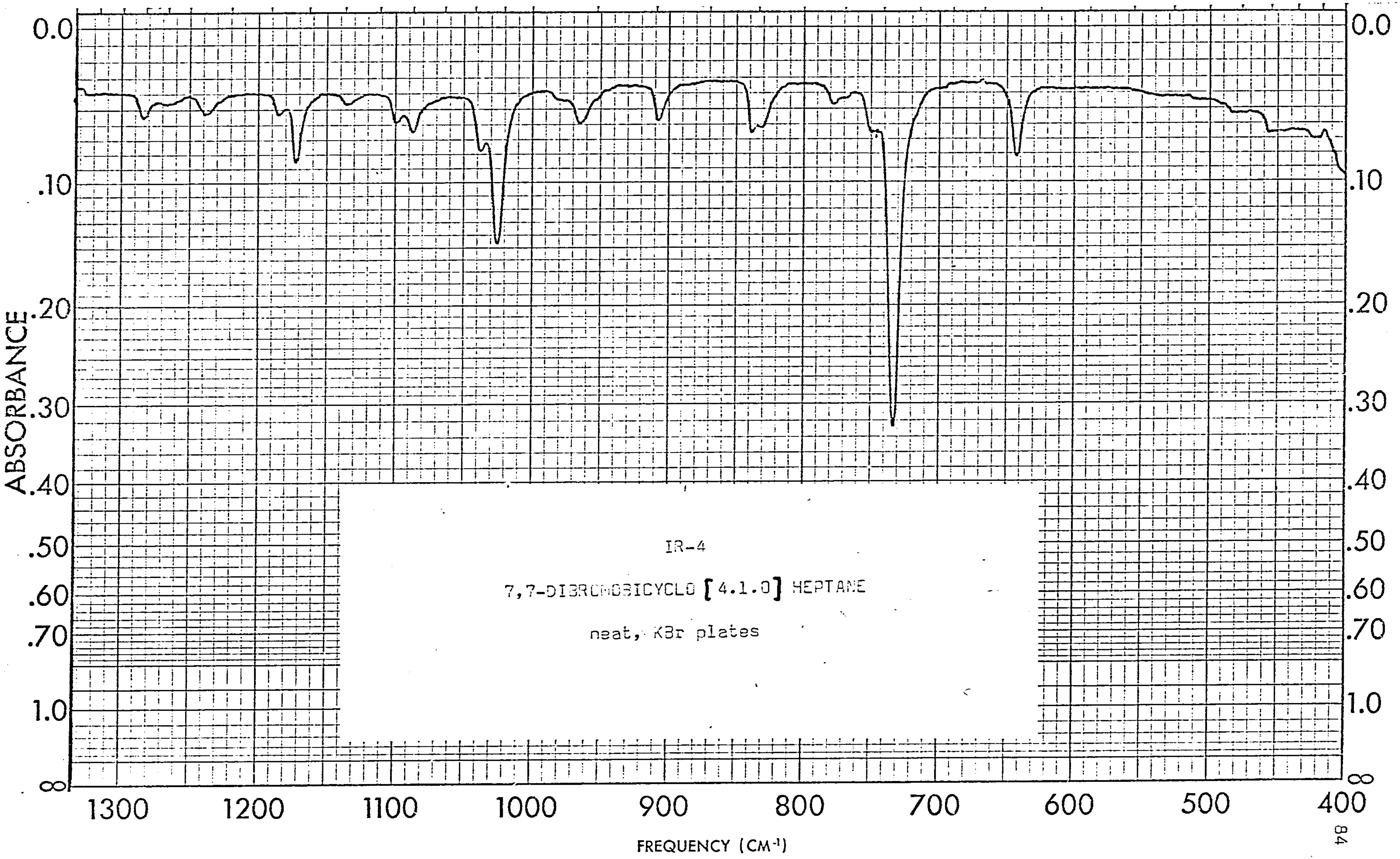
neat, KBr plates



IR-4

7,7-DIBROMOBICYCLO [4.1.0] HEPTANE

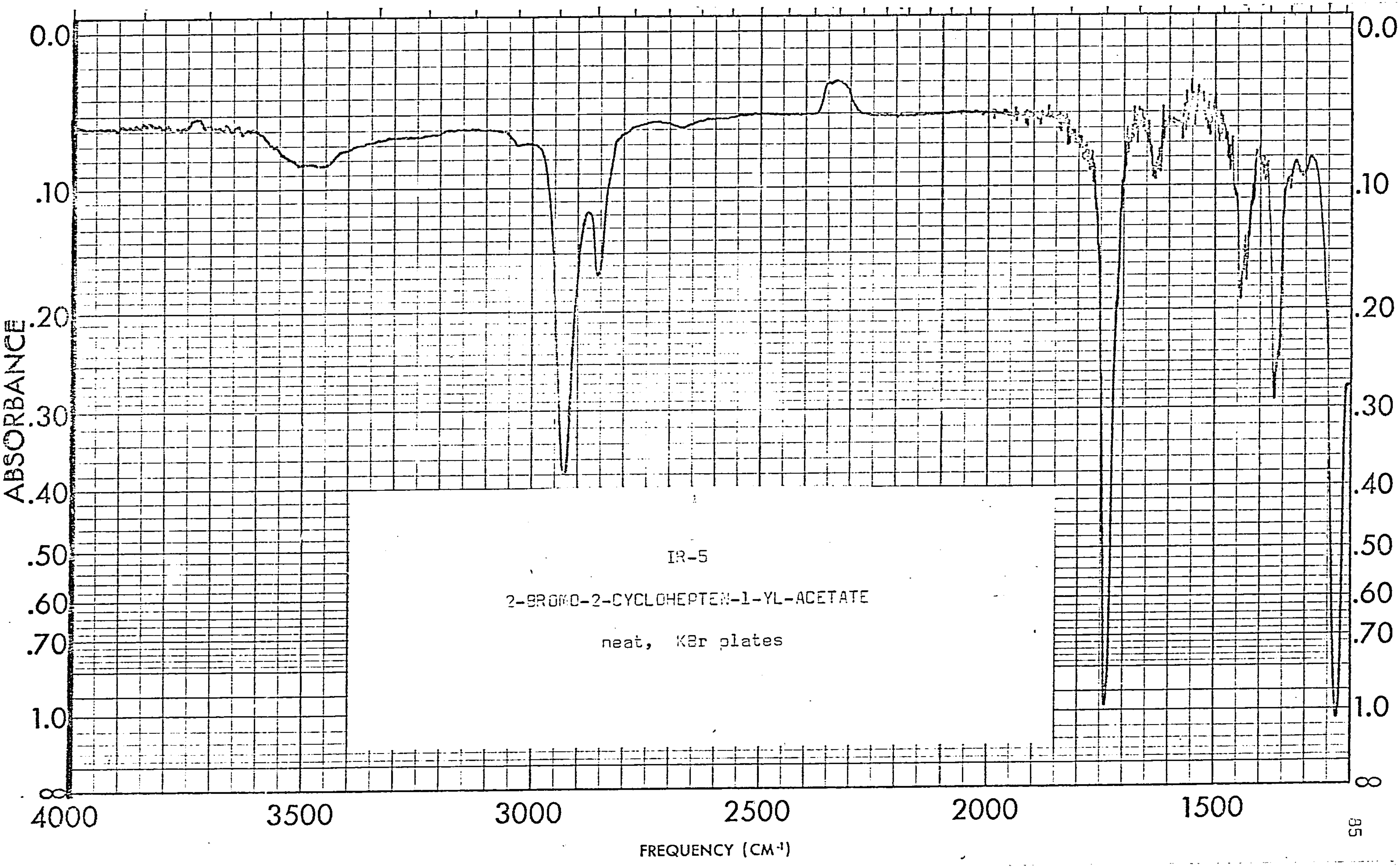
neat, KBr plates



