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THE REACTION OF
1-METHOXY-BICYCLO[3,2,0]
HEPTA-3,6-DIENE WITH DIHALOCARBENE

Thesis for the Degree of M. S.
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John Szendrey

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THE REACTION OF 1-METHOXY-BICYCLO [3,2,0]
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By

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ABSTRACT

The addition of dibromo- and dichloro-carbene to 1-methoxy-bicyclo[3,2,0]hepta-3,6-diene occurred in the less strained five-membered ring to give 6-methoxy-3,3-dihalo-tricyclo[4,2,0,0^{2,4}]octa-7-ene. One of the two vinyl proton n.m.r. absorptions in the spectrum of the former compound was assigned in previous literature to the four-membered ring. This assignment was used to follow the addition reaction.

The dihalocarbene adduct resisted ring opening under warm, basic conditions.

A Simmons-Smith reaction, which uses a $\text{Zn-CH}_2\text{I}_2$ adduct, was performed on the heptadiene and indicated a different mode of addition to the vinyl groups.

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INTRODUCTION

The bicyclic structure pentalene (I) belongs to



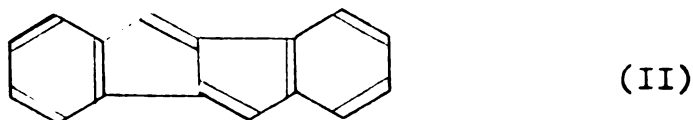
(I)

the class of compounds called pseudoaromatic. Its completely conjugated double bond system contains eight π -electrons and consequently, does not comply with Huckel's $(4N+2)$ rule for aromaticity. Both valence bond and molecular orbital methods of calculation suggested a larger delocalization energy than is expected from a compound that does not have aromatic character^{(1),(2)}. However, calculation by the molecular orbital method also suggested a high reactivity for pentalene⁽³⁾. These calculations indicate that the eight π -electrons can occupy four bonding orbitals and that the closest unoccupied orbital is one of zero energy. This zero energy level permits the molecule to be readily transformed into a dianion since there is a small difference between the highest occupied and the lowest unoccupied orbitals⁽²⁰⁾.

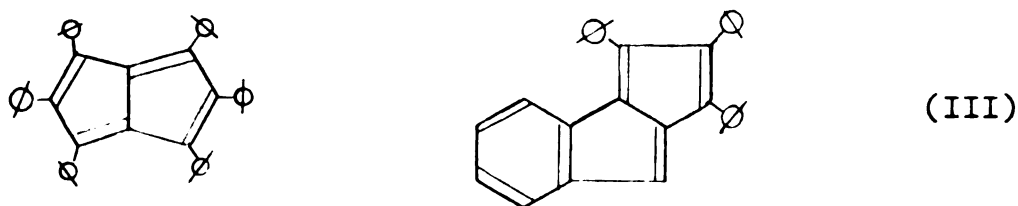
That pentalene is highly reactive is suggested by the many unsuccessful attempts to prepare it. The obvious routes for pentalene, hexahydropentalene and tetrahydropentalene by catalytic dehydrogenation have been unsuccessful^{(4), (5), (6)}.

Halogenation-dehydrohalogenation attempt on a tetrahydropentalene led to a gum upon reaction with n-bromosuccinimide⁽⁷⁾. A more recent approach was the attempt to degrade 2,4,6,8-tetra(dimethylamino)bicyclo[3,2,0]octane both by the Cope amine oxide technique and by the Hofmann exhaustive methylation procedure, both being unsuccessful⁽⁸⁾.

A derivative of pentalene that has been prepared is the fused dibenzopentalene (II)



Recently prepared derivatives, hexaphenylpentalene and triphenylbenzopentalene (III)⁽⁹⁾, have

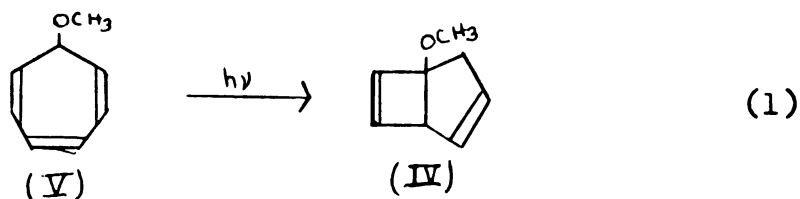


pentalene highly substituted.

The purpose of the work is to attempt the synthesis of less highly substituted derivatives of pentalene.

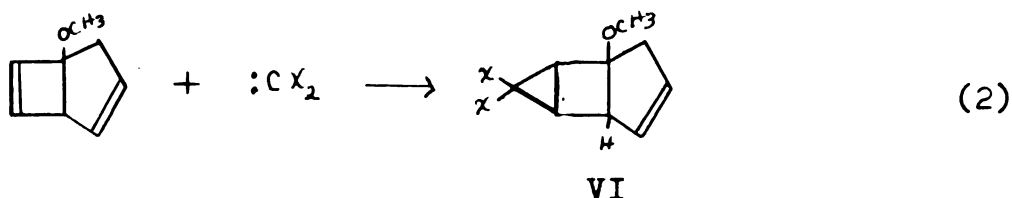
DISCUSSION

The approach attempted has its beginning in the compound, 1-methoxy-bicyclo [3,2,0] hepta-3,6 diene (IV).

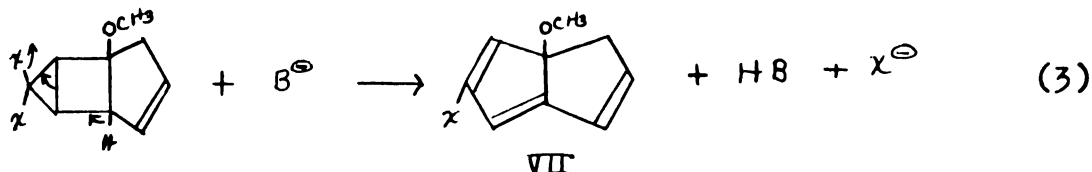


This compound was prepared by Chapman and Borden⁽¹⁰⁾ via the photoisomerization of 7-methoxycycloheptatriene (V). Compound (V) was readily available from a nucleophilic attack of methanol on tropenium fluoroborate⁽¹¹⁾.

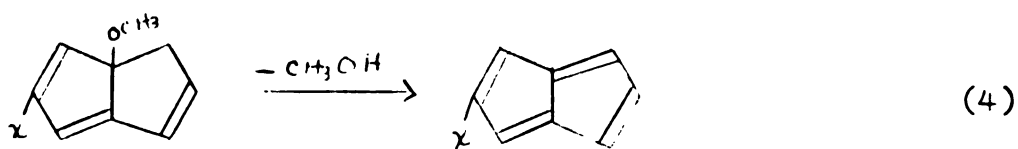
A dihalo-carbene addition to compound (IV) was proposed to lead to 5-methoxy-3,3-dihalotricyclo [3,3,0,0^{2,4}] octa-7-ene (VI) by addition of the carbene across the more strained double bond of the butadiene ring.



An abstraction of the bridgehead hydrogen by a base was to lead to ring opening according to reaction (3).



There then remains the removal of methanol from compound (VII) to lead to a derivative of pentalene, 3-halo-bicyclo [3,3,0] octa-2,4,6,8-tetraene.

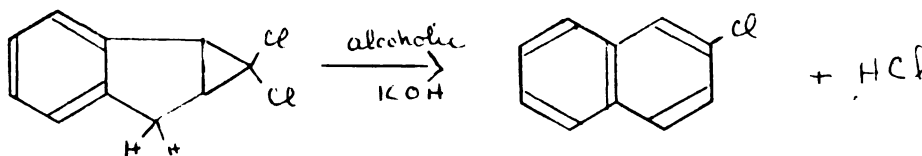


When both dichloro and dibromo carbene were reacted with the photo-product (IV) there was isolated in each case a compound that appeared to result from carbene addition to the cyclopentene double bond. This mode of addition is arrived at by noting the disappearance of a multiplet at $\tau = 4.27$ which had been assigned to the vinyl protons of the five membered ring of the photo-product. The vinyl protons which appear as a quartet at $\tau = 3.78$ are assigned to the cyclobutene ring because there is a 2.9 c.p.s. coupling constant apparent for the two doublets.

From previously reported n.m.r. spectra of analogous compounds^(16,17), there appears to be a possibility of assigning the $\tau = 4.27$ value to the four membered ring. The reported n.m.r. of bicyclo [3,2,0] hepta-3,6-diene is very similar to that reported here for the methoxy compound. A quartet between $\tau = 3.67$ and $\tau = 3.92$ due to a vinyl group in the former compound is also assigned to the four membered ring⁽¹⁶⁾. The bicyclo [3,2,0] hepta-2-ene which has the five membered ring saturated produces an n.m.r. spectrum with a closely spaced triplet (0.73 c.p.s.) at $\tau = 4.24$ ⁽¹⁷⁾. This triplet is not too different from the display at $\tau = 4.27$ obtained in the photo-product (IV) in possible coupling and multiplicity.

The photoproduct displays a more complicated high resolution spectrum with a higher multiplicity of four at $\tau = 4.27$. An environment of two methylene protons and a bridgehead proton could account for this complexity. The coupling constant of 2.9 c.p.s. in the quartet at $\tau = 3.78$ along with simple splitting in the high resolution of its doublet at $\tau = 3.74$ (this splitting probably due to the bridgehead proton) favors assigning this group to the cyclobutene ring.

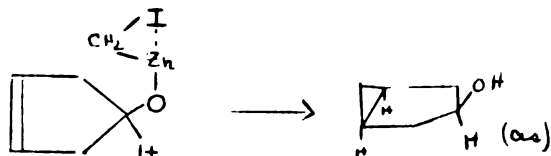
Attempts to open the cyclopropyl ring as, for example, in the following preparation of 2-chloronaphthalene⁽¹⁸⁾, were not successful.



Only starting material was isolated from the treatment of the dichlorocarbene addition product with 15% aq. sodium hydroxide and 15% alcoholic potassium hydroxide.

A different mode of reaction on the photoproduct with the Simmons-Smith reagent was apparent. The n.m.r. of the product in the reaction clearly indicated the presence of an absorption at $\tau = 4.09$ and the absence of a quartet at $\tau = 3.78$. This is probably due to the Simmons-Smith intermediate zinc compound directing the reaction through coordination with the oxygen of the methoxy group. A directing influence of an intermediate zinc compound in the Simmons-

Smith reaction has been postulated for the addition of methylene to an oxygen containing olefin⁽¹⁹⁾. Only cis-3-bicyclo 3,1,0 hexanol was obtained from cyclopenten-4-ol⁽¹⁹⁾:



The product in the Simmons-Smith reaction was unstable at room temperature. Upon standing, a brown residue began to form. This could be from a facile ring opening of the cyclopropyl group followed by a polymerization.

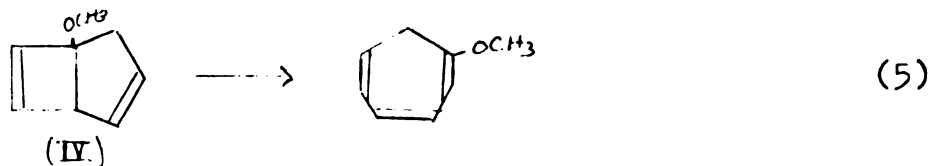
RESULTS

A. Nuclear magnetic resonance spectra of compound (IV)

Photolysis of 7-methoxy cycloheptatriene in dilute ether resulted in a 63% yield of compound (IV) which distilled between 30° - 32°C and about 8 mm pressure. An n.m.r. spectrum of the product showed the following: a clean quartet at $\tau = 3.78$ having a coupling constant of 2.9 c.p.s.; a complex quartet (or multiplet) at $\tau = 4.27$ which is 6 c.p.s. wide; a complex singlet at $\tau = 6.45$; a sharp singlet at $\tau = 6.76$ and a complex doublet at $\tau = 7.59$. This spectrum was interpreted by a method due to Chapman⁽¹³⁾ which relates the coupling constants of vinyl protons in cyclic structures with ring size. In a four-membered ring, this coupling would be 2.5 to 3.7 c.p.s.; for five-membered rings this would be from 5.4 to 7.0 c.p.s. From this interpretation the quartet at $\tau = 3.78$ is assigned to the vinyl protons in the cyclobutene portion of compound (IV) and the multiplet at $\tau = 4.27$ to the vinyl protons of the five-membered ring. This latter complex multiplet did not clearly indicate a 5.4 to 7.0 c.p.s. splitting and in fact was only 6.0 c.p.s. wide in its entirety. Additional assignments in this spectrum of compound (IV) are: the complex singlet at $\tau = 6.45$ to the bridgehead proton; the sharp singlet at $\tau = 6.76$ to the three methoxy protons and the doublet at $\tau = 7.59$ to the methylene protons of the five-membered ring.

B. Dihalo-carbene addition to compound (IV)

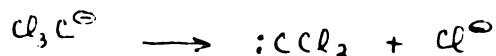
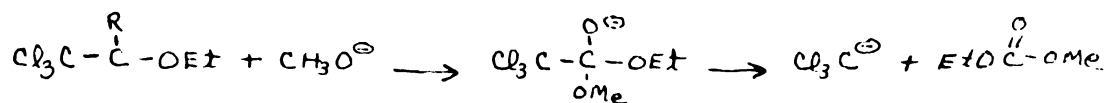
Because of a thermal rearrangement reported by Chapman and Borden⁽¹⁰⁾, (reaction 5), it was necessary to use low



temperature methods of obtaining dihalo-carbene addition to the bicyclooctadiene. Two sources of dihalo-carbene were used.

