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Mechanistic Studies of Alkylation of Cobalt(I) by Cyclobutyl Derivatives

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MECHANISTIC STUDIES OF ALKYLATION OF COBALT(I) BY CYCLOBUTYL DERIVATIVES

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MECHANISTIC STUDIES OF ALKYLATION OF COBALT(I)

BY CYCLOBUTYL DERIVATIVES

Thesis Approved

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Dr. D. H. Buchanan, Thesis Advisor

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Dr. J. W. Ellis

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Dr. C. D. Foote

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Dr. G. L. Henderson

Abstract

MECHANISTIC STUDIES OF ALKYLATION OF COBALT(I) BY CYCLOBUTYL DERIVATIVES

by

HAO KU

Under the supervision of Professor D. H. Buchanan

A study was initiated on the hypothesis, by Ugi and co-workers, that cyclopropyl, cyclobutyl, and cyclopentyl electrophiles might under go nucleophilic substitution reactions with retention of configuration.

The synthesis of benzocyclobutenol and 2-phenylcyclobutyl tosylate is described. The reactions of these tosylates with cobalt(I) "supernucleophiles" gave low yields of products which have not been purified sufficiently for assignment of stereochemistry.

Reaction of cyclopentyl tosylate and phenylethyl-

tosylate with the "supernucleophiles" cobaloxime(I) and cobalt(salen)(I) is discussed for the advance of future work.

Acknowledgement

I would like to express my sincere appreciation to Dr. D. H. Buchanan for suggesting the problem and for providing guidance, inspiration and assistance throughout the investigation.

I give thanks to the other members of the faculty and graduate students for their interest and help.

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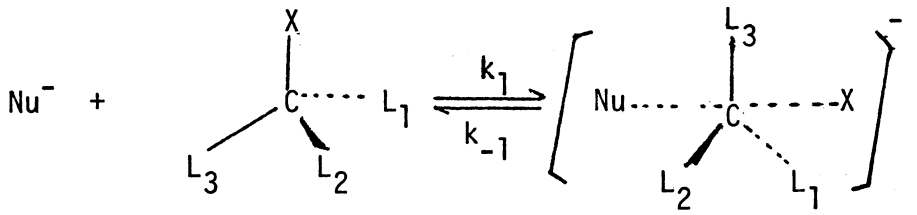
Introduction:

This research project essentially deals with the synthesis of four member ring derivatives and their reactions with low-valent organocobalt complexes in order to gain deeper insight into the chemistry of vitamin B_{12} model compounds and into the mechanism of the nucleophilic substitution (S_N2) reaction (eq 1).

$$Nu^- + R\text{-}X \longrightarrow Nu\text{-}R + X^- \qquad (1)$$

by which a nucleophile (Nu^-) displaces a leaving group (X) from electrophiles (R-X) in which R is a small ring.

The S_N2 reaction is one the most fundamental and ubiquitous reactions in all of chemistry. The second-order kinetics and configurational inversion were qualitatively accounted for in a satisfying manner by Lewis[1] who suggested that a new bond is formed to the central carbon atom as the old bond is broken, with the action occurring simultaneously at opposite ends of the carbon tetrahedron (Scheme I). Scheme I: Nu^- = nucleophile, X^- = electronegative leaving group, L = ligand.



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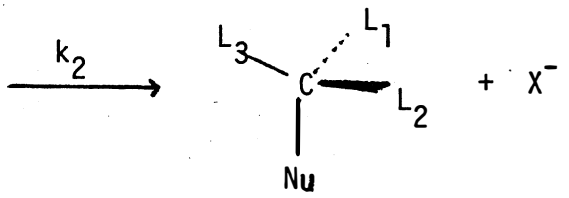

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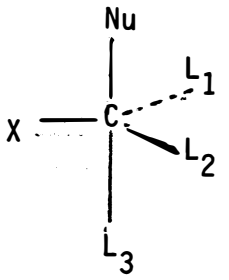
In the classical S_N2 mechanism the trigonal-bipyramidal species 3 is a transition state with apical entering and leaving groups which by apical departure of X^- leads to the inverted product 4. This inversion mechanism has been known a good many years.