IR-4

7,7-DIBROMOBICYCLO [4.1.0] HEPTANE

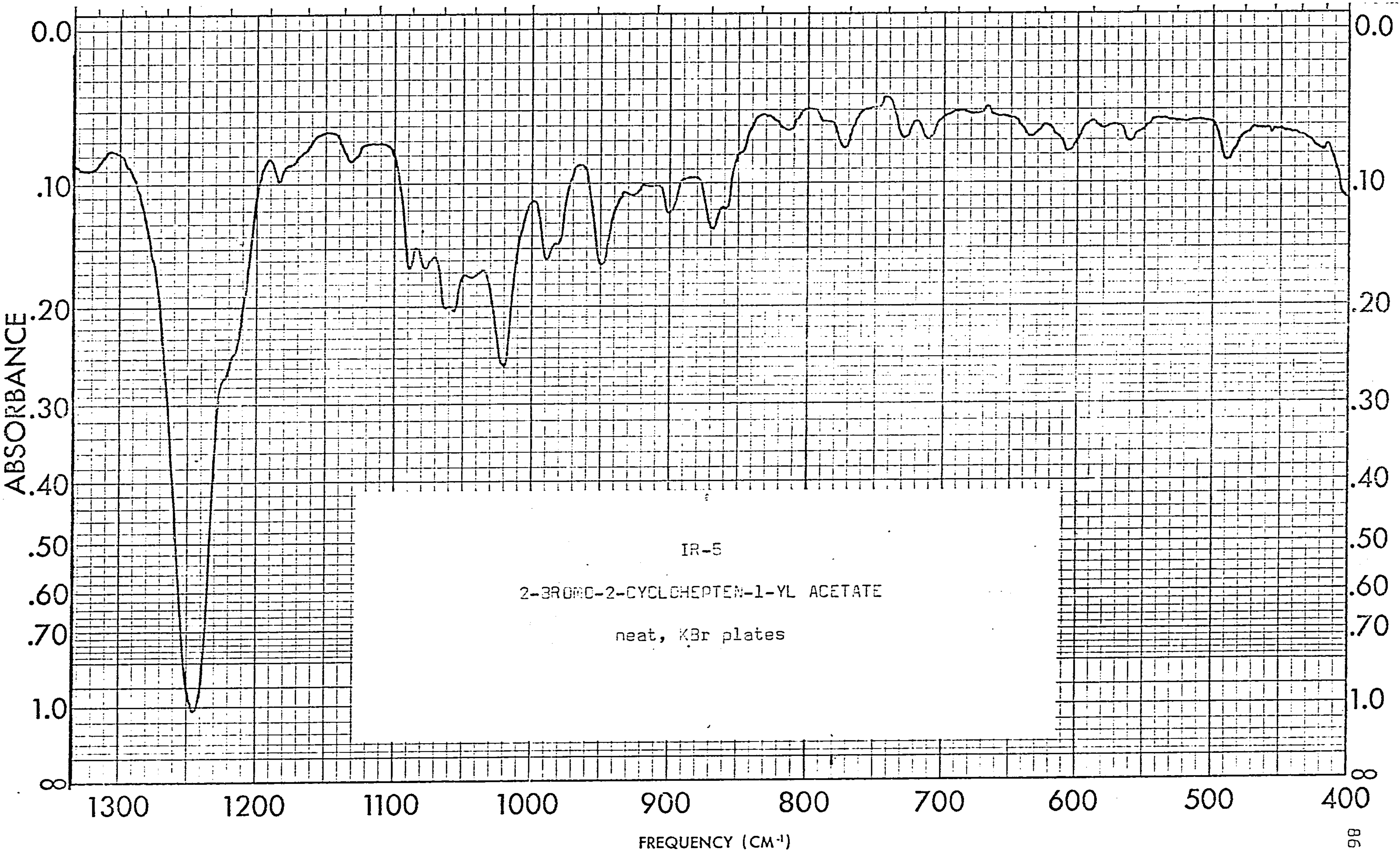
neat, KBr plates



IR-5

2-BROMO-2-CYCLOHEPTEN-1-YL-ACETATE