1. Dichlorocarbene from trihaloacetate esters.

Ethyl trichloroacetate was reported to produce dichlorocarbene in the presence of alkoxide ion at ice temperature and, in the presence of olefins, gave a higher yield of 1,1-dichlorocyclopropanes (80%) than obtained when chloroform was used as the source of carbene⁽¹²⁾.



This reaction was performed on compound (IV) in pentane and yielded a distillable product that crystallized from pentane as low melting ($44^\circ\text{--}46^\circ\text{C}$) white crystals that analyzed for the empirical formula $\text{C}_9\text{H}_{10}\text{OCl}_2$. The mass spectrum of this compound indicated a molecular weight of 204 and the presence of two chlorine atoms by isotope distribution. A $\text{C}_3\text{H}_2\text{Cl}_2$ fragment was evident as a metastable ion corresponding to the $m/e = 203$ to $m/e = 95$ transition occurring in one step.

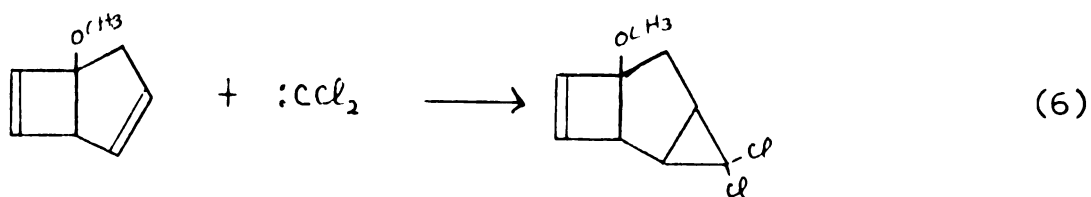
Nuclear magnetic resonance spectra indicated that this compound had originated from a dichlorocarbene addition across the double bond of the five-membered ring. The quartet at $\tau = 3.78$ was still present in the product and its assignment to a four-membered ring was interpreted, as in the bicyclooctane, from a 2.9 c.p.s. coupling constant. High resolution n.m.r. showed only secondary splitting in the left hand doublet. That absorption at $\tau = 4.27$, present in (IV) and assigned to the five-membered ring, was now absent. The bridgehead hydrogen in the product was displayed as a more distinct peak at $\tau = 6.69$ and the methoxy hydrogens were at $\tau = 6.79$.

A more complex array of peaks centered around $\tau = 7.9$ occurred in the product. The complexity is due to the cyclopropyl hydrogens which have absorbed down field from their normal positions and occur under the two methylene hydrogens.

The ratios for these areas of absorption were:

$$\tau = 3.78 : \tau = 6.69 ; \tau = 6.79 : \tau = 7.9 :: 2 : 1 : 3 : 4.$$

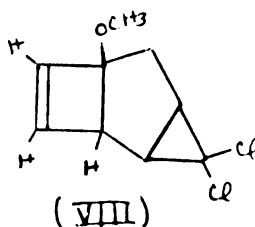
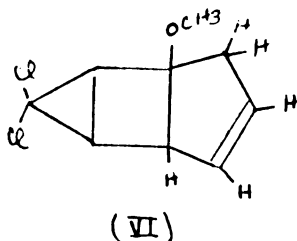
Disappearance of the complex multiplet at $\tau = 4.27$ and assignment of this to the vinyl protons of the five-membered ring according to Chapman's interpretation of the n.m.r. spectrum of the bicyclooctadiene (IV)⁽¹³⁾ is used here as an indication of carbene addition by way of reaction(6).



It is surprising that some or all of the reaction did not occur at the more strained double bond of the four-membered ring. A modification of Chapman's interpretation in the following way would indicate carbene addition across the cyclobutene of (IV):

The nuclear magnetic resonance absorption due to the vinyl protons of the five-membered ring was noted by Chapman as being too complex for interpretation. An expected coupling constant of from 5.4 to 7.0 c.p.s. for these protons is not apparent from our spectra of compound (IV). But, any coupling constant for the hydrogens at $\tau = 4.28$ could not be near 5.4 c.p.s. because the entire absorption is only 6 c.p.s. wide. Chapman states that the coupling constant increases with ring size. If this is taken in a broader sense in which the 2.9 c.p.s. coupling is considered to be larger than that of some smaller coupling in the display at $\tau = 4.28$, then the 2.9 value belongs to the five-membered ring. This would indicate addition of the carbene across the more strained four-membered ring.

The high resolution n.m.r. spectrum of the dichlorocarbene adduct, however, favors the structure written as compound (VIII)



Simple secondary splitting in the left hand doublet of the quartet centered at $\tau = 3.78$ is probably due to a vinyl proton coupling with the bridgehead proton. A more complex display of splitting would be expected for the coupling with two methylene protons and the bridgehead proton of structure (VI).

Two arguments were presented above: one assigning the multiplet at $\tau = 4.28$ to the five-membered ring and one assigning it to the four-membered ring. For comparison there is presented n.m.r. data from the literature for two compounds. The first,⁽¹⁴⁾ structure (IX), is similar to the photoproduct (IV).



The two vinyl protons of the cyclobutene were assigned as a quartet with its doublets centered at $\tau = 3.67$ and $\tau = 3.92$ each having a 3.0 c.p.s. coupling constant. Coupling with ring juncture was not detected. The cyclopentene proton absorption was centered at $\tau = 4.36$ and appeared as a multiplet. The second,⁽¹⁷⁾ structure X, assigns the vinyl protons

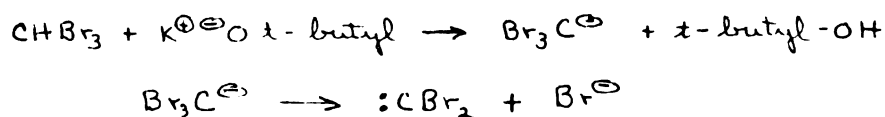


(X)

as a singlet at $\tau = 4.24$ which, under high resolution conditions, appears as a closely spaced (0.73 c.p.s.) triplet.

2. Dibromocarbene from bromoform

The well-known method generating dibromocarbene from bromoform and potassium *t*-butoxide⁽¹⁴⁾ was used.



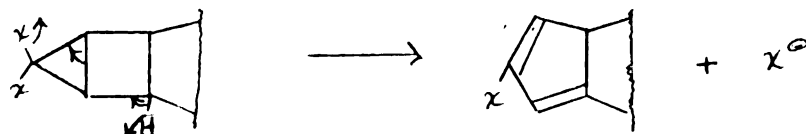
White crystals obtained from this reaction on the bicyclo-octadiene (IV) melted at $58.5^{\circ}\text{--}60.5^{\circ}\text{C.}$, somewhat higher than the dichlorocarbene adduct. These also were obtained from distilled product crystallized from pentane. They analyzed for the empirical formula, $\text{C}_9\text{H}_{10}\text{OBr}_2$. Mass spectrometry indicated a molecular weight of 292 which arises from a mass of 79.0 for Br. The meta stable fragment $\text{C}_3\text{H}_2\text{Br}^+$ was apparent from the transition $m/e = 277$ to $m/e = 80$. This $m/e = 277$ peak arises from $(M-15)^+$ which indicates a loss of a $-\text{CH}_3$; a different breakup than that from the dichlorocarbene adduct.

Here again the n.m.r. display was similar to the dichloro adduct. The quartet at $\tau = 3.78$ remained in the product with a 2.9 c.p.s. splitting; the methylene region became more complex due to the cyclopropyl hydrogens and the

τ = 4.28 multiplet was gone.

C. Attempts to open the cyclopropane ring of compound (VIII)

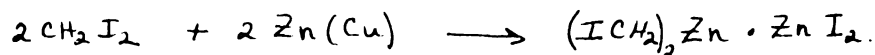
A cyclopropyl group fused to a four or five-membered ring was expected to open up to the next higher ring system quite readily in the presence of base.



Treatment of the dichloro adduct dissolved in hexane with a fifteen per cent aqueous sodium hydroxide solution for fifteen minutes yielded only starting dichloro adduct. Subsequent treatment of this adduct in refluxing hexane with a fifteen per cent solution of potassium hydroxide in methanol gave the same results.

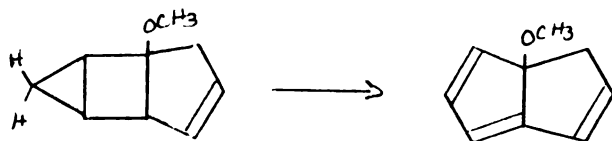
D. Simmons-Smith reaction of compound (IV)

The Simmons-Smith reaction produces a fused cyclopropyl group in a way that is analogous to a Grignard reaction rather than through a carbene intermediate.



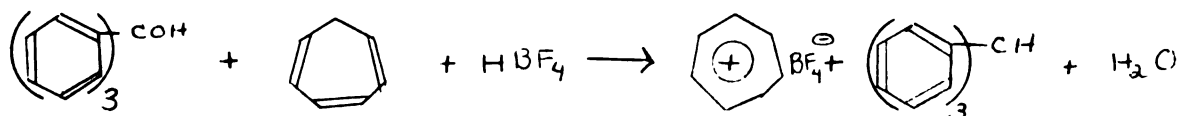
This reaction performed on the cyclooctadiene (IV) gave a liquid product that was somewhat unstable. A pentane solution of the distilled product, upon standing overnight, became green and a brown solid residue began separating. This solution was cleared with activated carbon, the pentane stripped under blowing N_2 gas and an n.m.r. taken in CCl_4 .

An interesting event in this reaction was apparent when the n.m.r. indicated that the quartet at $\tau = 3.27$ was gone but that the vinyl protons at $\tau = 4.28$ were still present. The solution used for n.m.r. was dilute and a clean display was not obtained but the presence and absence of the above absorptions and the different mode of addition to (IV) were apparent. This CCl_4 solution was allowed to stand overnight in the n.m.r. tube and after this time the green color and brown residue were present again. This may be an indication that the Simmons-Smith type of methylene added to the vinyl of the four-membered ring and that a facile ring opening had occurred. This ring opening then would give a compound, close to pentalene, that polymerizes readily.



EXPERIMENTAL

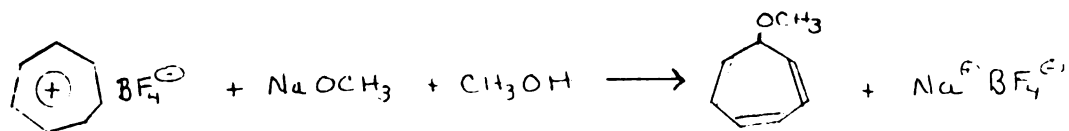
A. Preparation of Tropenium fluoroborate⁽¹⁵⁾



Triphenyl carbinol (80 g, 0.308 mole) was dissolved in 800 ml. of acetic anhydride by heating on a steam bath in a two-liter round bottom flask. After this solution had cooled to room temperature, there was slowly added 50 ml. of 48% fluoroboric acid while the flask was cooled in an ice bath and the contents were stirred. The carbinol dissolved rather quickly upon heating and recrystallized upon cooling to room temperature. An amber-red color developed upon adding the HBF_4 .

While the contents were stirring and cooling continued, there was added 27.6 g (0.3 mole) of cycloheptatriene. The expected salt began to come out of solution and the amber-red color disappeared upon complete addition of the cycloheptatriene. Two pounds of anhydrous ether were used to precipitate the remainder of the salt. The precipitate was filtered and washed three times with anhydrous ether giving 38.5 g of fine white solid. Two more crops of crystals were obtained giving 11.0 g more of salt.

The theoretical yield based on 0.3 mole of cycloheptatriene was 53.5 g; per cent yield was 92.5.

B. Preparation of 7-methoxy-1,3,5-cycloheptatriene (11)

A mixture containing 50 g of tropenium fluoroborate, 18 g of free flowing sodium methoxide and 336 ml. of absolute methanol was stirred for one hour, allowed to stand overnight and stirred for an additional hour. A white solid, different in appearance than the tropenium fluoroborate, separated out. (The amount of the solid in each preparation of 7-methoxy-cycloheptatriene appeared to be more than a trace as described in ref. 9). The mixture was then diluted with 360 ml. of petroleum ether (30°-60°C) and extracted four times with 270 ml. of water. Each water extract was back extracted four times with 60 ml. of petroleum ether. The combined organic layers were stripped of solvent. Stripping was accomplished on a rotary evaporator without external heat. During the subsequent distillation the receiver was cooled in a dry-ice acetone bath to prevent loss of product.

There was obtained 26.5 g of material distilling at 43°-44°C (6 mm). The yield was 77.5%. This material had a retention time of 10.1 min. when run isothermally on a glc column at 99°C. Other material eluted, but these (retention time between 0 and one min. and 16.7 min. at 99°C) may have been decomposition products since at 91°C the middle peak increased substantially over the other two (13.4 min. for the middle peak at 91°C).