In the bimolecular S_N2 process, the transformation of the tetra-coordinate carbon compound into the pentacoordinate species results from an attack on any face (see 5 - 7) of the tetrahedron by the nucleophile such that the entering group assumes an apical position in the intermediate. If the steric requirements for both apical entry and departure are not fulfilled, no nucleophilic substitution via penta-

coordinate species takes place.[2]



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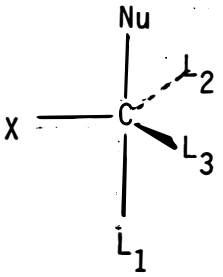

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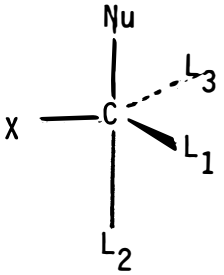
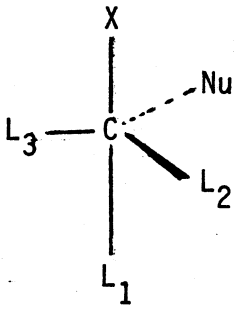


7

Reorganization of (5) - (7) by BPR or TR processes[3] (BPR = Berry pseudorotation, TR = turnstile rotation) forms (8) which by apical departure of X^- leads to (9), with retention of configuration.



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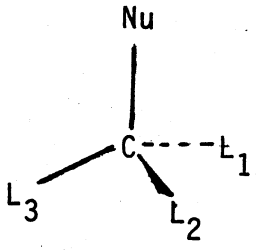

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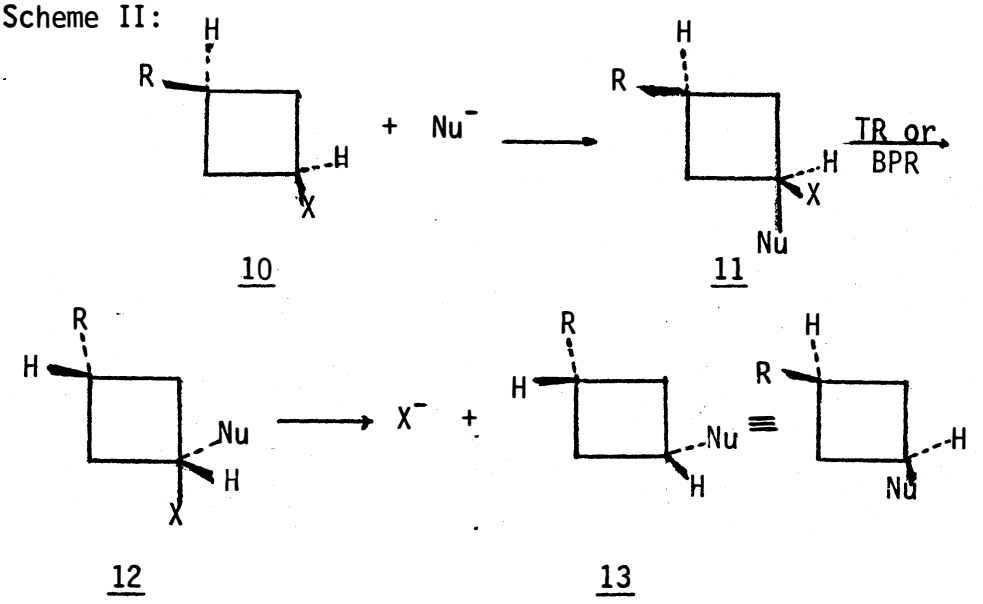
An S_N2 process with retention of configuration is predicted by Ugi[4] if a cyclopropyl, cyclobutyl, or cyclopentyl

derivative undergoes a nucleophilic substitution under conditions where the bimolecular S_N2 process is faster than the competing S_N1 process.