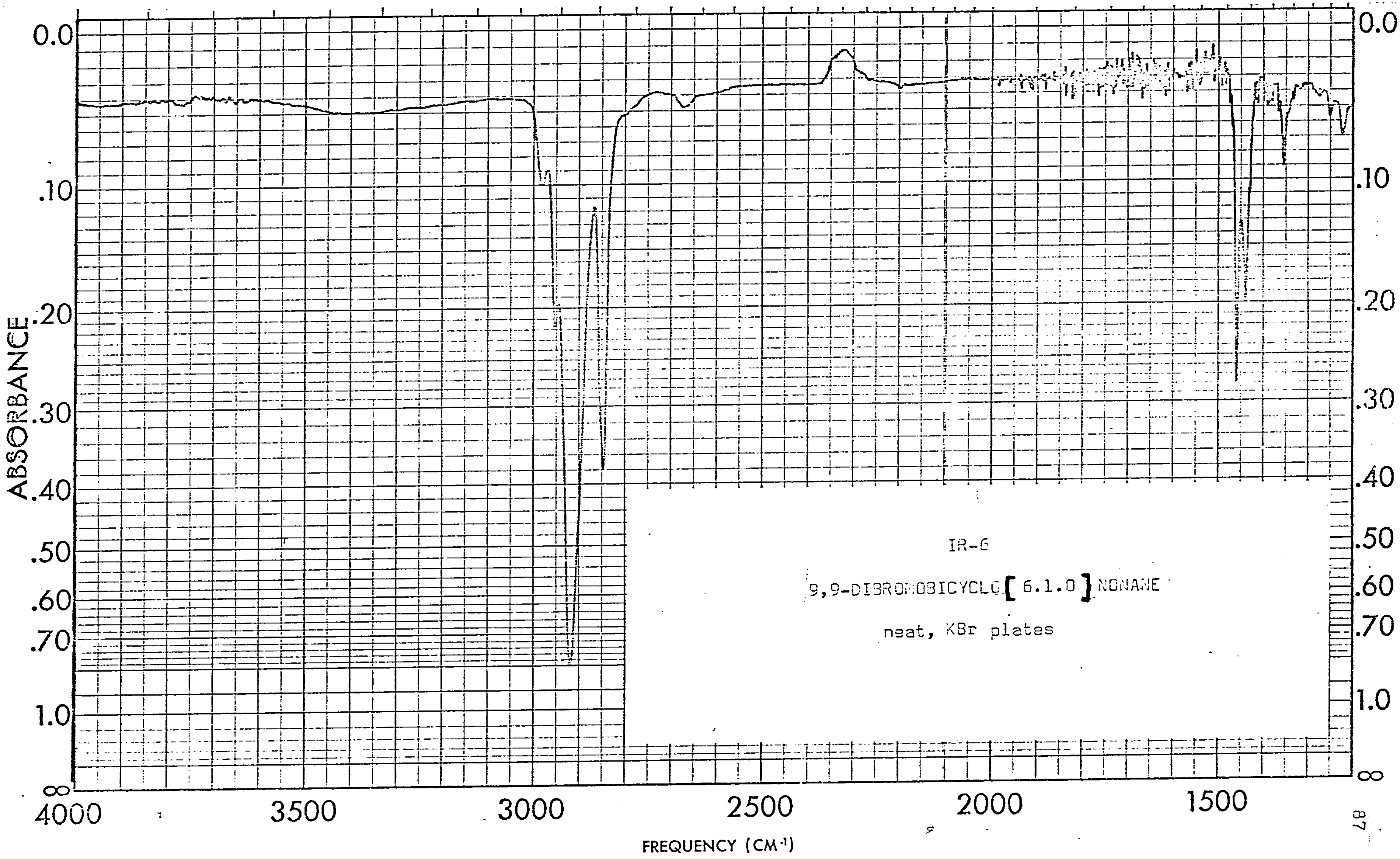
neat, KBr plates



IR-5

2-BROMO-2-CYCLOHEPTEN-1-YL ACETATE

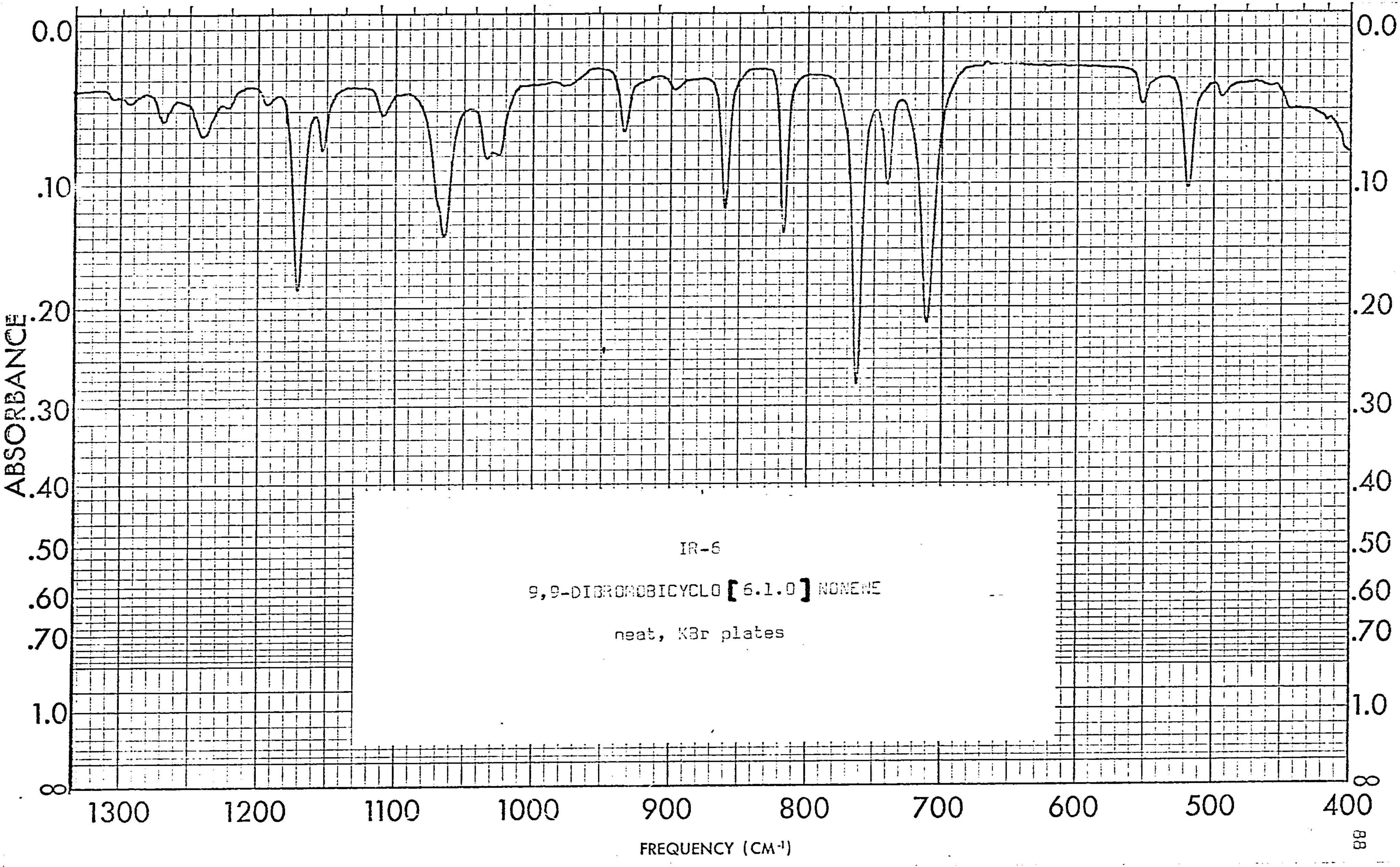
neat, KBr plates