C. Preparation of 1-methoxy bicyclo[3,2,0]hepta-3,6-diene,
(IV)⁽¹⁰⁾

To six pounds (about 3800 ml.) of anhydrous ether (contained in a five-liter, three necked, round bottom flask which was equipped with a 60/50 standard joint to fit a quartz immersion well) was added 11.0 g of freshly, redistilled 7-methoxy-1,3,5-cycloheptatriene. A slow stream of oxygen free, dry nitrogen was bubbled through the solution and stirring was accomplished with a two-inch Teflon coated magnetic stirring bar. To the five-liter flask were attached two water cooled condensers, one a Liebig type and the other a Friedrich type closed off with a drying tube containing calcium chloride. The ether solution was photolyzed for ten hours by means of a high pressure mercury arc lamp (Hanovia, 450 watt) contained in the water cooled quartz immersion well. After the photolysis, 50 g of MgSO_4 were added to the ether solution. After filtering off the MgSO_4 , the ether was stripped away portionwise on a rotary evaporator. Each portion of ether solution was filtered through a cone of MgSO_4 . The concentration was carried to about 100 ml. on the rotary evaporator. Further stripping was accomplished by dripping the 100 ml. of solution into a 15 ml. round bottom flask equipped with a distilling head. The flask was warmed by means of an oil bath. Distillation of the residue under vacuum gave 7.0 g of material distilling at $33^\circ\text{--}35^\circ\text{C}$ (10 mm). Distillation was

performed in a micro-Vigreux column equipped with a water-cooled condenser and three rotating receivers. This 7.0 g was collected in the second receiver after a few drops were obtained in the first. In order to prevent the product from distilling into the dry-ice trap of the pumping assembly, the receiver flask and head were cooled with a dry-ice acetone bath.

Other photolysis reactions of 7-methoxy-cycloheptatriene were run for six and 12½ hours. The longer time gave a better yield (63%) of product.

A glc of this product had very minor peaks eluting at 0.7 min. and 7.2 min. at 97°C; a large major peak eluted after 5.2 min.

Nuclear magnetic resonance spectrum of the photo-product in CCl_4 solution showed the following: quartet at $\tau = 3.78$; complex multiplet at $\tau = 4.28$, a broad singlet at $\tau = 4.45$, a sharp singlet at $\tau = 6.76$ and a doublet at $\tau = 7.59$ in the respective ratios of 2:2:1:3:2.

D. Reaction of (IV) with dichlorocarbene

To a 100 ml., three-necked flask, equipped with a stirring bar, nitrogen inlet, dropping funnel and water cooled condenser closed with a drying tube was placed 2.0 g (0.037 mole) of NaOCH_3 and 10 ml. of pentane. This mixture was stirred with the bar and cooled by means of an ice bath. There was then added through the dropping funnel, 4.0 g (0.0328 mole) of the

photo-product (IV) dissolved in 5 ml. of pentane. Then there was added, over a period of 15 minutes, a solution of 7.1 g (0.037 mole) of ethyl trichloroacetate in 5 ml. of pentane. Nitrogen sweep and ice bath cooling were continued during these additions and during the eight hours for which the reaction was stirred. A brown color that formed when the diolefin was added to the base changed to a light tan after eight hours. To this tan mixture, containing what appeared to be solid material, was added 30 ml. of water when, after stirring, there remained two liquid phases. The organic layer was separated and the aqueous layer washed four times with 20 ml. of petroleum ether (30°-60°C). Combined organic layers were washed once with water, dried with MgSO_4 , and organic solvent stripped off on a rotary evaporator without external warming. Distillation of the residue was best carried out in a one-piece micro-distilling apparatus that had an air cooled side arm attached to a one dram vial as a receiver. Material was obtained at an oil bath temperature between 70°-80°C (1.0 mm). This liquid solidified upon cooling the vial on a piece of dry ice and the crystals dissolved in a small amount of pentane. Recrystallization three times from pentane gave 1.1 g (16% yield) of crystals that melted at 45°-46°C.

Anal: Calcd. for $\text{C}_9\text{H}_{10}\text{OCl}_2$: C, 52.71%; H, 4.91% Found: C, 52.80%; H, 5.02%. N.m.r. in CCl_4 : quartet at $\tau = 3.80$ with a coupling of 2.9 c.p.s.; sharp singlet at $\tau = 6.70$;

sharp singlet at $\tau = 6.80$ and a complex array between $\tau = 7.74$ and $\tau = 8.04$ in the respective ratios of 2:1:3:4.

E. Reaction of compound (IV) with dibromocarbene

A solution of potassium t-butoxide in t-butanol was prepared by reacting about 1.2 g (0.0308 mole) of potassium in 150 ml. of t-butanol which had been dried over CaH_2 . The excess t-butanol was then stripped off using vacuum and slight warming until a white powder was left. The 250 ml., three-necked flask, which was equipped with a condenser, drying tube, N_2 inlet and dropping funnel, was then swept with nitrogen and 15 ml. of pentane added. After cooling the flask in an ice bath, there was added three g (0.0246 mole) of compound (IV) dissolved in five ml. of pentane. A 6.5 g (0.0257 mole) sample of bromoform was added dropwise and the dropping funnel washed down with five ml. of pentane. Ice-bath cooling and nitrogen sweep was continued for six hours while the reaction mixture was stirred using a magnetic bar. After this time the ice bath was taken away and the mixture allowed to stand at room temperature for one hour. To this mixture was added 45 ml. of water. Stirring caused solution of a solid phase and two liquid phases then separated. The organic phase was separated from the bottom aqueous phase and the aqueous phase washed three times with 20 ml. portions of petroleum ether ($30^\circ\text{--}60^\circ\text{C}$). Organic layers were combined and washed twice with 10 ml. portions of water. This was dried using

MgSO₄ and stripped of solvent on a rotary evaporator.

Residue from this was distilled through the one-piece micro distilling apparatus. Material distilled at about 105°C and was crystallizable at room temperature from pentane. The melting point of these crystals was 58.5°-60.5°C. Analysis, after passing a chloroform solution of these crystals through a three-inch silica gel column, was:

Calc. for C₉H₁₀OBr₂: C, 36.77%; H, 3.42% Found: %C, 36.88; %H, 3.21. N.m.r. in CCl₄: quartet at τ = 3.80 with coupling constant of 2.9 c.p.s.; sharp singlet at τ = 6.80 with slight broadening at τ = 6.78; a complex array between τ = 7.70 and τ = 8.25 in the respective ratios of 2:4:4.

F. Effect of base on the dichloro adduct

An infra-red analysis of one preparation of the dichloro adduct showed the presence of two carbonyl absorptions; one at 5.68 μ and one at 5.73 μ . These could arise from the starting ethyl trichloroacetate or the product ethoxy methoxy ketone.

About one gram of the dichloro adduct was dissolved in about two ml. of hexane. To this was added two ml. of a 15% aqueous solution of NaOH. This two-phase system was heated under a cold finger for 15 minutes. The two layers were separated; the aqueous layer washed three times with one ml. of hexane each and the combined organic layers were washed once with water. After drying with MgSO₄ the organic layer

was stripped of solvent with blowing nitrogen. The resulting infra-red still had one carbonyl at 5.73μ (the one at 5.68μ was gone); the rest of the spectra remained the same.

Repeating the above treatment using a 15% solution of potassium hydroxide in methanol and extracting with hexane after adding water caused the carbonyl to disappear from the infrared trace. The residue gave crystals from pentane. These crystals melted at 44° - 46°C .

A similar treatment with a 20% solution of potassium hydroxide in methanol but refluxing for six hours gave crystals that displayed the same n.m.r. as an untreated sample of the dichloro adduct.

G. Simmons-Smith reaction on compound (IV)

A Zn-Cu couple was prepared by placing 0.009 g of cupric acetate monohydrate in one ml. of glacial acetic acid contained in a 15 ml. round bottom flask. This was heated on a steam bath until cupric acetate dissolved. There was then added 0.63 g of 30 mesh Zn while the solution was still hot. The mixture was shaken for a few minutes and the acetic acid decanted. Three, one ml., portions of acetic acid followed by three, one ml., portions of ether were used to wash the couple.

A small condenser was attached to the flask and two ml. of ether was added to the Zn(Cu) couple. By means of a capillary pipette there was added a few drops of methylene

iodide to start the reaction. This mixture became cloudy upon slight warming. There was then added a solution of 0.55 g (0.0045 mole) of the diolefin and 1.61 g (0.006 mole) of methylene iodide. Part of this 0.006 mole of CH_2I_2 was added as a few drops previously. This addition was accomplished down the small condenser by means of a capillary pipette and took about 10 min. The stirred solution was decanted into a small (25 ml.) separatory funnel containing ice and five ml. of 1 normal HCl. This ether layer sank to the bottom but shaking brought it to the top. After the ether layer was separated it was washed with a second five ml. portion of HCl and then with three, five ml., portions of water. The combined water layers were washed with a ten ml. portion of ether and the combined ether layers dried over K_2CO_3 .

After concentrating the ether solution there was obtained a glc at 95°C . Two peaks above the product peak which eluted at 6.0 minutes were obtained: a minor peak at 10.3 min. and a major peak at 15.3 min. The residue was distilled through the small, one piece distilling apparatus to give two cuts. The first was distilled over at an oil bath temperature of $58^\circ\text{--}65^\circ\text{C}$ and a pressure of about 8 mm; the second at an oil bath temperature of $65^\circ\text{--}85^\circ\text{C}$ and a pressure between 8 mm and 4 mm.

The second pentane solution, upon standing overnight became green and a brown solid residue began to separate. This residue was filtered after adding a little Norit-A (carbon) and

the pentane stripped of under blowing nitrogen. A glc of the pentane solution before stripping indicated very slight amounts of both the starting compound (IV) and the peak at 10.0 min. were present in the product. The residue was taken up in a few drops of CCl_4 and filtered into an n.m.r. tube.

The n.m.r. trace, although run on a dilute sample, clearly indicated the presence of the vinyl protons at $\tau = 4.1$ and the absence of any absorption between $\tau = 2$ and $\tau = 4$.

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APPENDIX

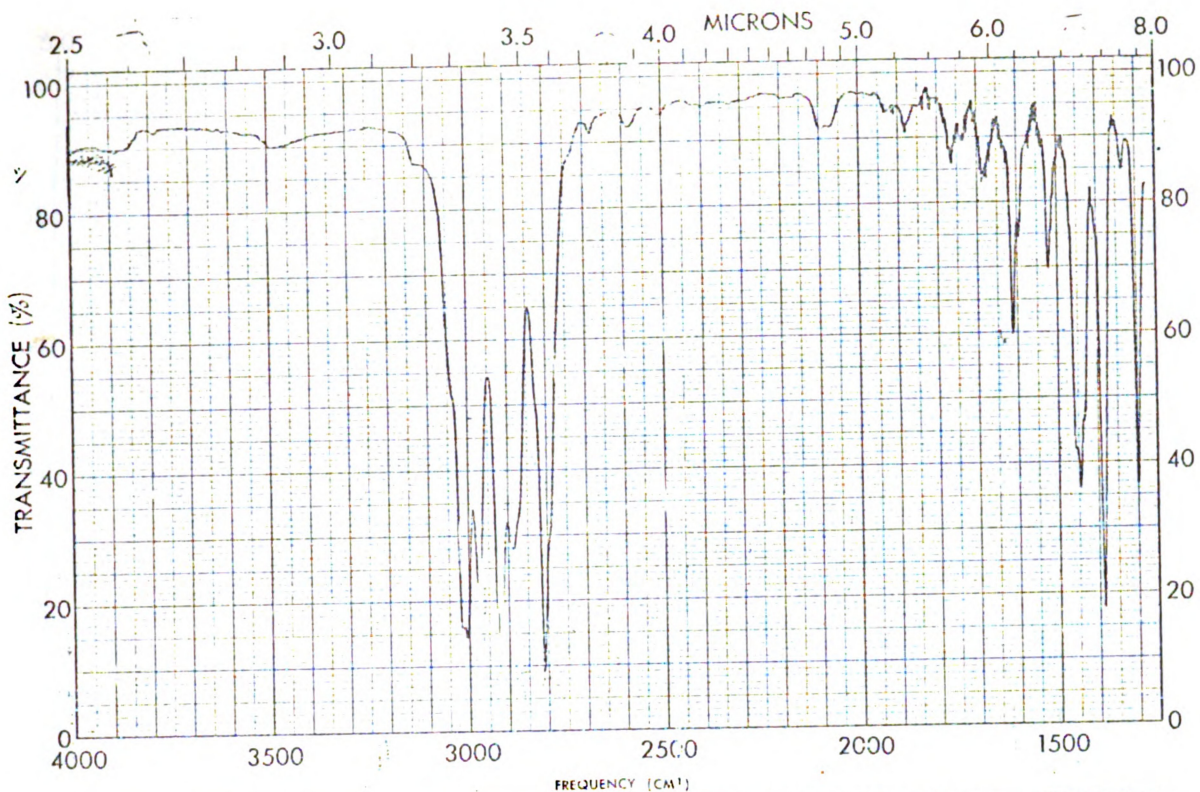
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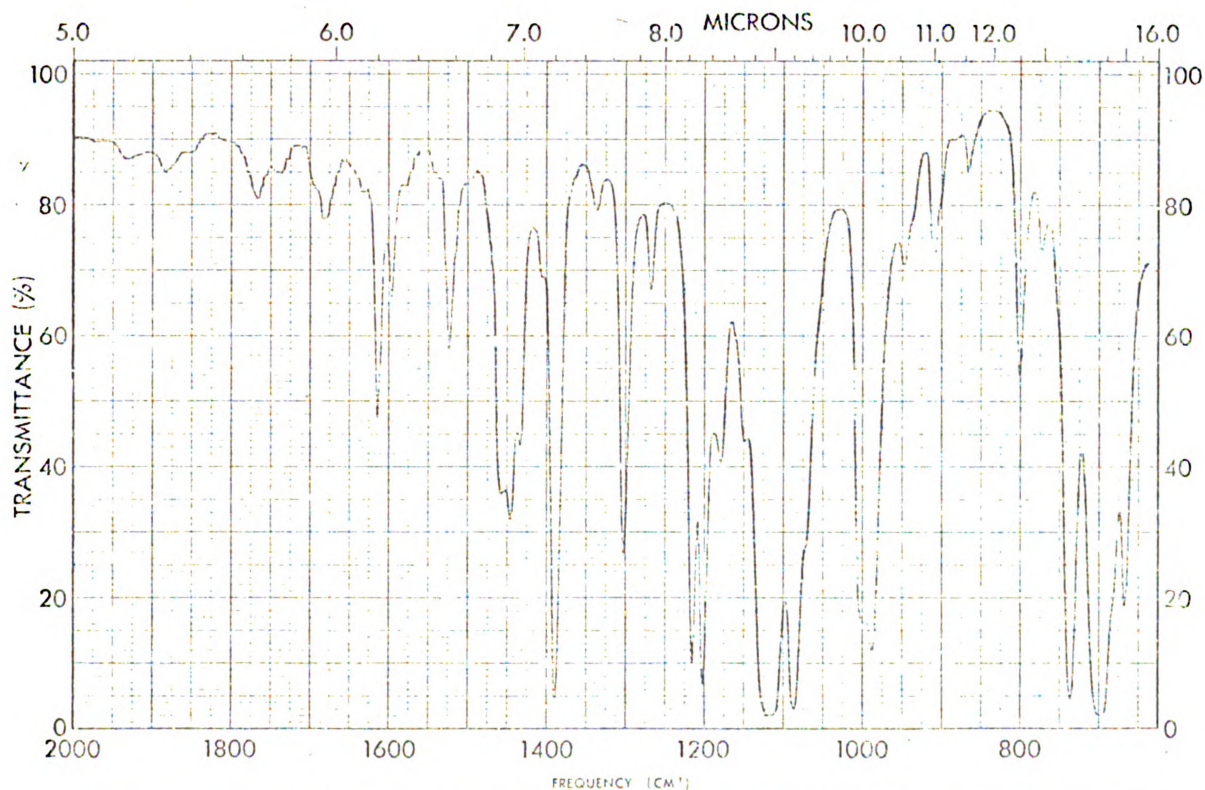
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FIG. 1