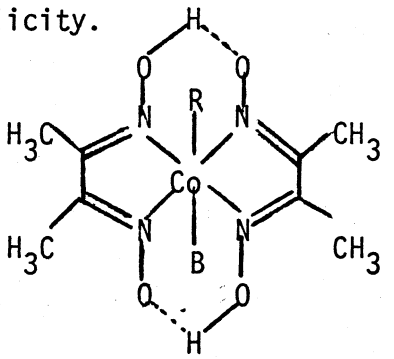
Penta-coordinate molecules with a trigonal-bipyramidal skeleton possessing diequatroial three to five-membered rings are of such high energy that reaction would probably proceed through a BPR or TR processes in the transition state. For example, if a cyclobutyl derivative (10) undergoes a nucleophilic substitution S_N2 process, apical attack by Nu^- on (10) can only lead to (11); apical departure of X^- is only possible after a rearrangement (11) - (12) (Scheme II). This leads to the prediction of retention of configuration on these substitution reactions.

Scheme II:



Unfortunately small ring alkyl halides and tosylates react extremely slowly, if at all, via S_N2 reactions[2]. The facility with which direct displacement reaction occurs on cycloalkane derivatives is markedly dependent on the size of the ring and on the nucleophilicity of the substituting group. Hence the powerful nucleophiles cobalt(I) are introduced. They are orders of magnitude faster than the typical nucleophiles[5].

Complexes of cobalt in the +1 oxidation state with planar chelates form spin-paired Co(I) (d^8) derivatives such as cobaloximes(I)(14) (complexes of cobalt with bis(dimethylglyoximato) ligand) and cobalt(salen)(15) (salen = bis(salicylaldehyde)ethylenediiminato). These are the most nucleophilic compounds known[6,7]. The highest occupied orbital in the cobalt(I) species is the weakly antibonding d_{z^2} orbital[8], whose directional characteristics and high charge density give it the high nucleophilicity.



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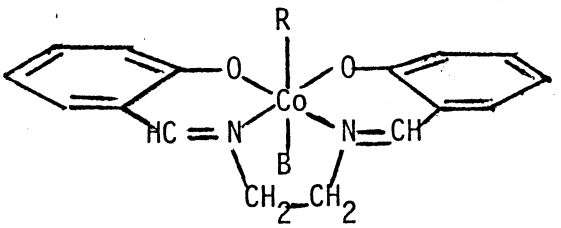
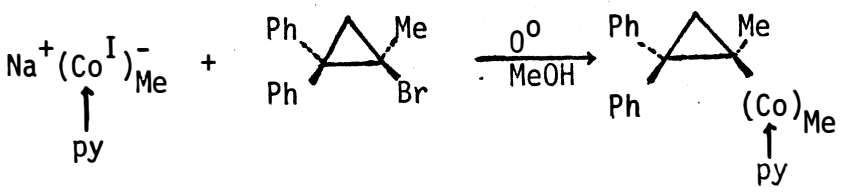


15

The reaction of alkyl halides with cobaloximes(I) proceeds by second order kinetics[5] and configurational inversion[9]. The observed second order rate law eliminates the possibility of a S_N1 mechanism, however, it does not discriminate between a classical S_N2 mechanism and an electron-transfer process involving free radicals as intermediates. Recently studies of the reaction of pyridine [bis(dimethylglyoximato)]cobalt(I) and 1-methyl-2,2-diphenylcyclopropyl bromide (eq 2) and five possible mechanisms for the reactions of low-valent metal ions and alkyl halides are discussed by Jensen and Buchanan[10]. Although inversion at carbon was shown for reactions at cyclohexyl and open chain centers, the stereochemistry of displacement at small rings is still unknown.