IR-6

9,9-DIBROMOBICYCLO[6.1.0]NONANE

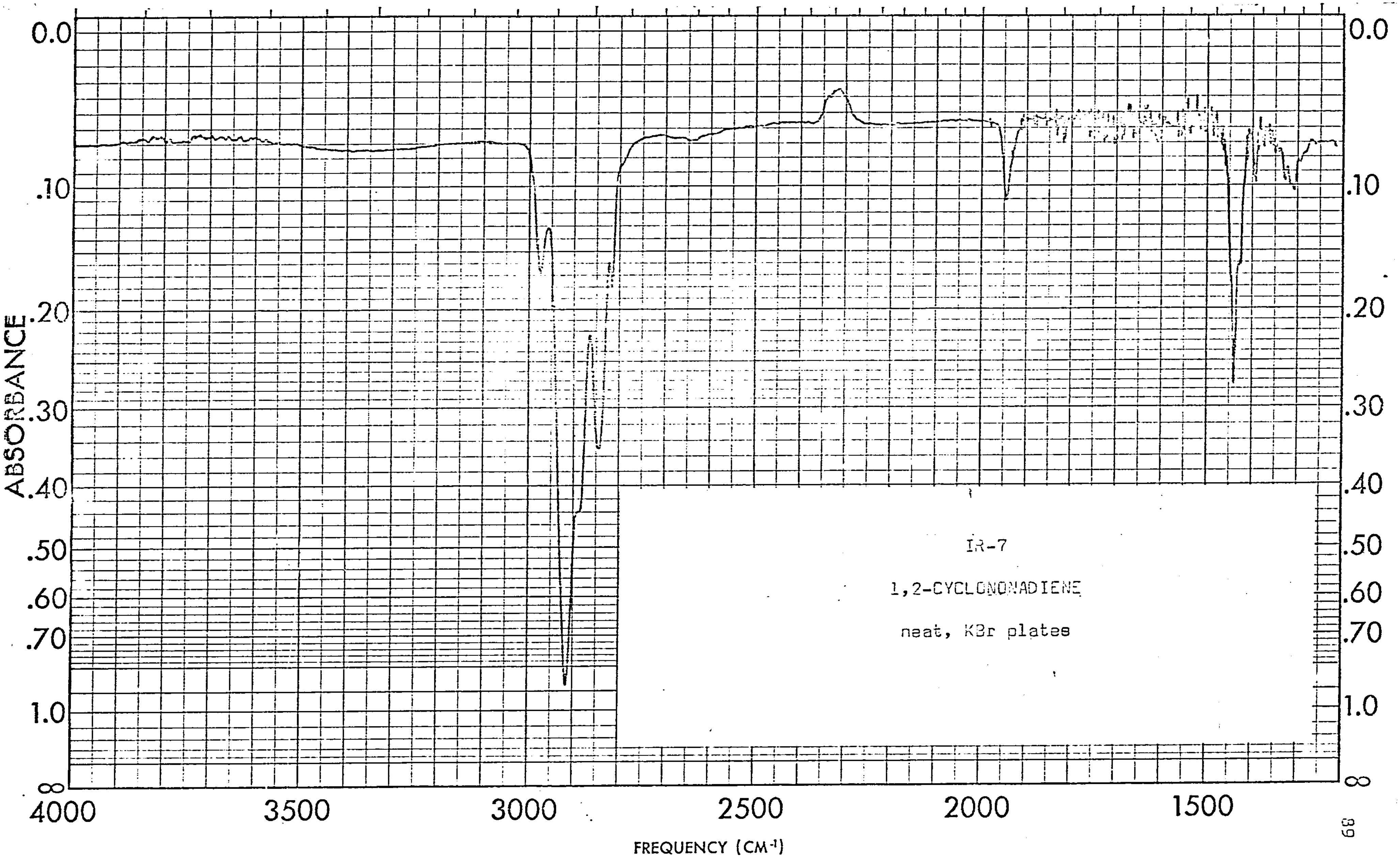
neat, KBr plates



IR-6

9,9-DIBROMOBICYCLO [6.1.0] NONENE