SAMPLE <chem>CC(=O)OC1=CC=CC=C1</chem>	CURVE NO. 2	SCAN SPEED <i>fast</i>	OPERATOR <i>J.P.S.</i>
ORIGIN From IR 35" + Microns in CH ₂ N	CONC. -	SLIT <i>N</i>	DATE <i>20 Oct 66</i>
SOLVENT <i>pressed film</i>	CELL PATH	REMARKS	
PART NO. 237-1034	REFERENCE <i>Fig 3</i>		

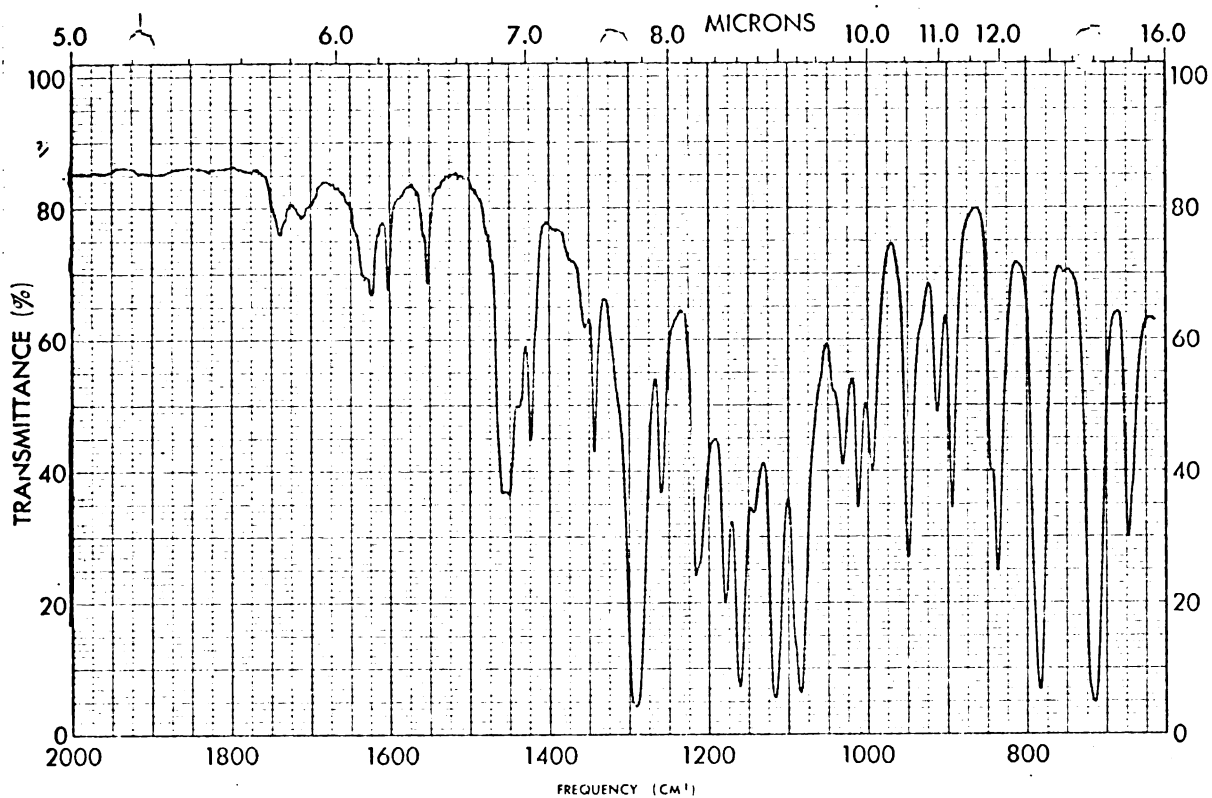
PERKIN-ELMER



SAMPLE <chem>CC(=O)OC1=CC=CC=C1</chem>	CURVE NO. 2	SCAN SPEED <i>fast</i>	OPERATOR <i>J.P.S.</i>
ORIGIN From IR 35" + Microns in CH ₂ N	CONC. -	SLIT <i>A1</i>	DATE <i>20 Oct 66</i>
SOLVENT <i>pressed film</i>	CELL PATH	REMARKS	
PART NO. 237-1035	REFERENCE <i>Fig 3</i>		

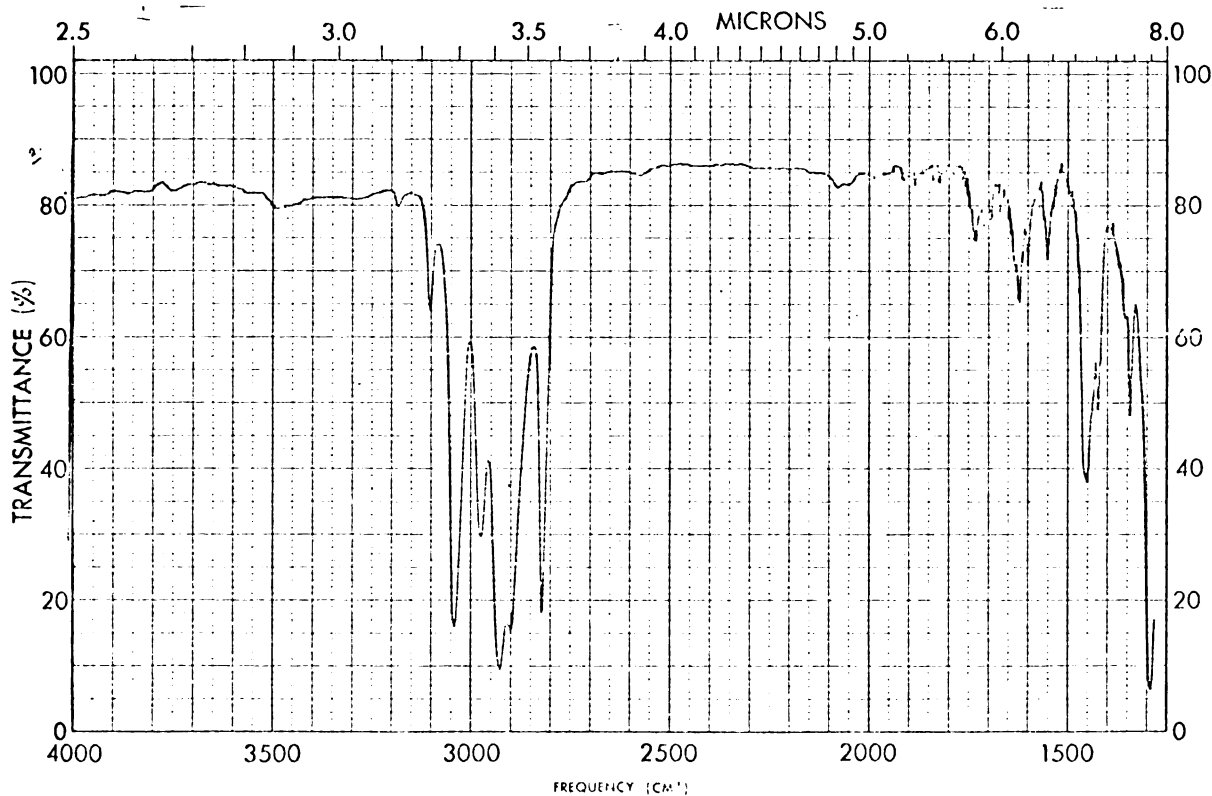
PERKIN-ELMER

Fig 2.



SAMPLE <u>11</u>	CURVE NO. <u>5</u>	SCAN SPEED <u>fast</u>	OPERATOR <u>J. G. Smith</u>
ORIGIN <u>by of 7-methoxy-cycloheptatriene</u>	CONC. _____	SPLIT <u>M</u>	DATE <u>Dec 1966</u>
SOLVENT <u>pressed film</u>	CELL PATH _____	REMARKS _____	
PART NO. 237-1035	REFERENCE <u>pp. 2</u>		

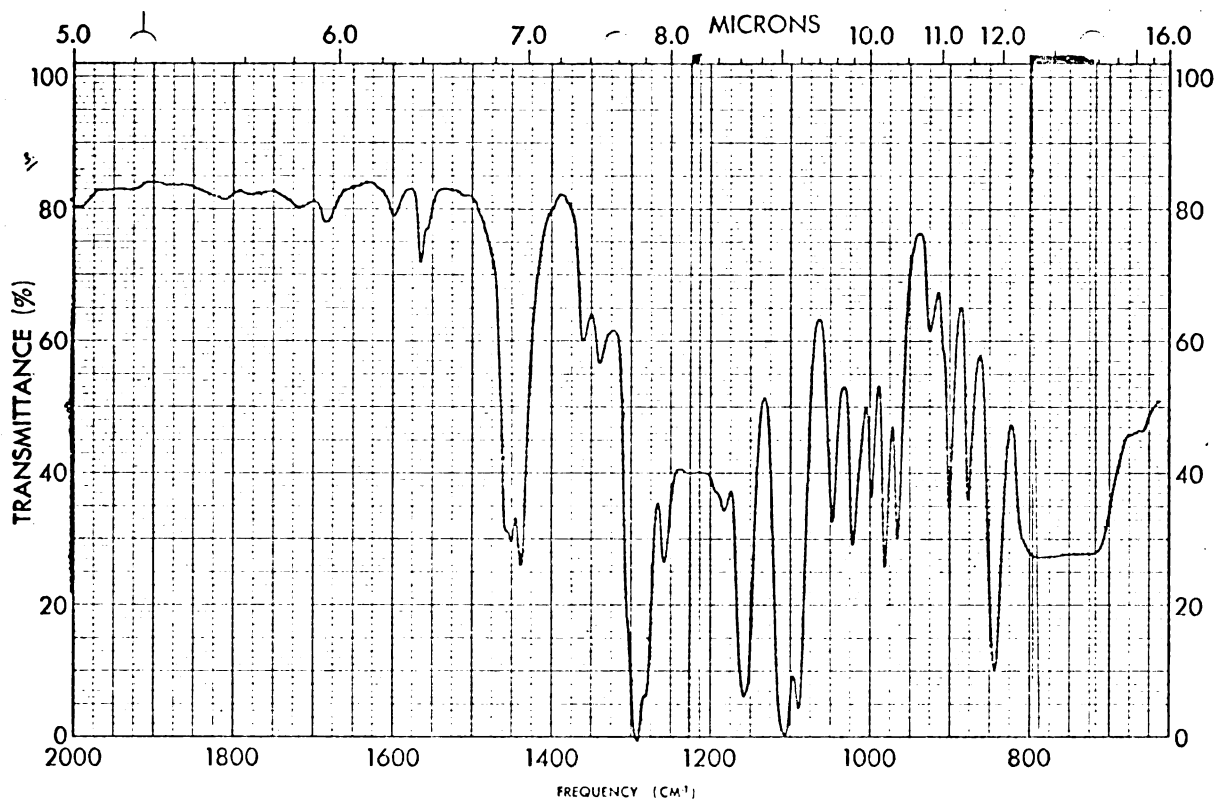
PERKIN-ELMER



SAMPLE <u>11</u>	CURVE NO. <u>5</u>	SCAN SPEED <u>fast</u>	OPERATOR <u>J. G. Smith</u>
ORIGIN <u>by of 7-methoxy-cycloheptatriene</u>	CONC. _____	SPLIT <u>M</u>	DATE <u>Dec 1966</u>
SOLVENT <u>pressed film</u>	CELL PATH _____	REMARKS _____	
PART NO. 237-1034	REFERENCE <u>pp. 2</u>		

PERKIN-ELMER

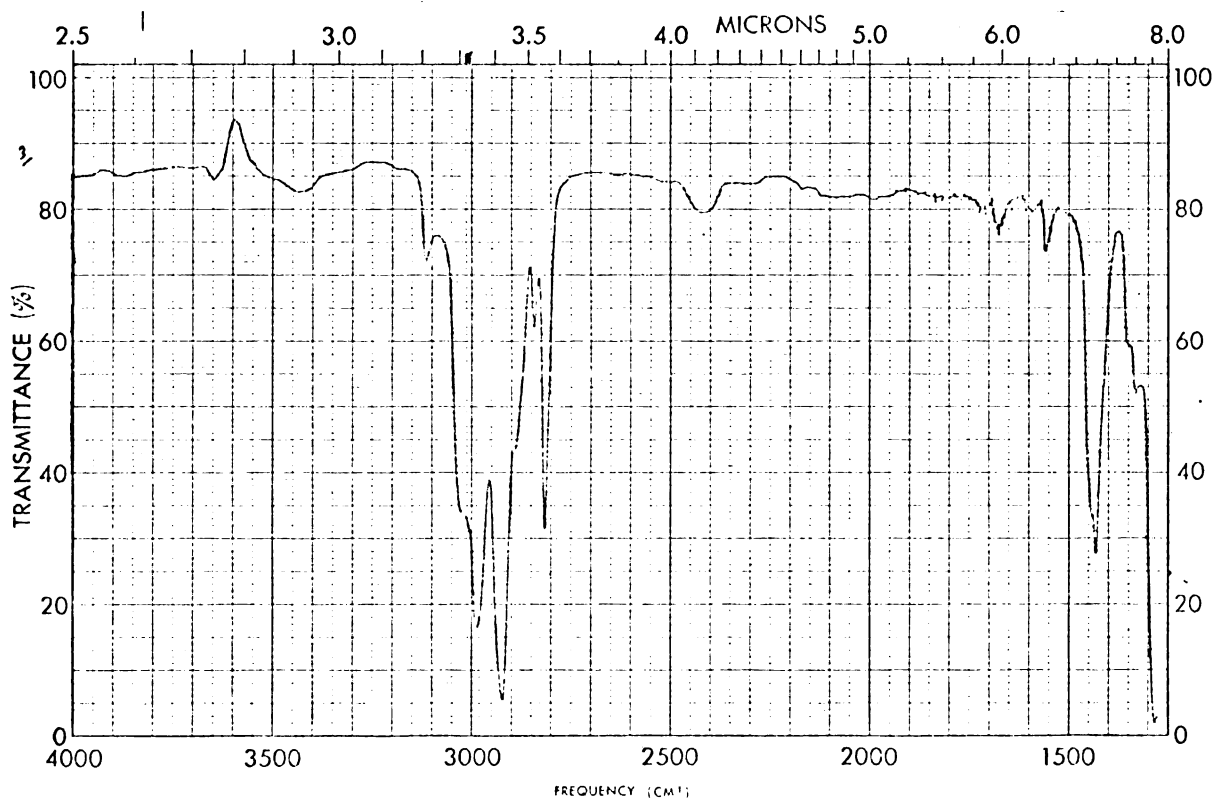
FIG. 3



SAMPLE <chem>CC1=CC=CC=C1C(=O)O</chem>	CURVE NO. 21	SCAN SPEED Fast	OPERATOR J.D.
ORIGIN <chem>CC1=CC=CC=C1C(=O)O</chem>	CONC.	SUIT N	DATE 11/10/66
SOLVENT <chem>CHCl3</chem>	CELL PATH	REMARKS	
REFERENCE			

PART NO. 237-1035

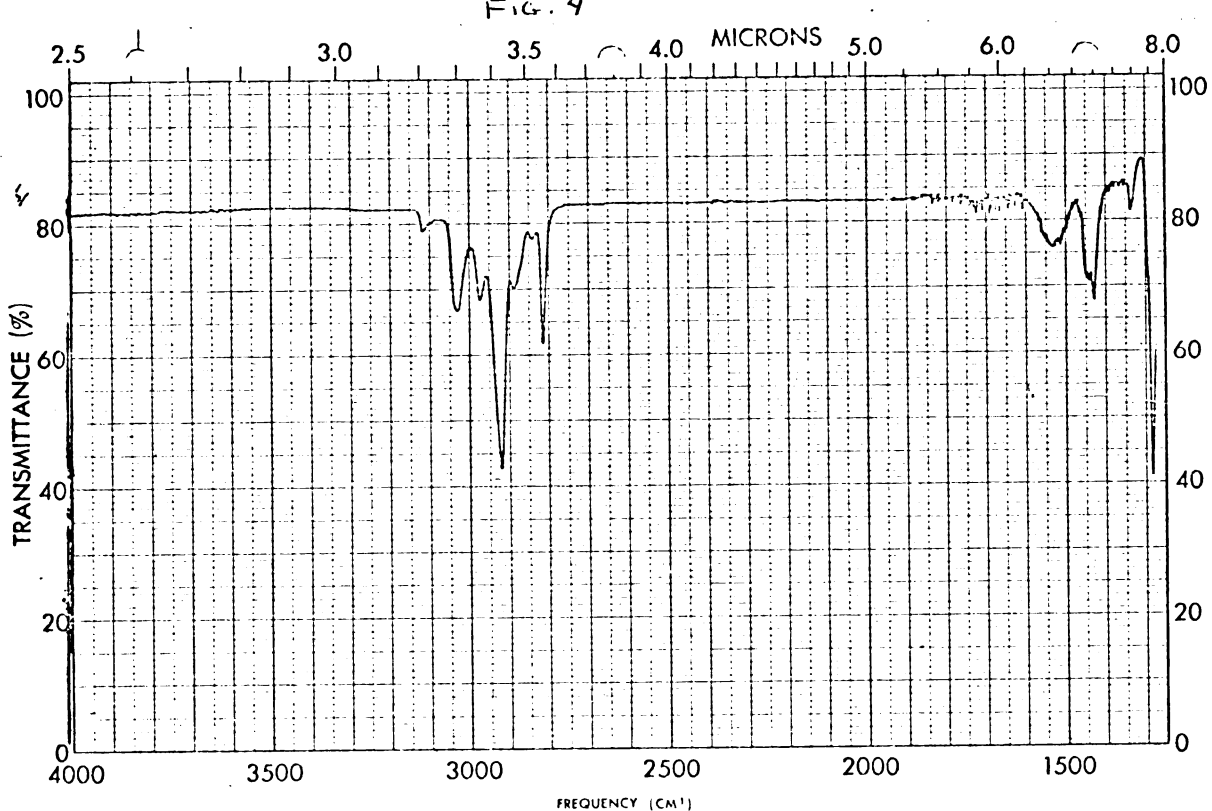
PERKIN-ELMER



SAMPLE <chem>CC1=CC=CC=C1C(=O)O</chem>	CURVE NO. 21	SCAN SPEED Fast	OPERATOR J.D.
ORIGIN <chem>CC1=CC=CC=C1C(=O)O</chem>	CONC.	SUIT N	DATE 11/10/66
SOLVENT <chem>CHCl3</chem>	CELL PATH	REMARKS	
REFERENCE			

PART NO. 237-1034

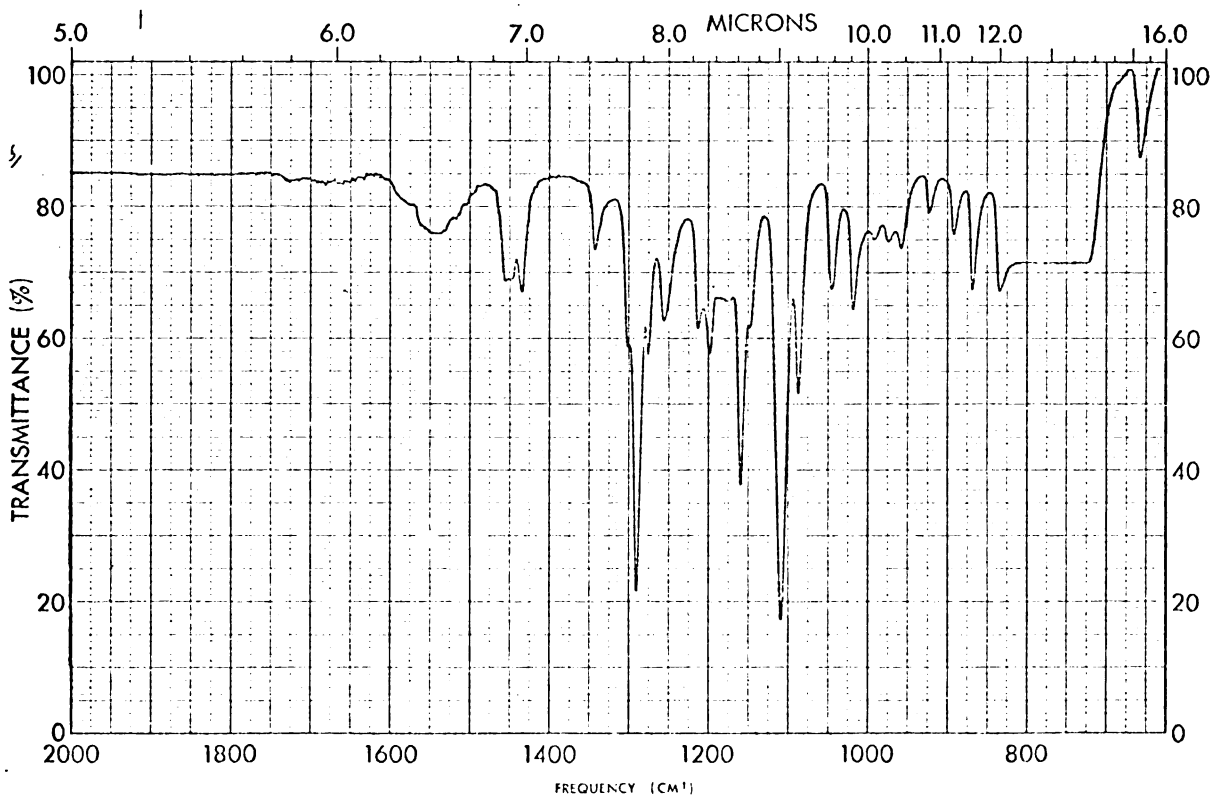
PERKIN-ELMER



SAMPLE <chem>CC(=O)OC1=CC=CC=C1</chem>	CURVE NO. 19	SCAN SPEED #100	OPERATOR JBS
ORIGIN <chem>CC(=O)OC1=CC=CC=C1</chem>	CONC. A.S.V.	SIT. N	DATE 11/26/66
SOLVENT <chem>CCl4</chem>	CELL PATH.	REMARKS	
REFERENCE <chem>CCl4</chem>			