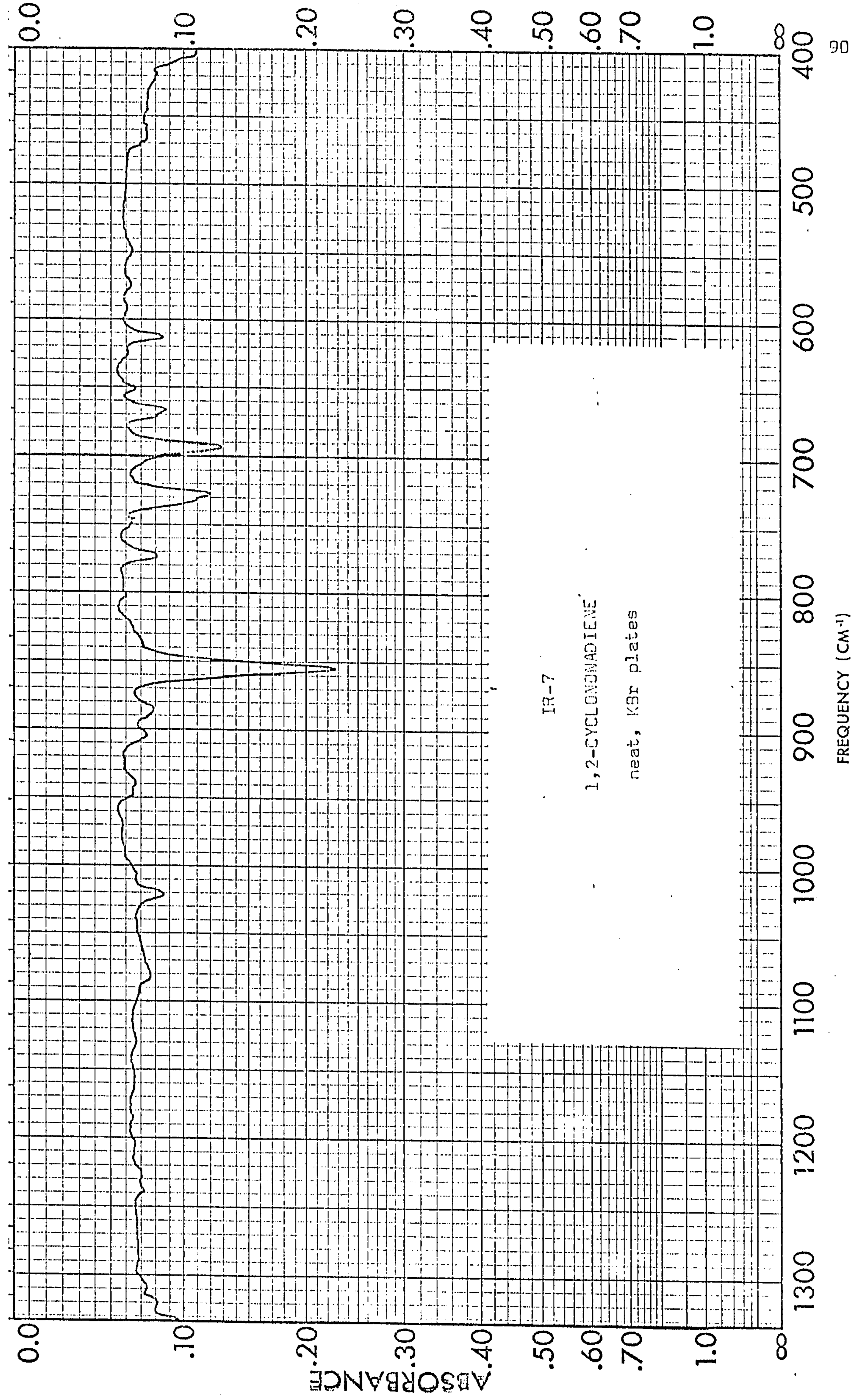
neat, KBr plates

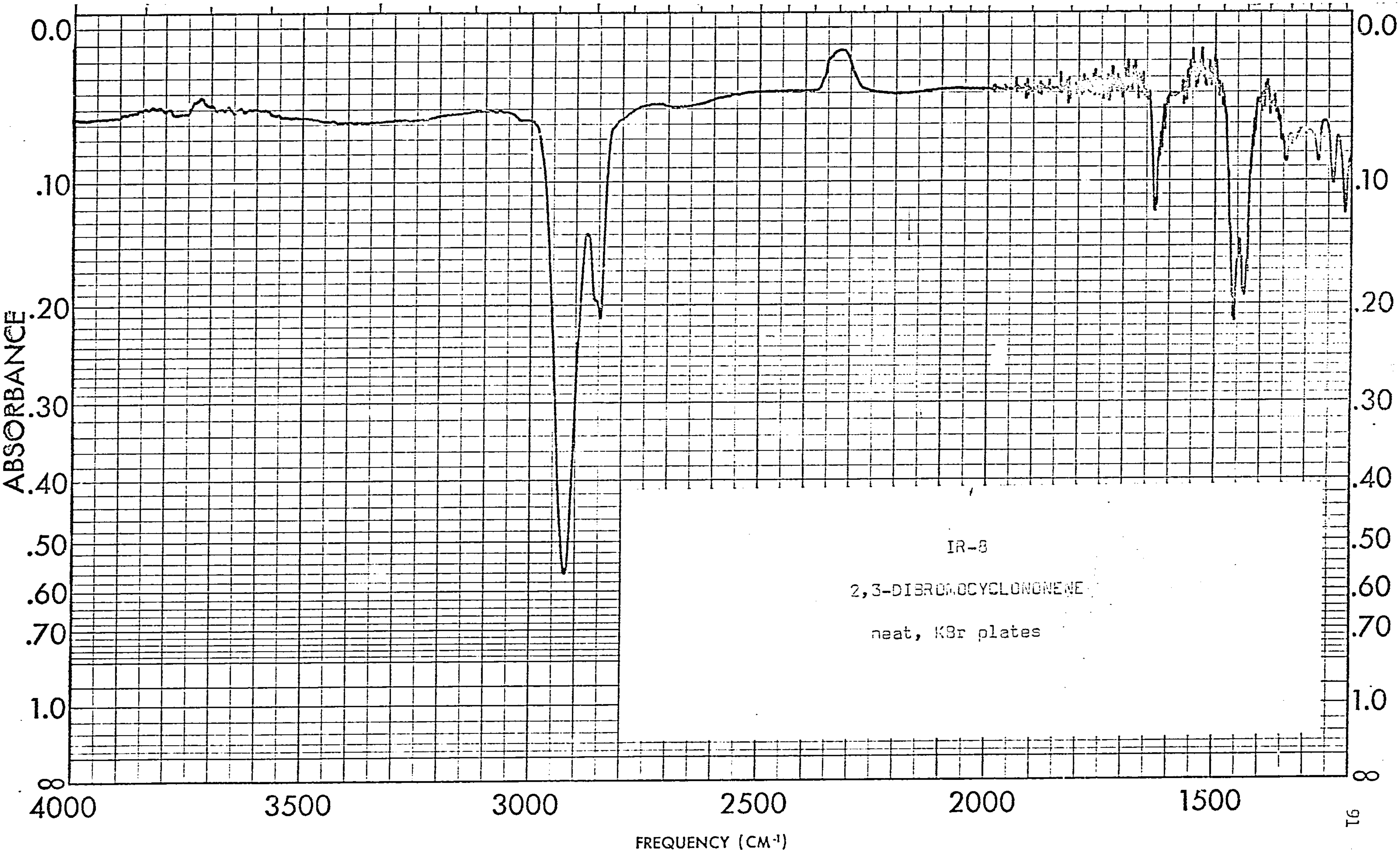


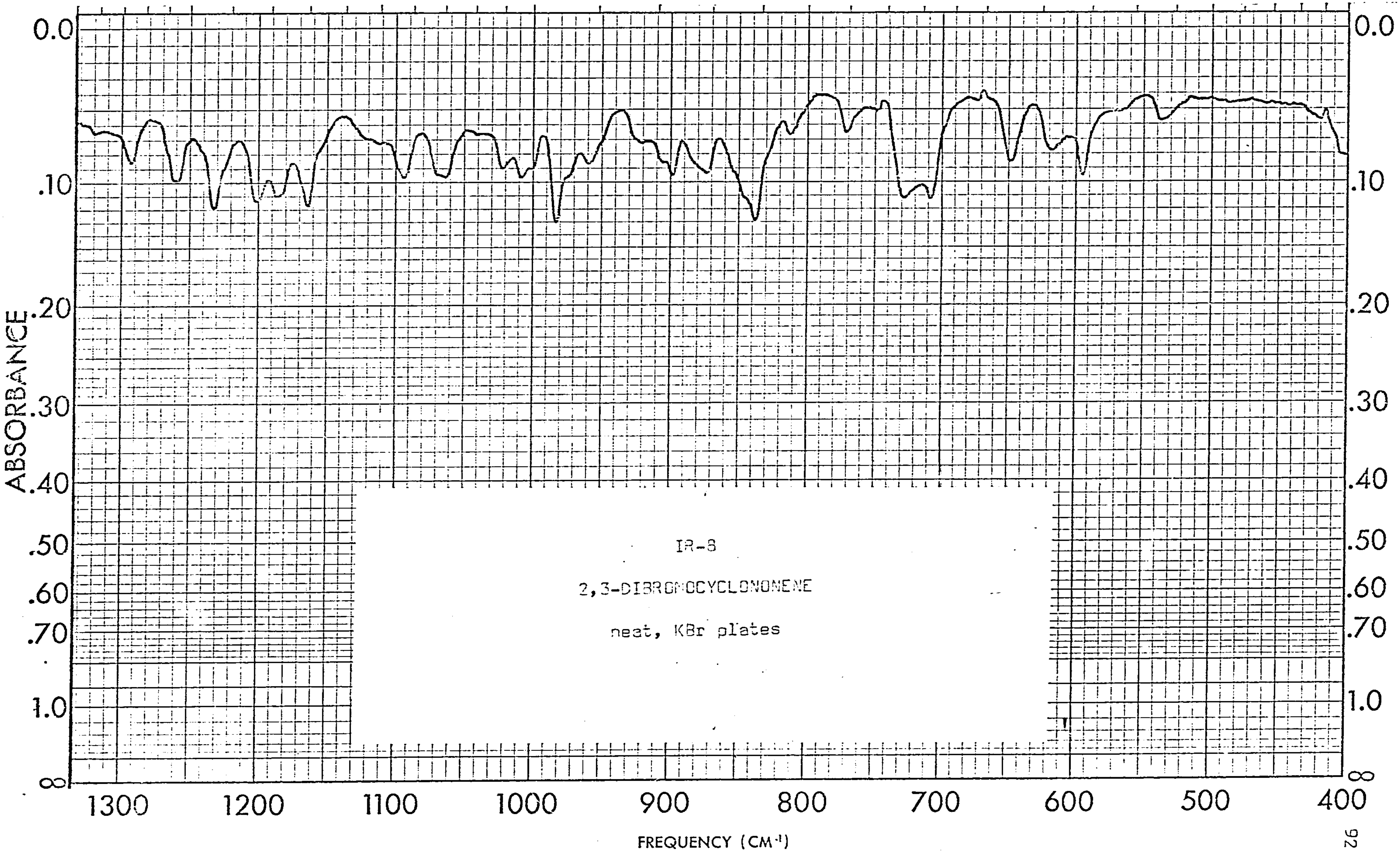
IR-7

1,2-CYCLONONADIENE

neat, KBr plates


IR-7
1,2-CYCLONONADIENE
neat, KBr plates
ABSORBANCE
0.0
.10
.20
.30
.40
.50
.60
.70
1.0
∞
FREQUENCY (CM⁻¹)
1300
1200
1100
1000
900
800
700
600
500
400


IR-8
2,3-DIBROMOCYCLONONENE
neat, KBr plates
ABSORBANCE
0.0
.10
.20
.30
.40
.50
.60
.70
1.0
∞
4000
3500
3000
2500
2000
1500
FREQUENCY (CM⁻¹)