PART NO. 237-1034

PERKIN-ELMER

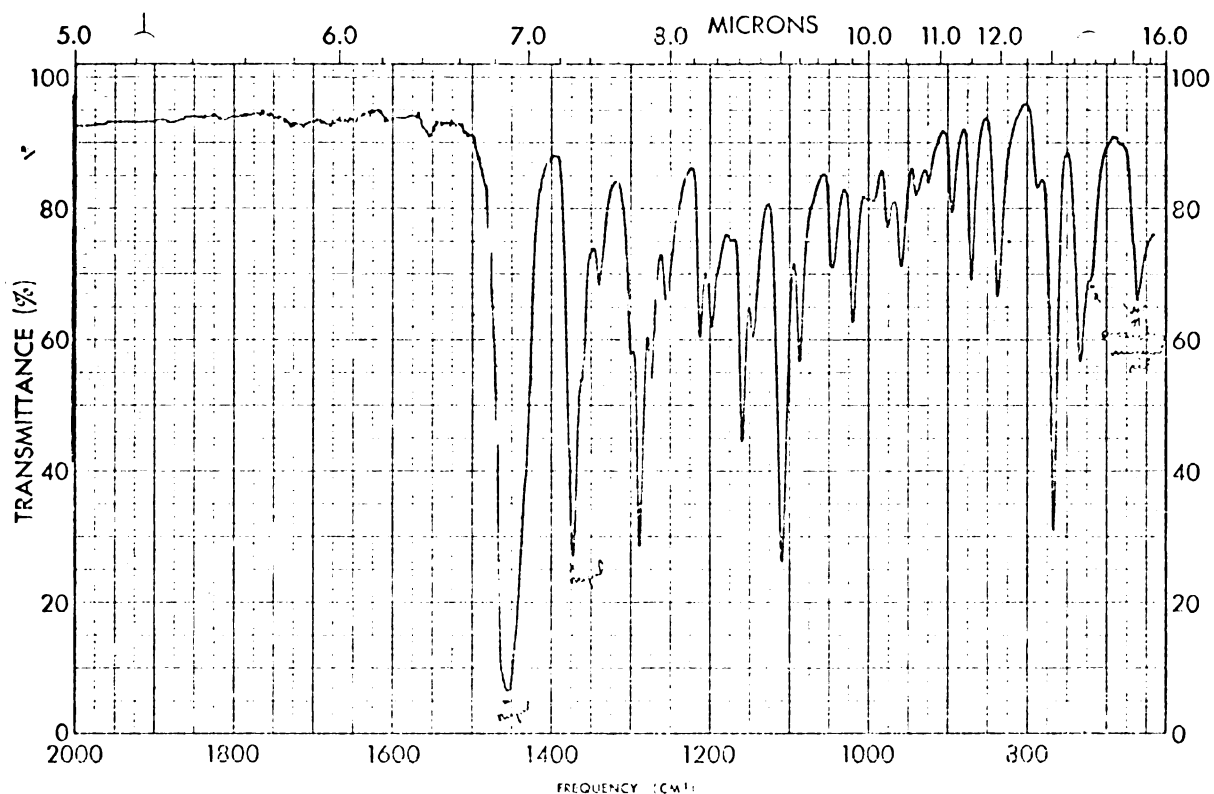


SAMPLE <chem>CC(=O)OC1=CC=CC=C1</chem>	CURVE NO. 19	SCAN SPEED Fast	OPERATOR JBS
ORIGIN <chem>CC(=O)OC1=CC=CC=C1</chem>	CONC. A.S.V.	SIT. N	DATE 11/26/66
SOLVENT <chem>CCl4</chem>	CELL PATH.	REMARKS	
REFERENCE <chem>CCl4</chem>			

PART NO. 237-1035

PERKIN-ELMER

Fig 5



SAMPLE <i>CCl₄</i>	CURVE NO. <i>20</i>	SCAN SPEED <i>Fast</i>	OPERATOR <i>JHS</i>
ORIGIN <i>CCl₄</i>	CONT.	SUT. <i>N</i>	DATE <i>1-11-66</i>
SOLVENT <i>mineral oil</i>	CELL PATH	REMARKS <i>rec'd. of 1st run</i>	
	REFERENCE <i>mineral oil</i>	<i>absent in CCl₄ solution of this compound</i>	

PART NO. 237-1035

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FIG. 6

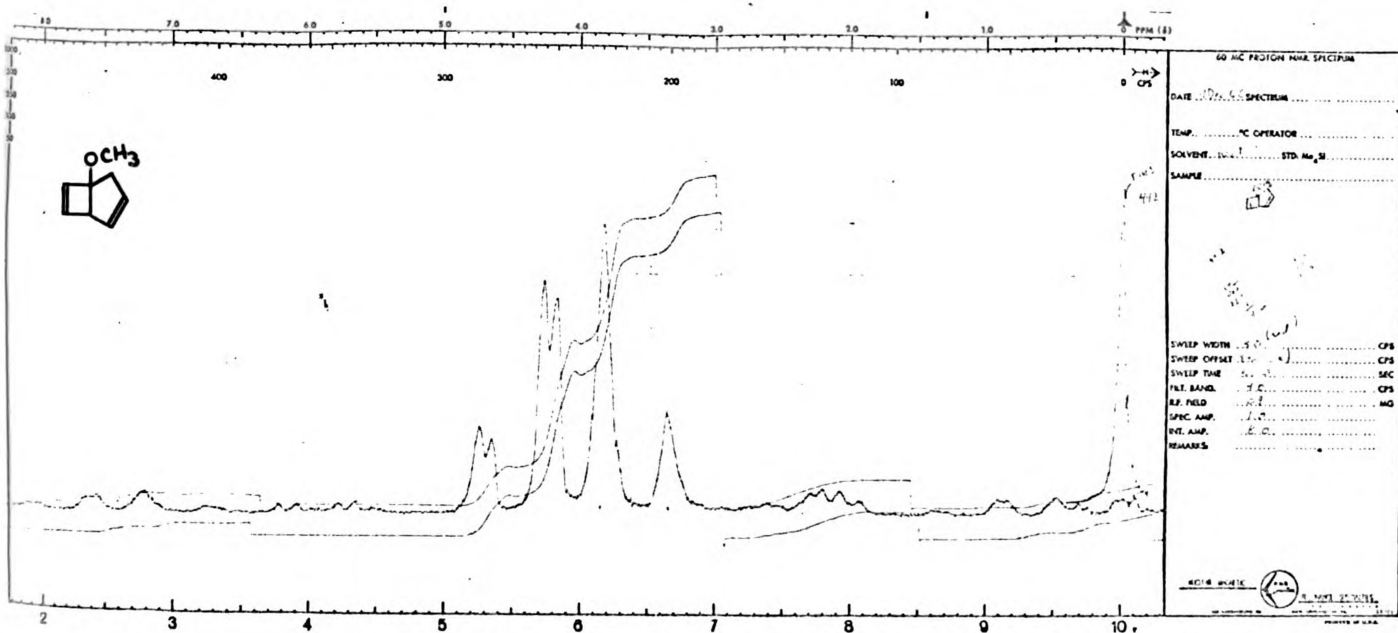
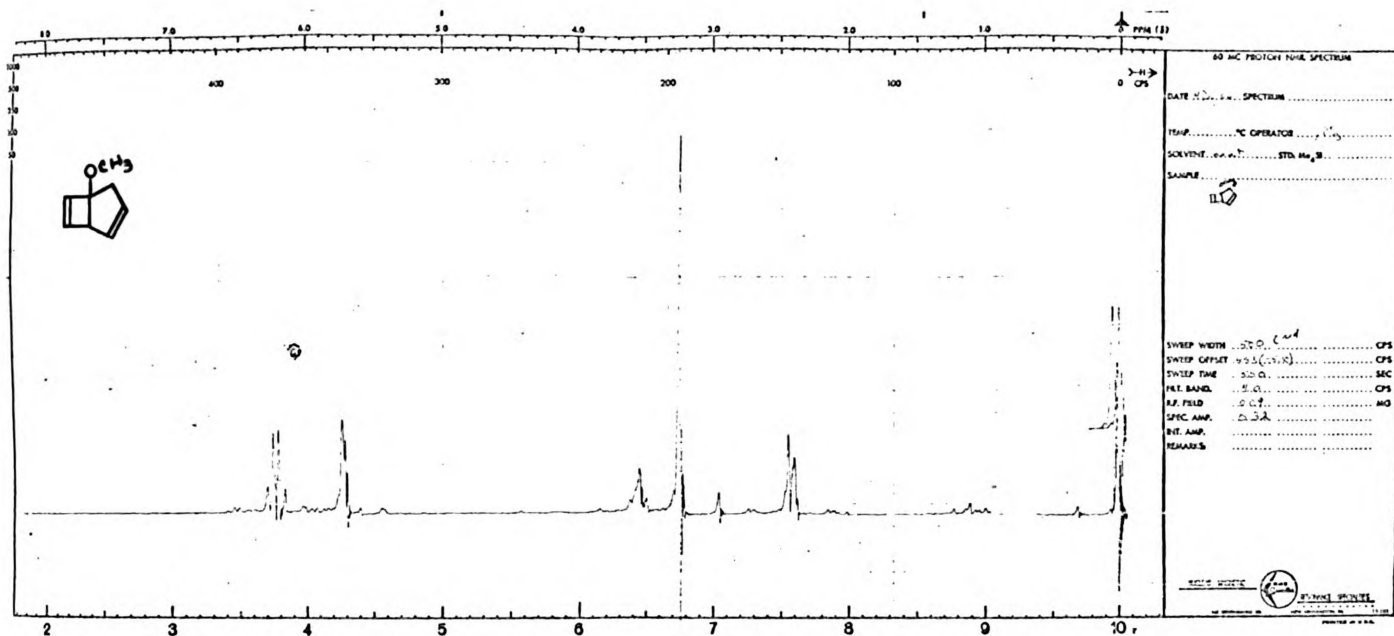


FIG. 7.

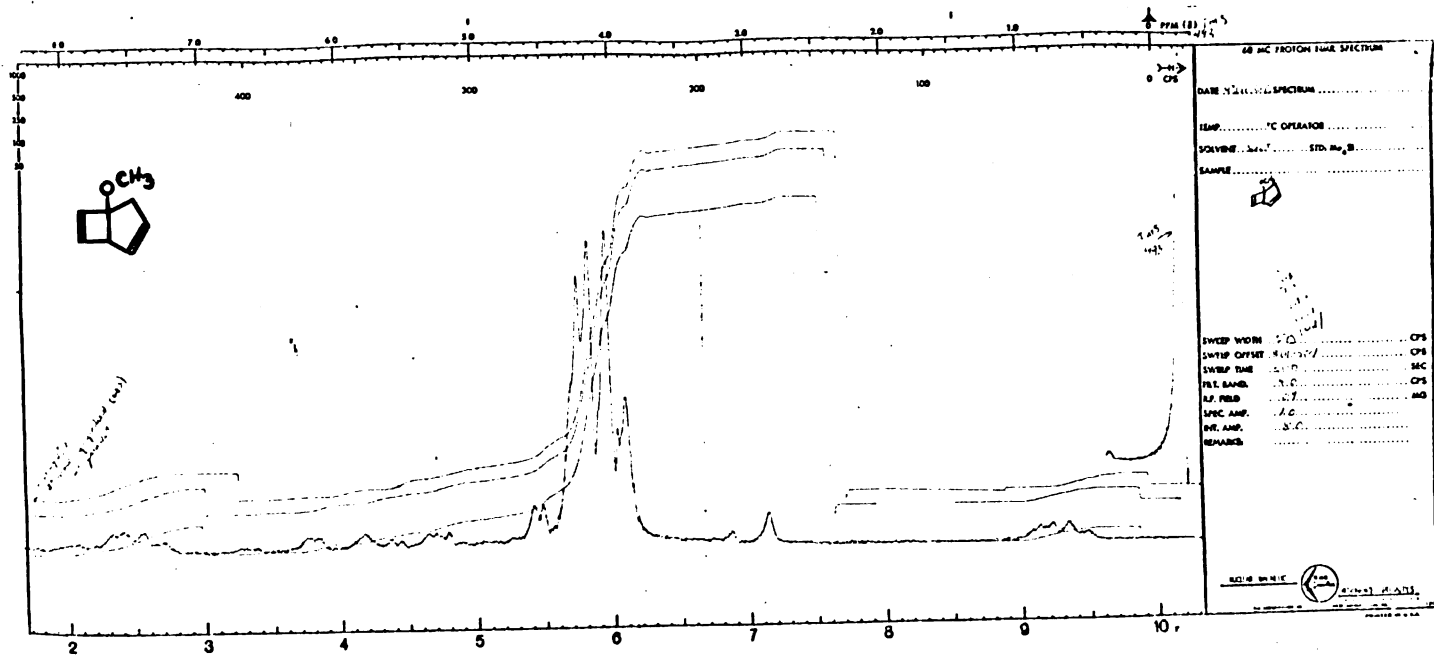
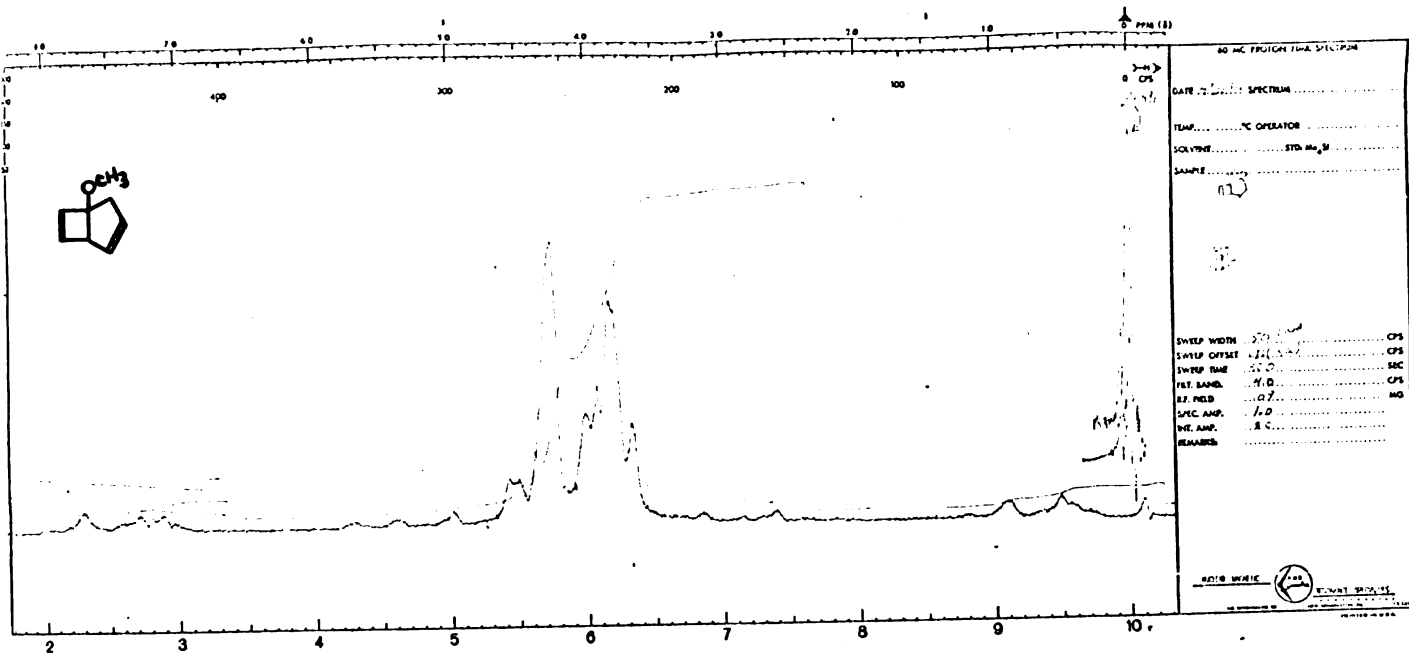