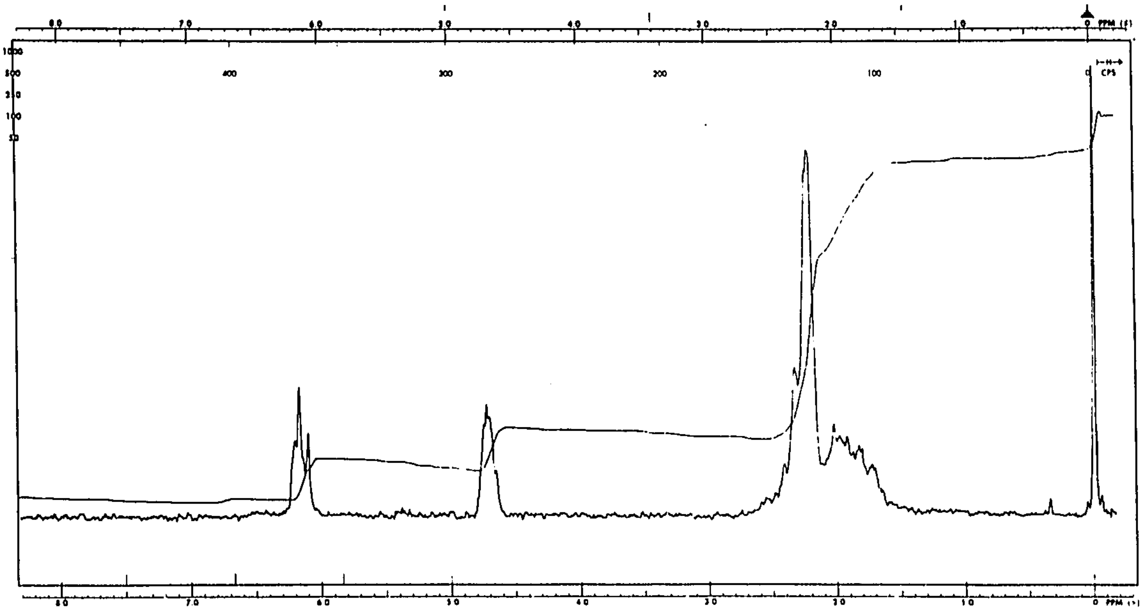


IR-8

2,3-DIBROMOCYCLONONENE

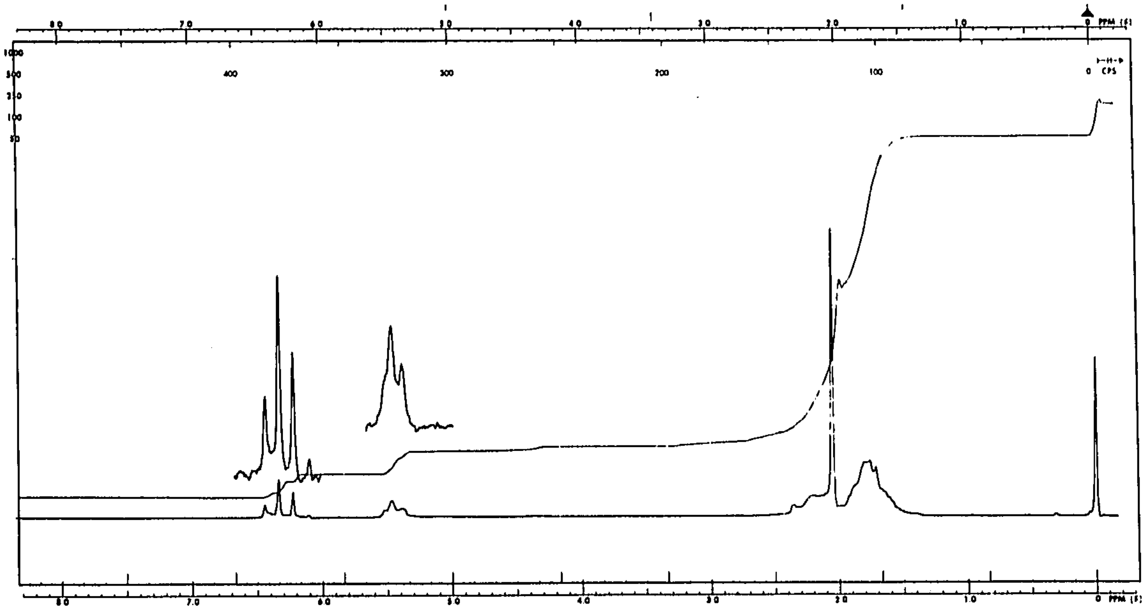
neat, KBr plates

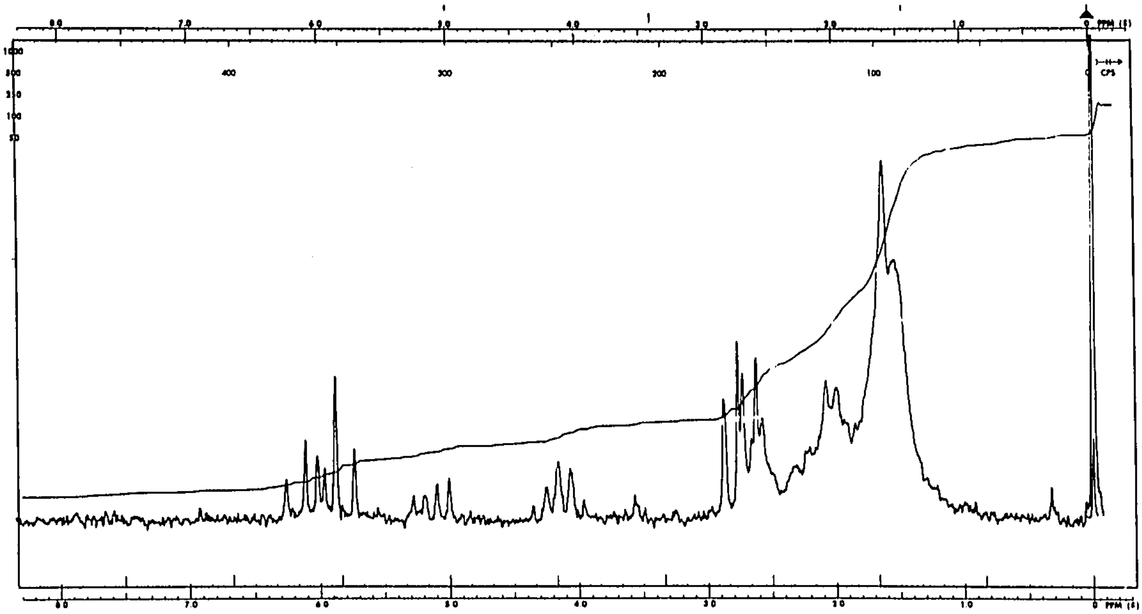
APPENDIX B



NMR-1
2,3-DIBROMOCYCLOHEXENE
Solution in CCl_4 plus 1% TMS

NMR-2
2-BROMO-2-CYCLOHEPTEN-1-YL ACETATE
Solution in CCl_4 plus 1% TMS





NMR-3
MIXTURE OF CIS- AND TRANS-2,3-DIBROMOCYCLONONENE
Solution in CCl_4 plus 1% TMS

NMR-4
TRANS-2,3-DIBROMOCYCLONONENE
Solution in CCl_4 plus 1% TMS