FIG. 8

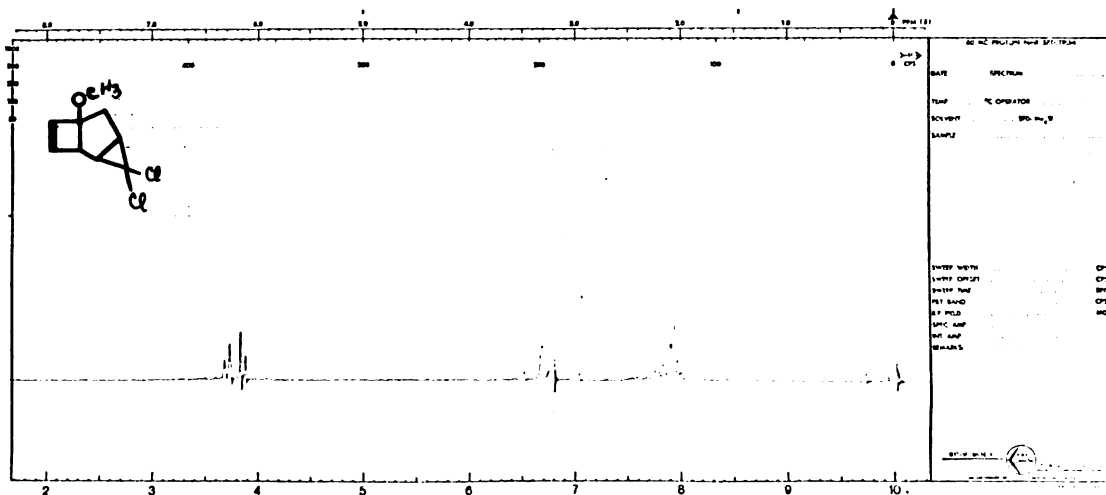
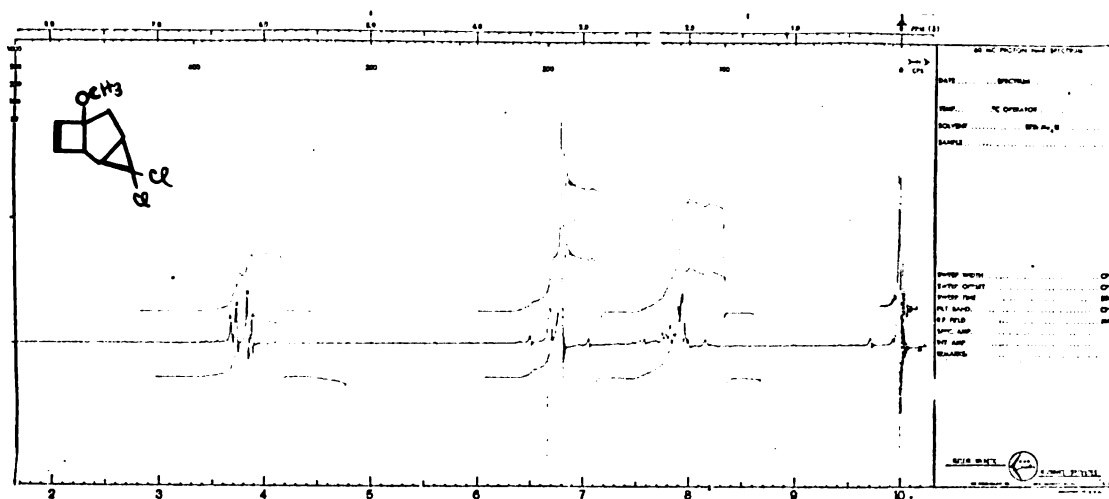


FIG. 9

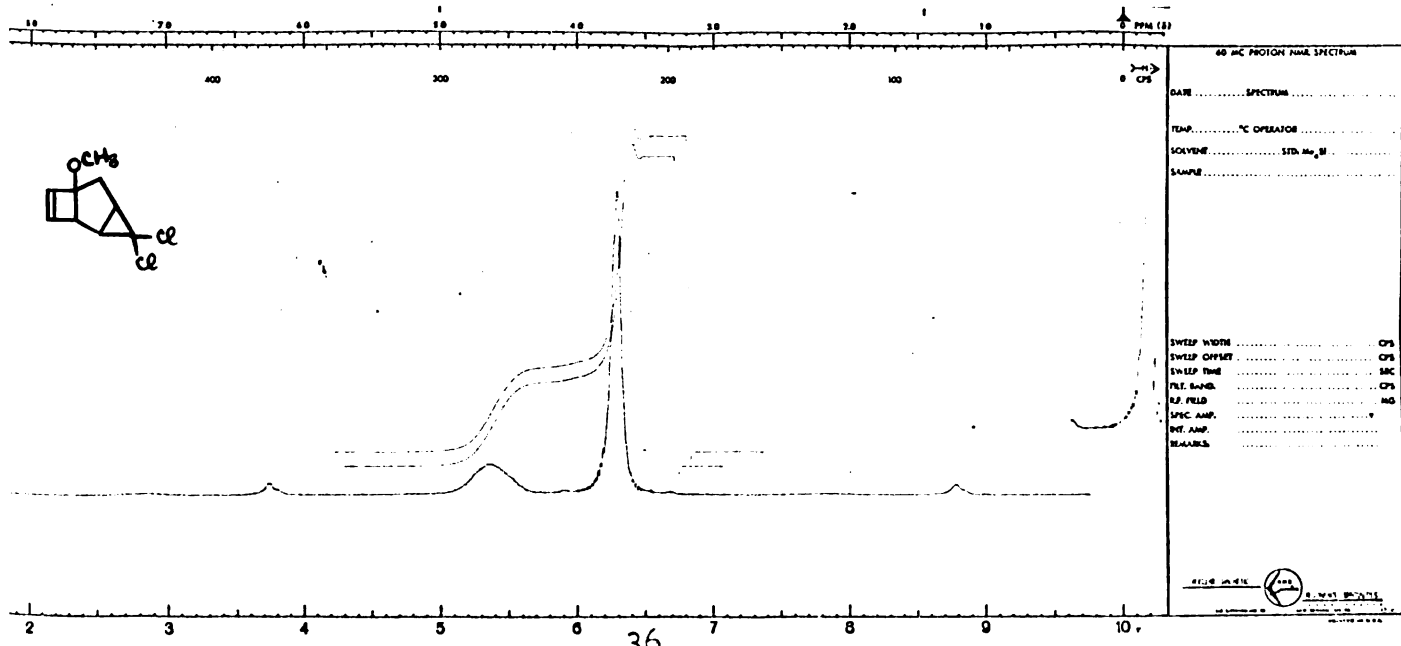
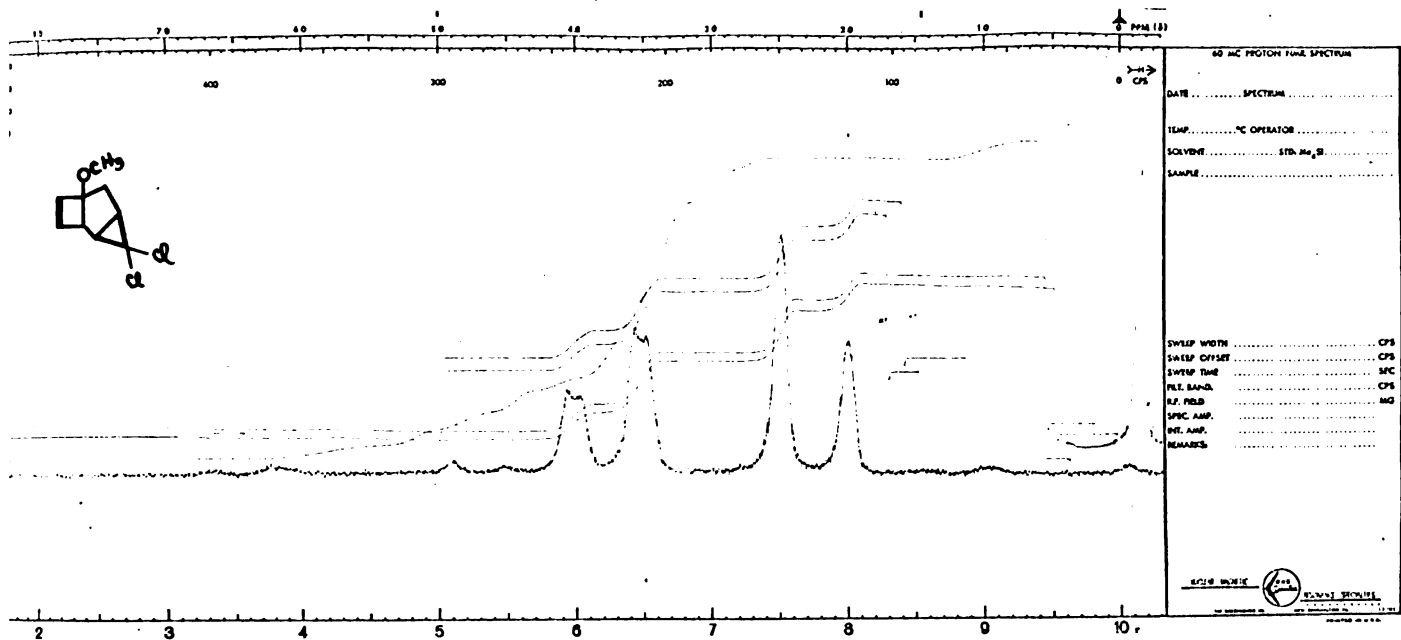


FIG 10.

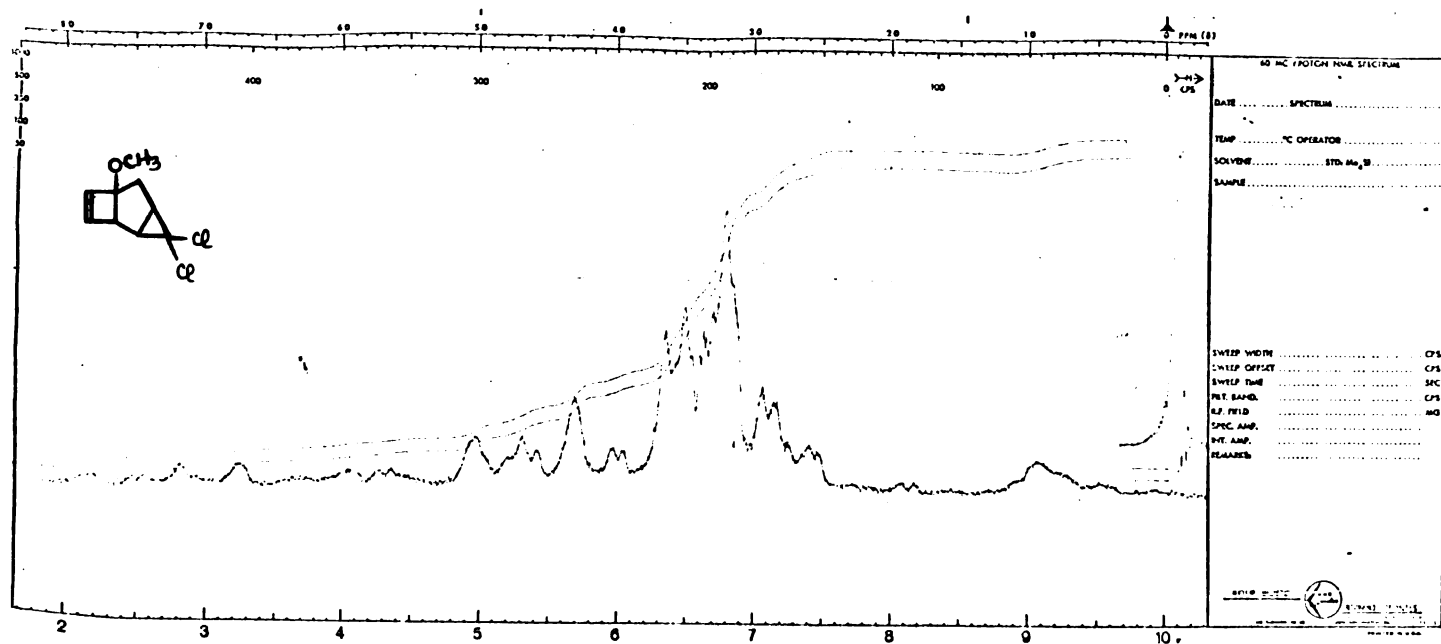
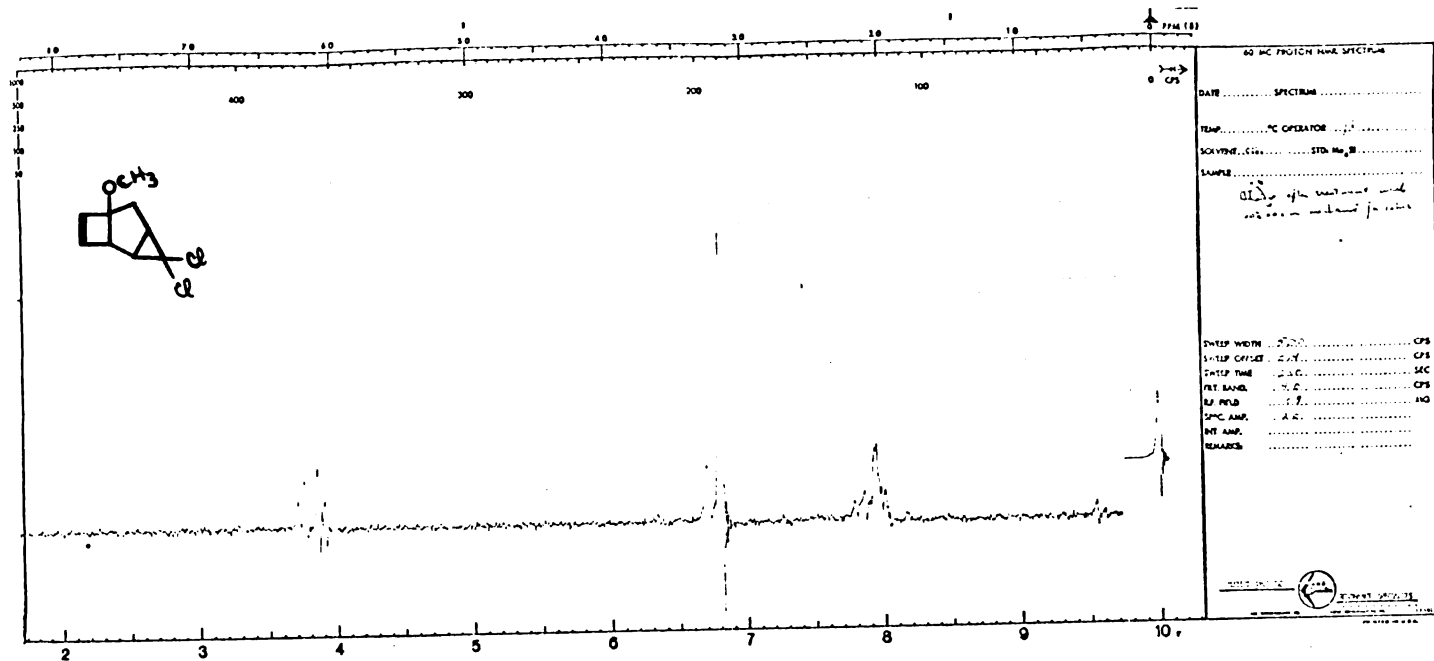


FIG. 11

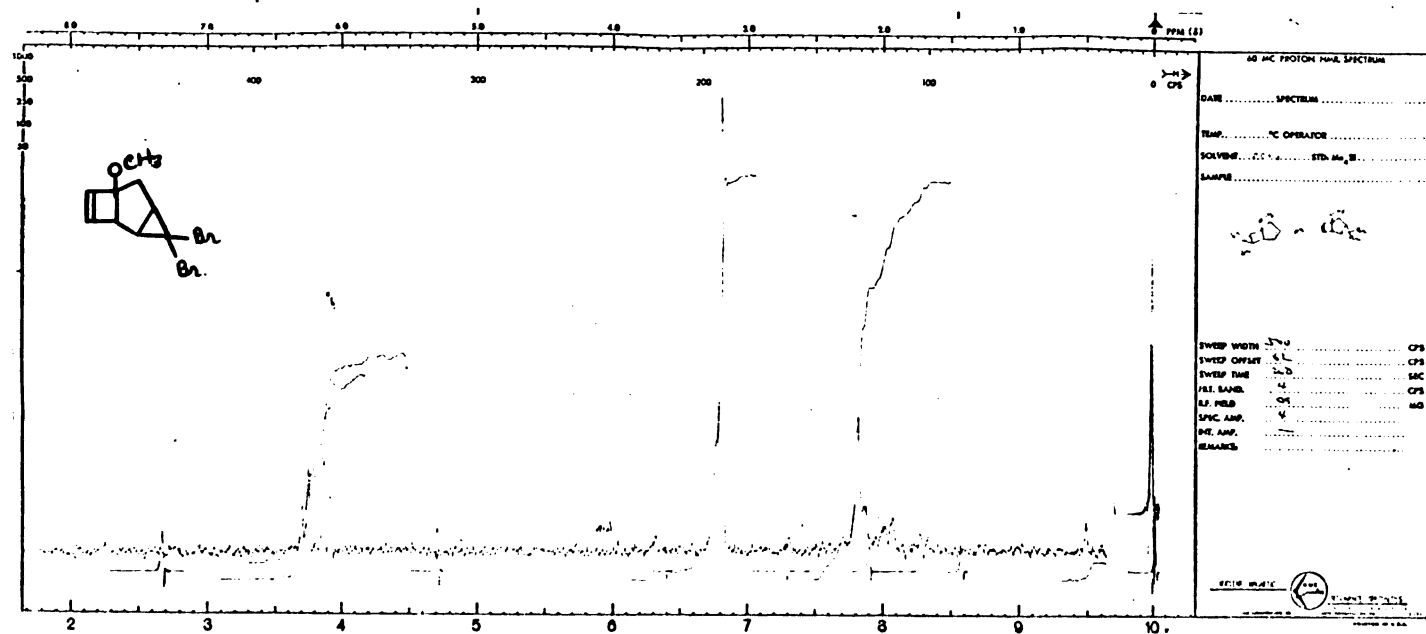
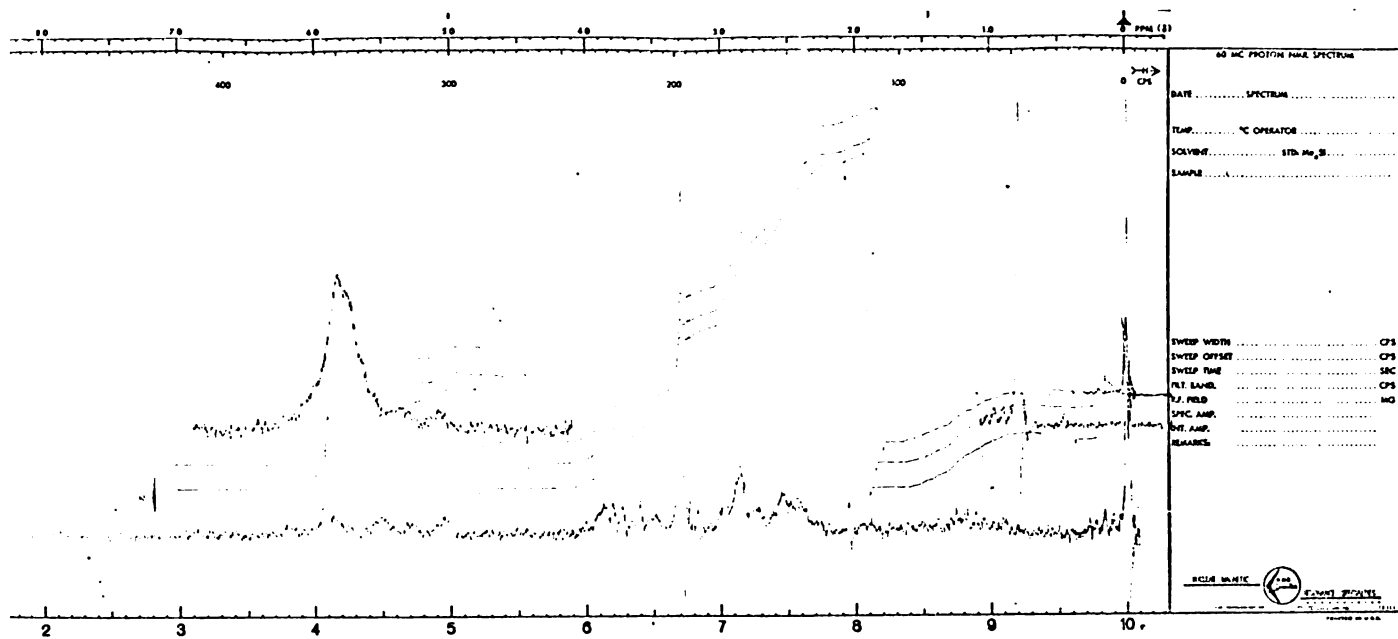
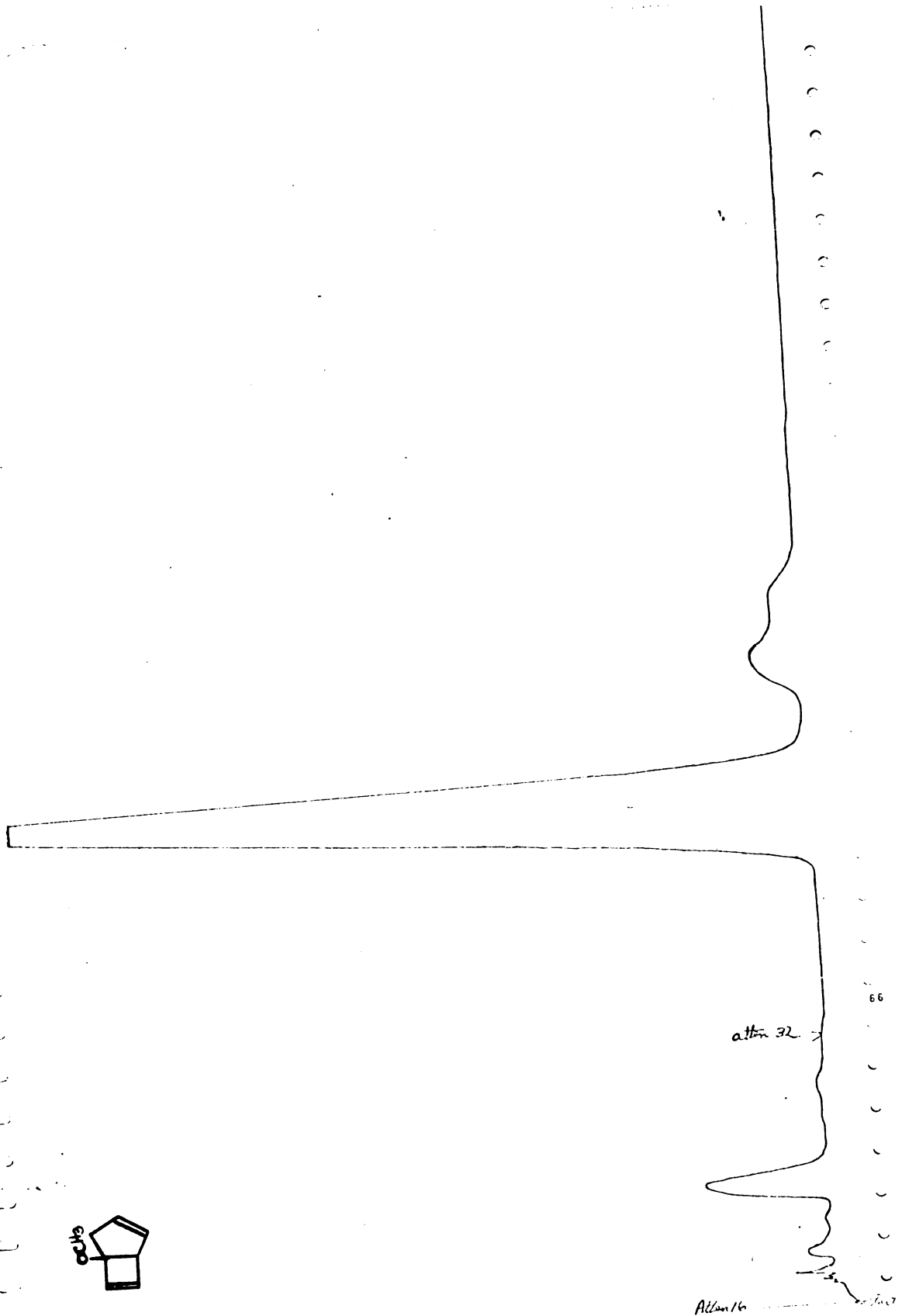



Fig 12.




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