(2)

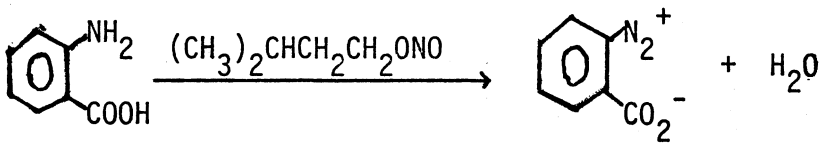
The stereochemistry of the alkylcobalt complexes can be determined from nmr coupling constants of the vicinal protons on the ring. Having on hand cis and trans starting materials and the cobalt derivatives of each will allow for cross checking of assignments.

In the course of studying the stereochemistry of alkylation of Co(I) as a test of the Ugi hypothesis, 1,2-disubstituted cyclobutyl derivatives were prepared.

Results and Discussion.

Synthesis of Benzocyclobutenol.

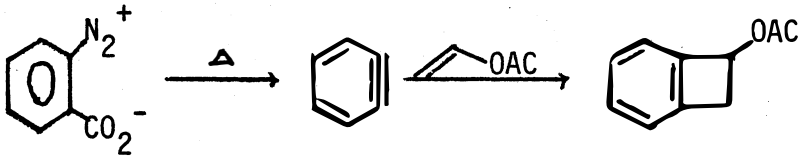
Starting with anthranilic acid(16), benzenediazonium-2-carboxylate(17)[11] was prepared as shown in equation 3.



16 17

$$+ \ (CH_3)_2CHCH_2CH_2OH \qquad (3)$$

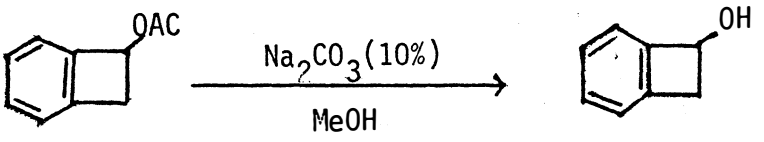
and the converted to benzocyclobutenyl acetate(18) via benzyne formation[12] (eq 4).



(4)

17 18

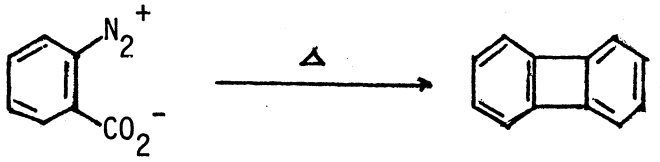
This was followed by basic hydrolysis to yield benzocyclobutenol[13] (eq 5) in overall 8% yield.



(5)

18 19

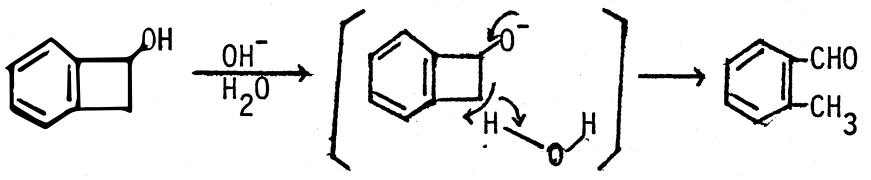
The reaction of benzyne with vinylacetate gave 26.5% of benzocyclobutenyl acetate. The low yield was presumbly due to the side reaction (biphenylene(20) formation) (eq 6).



(6)

17 20

The basic hydrolysis of 18 gave a yellow oily mixture. After benzocyclobutenol was isolated from the mixture, the residue was analyzed by nmr and was shown to be impure starting material. The impurity in the starting material was believed to be o-tolualdehyde(22), from the basic cleavage of benzocyclobutenal via an alkoxide intermediate(21) (eq 6).



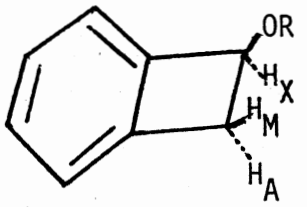
(7)

19 21 22

Some simple analogs of this reaction are to be found in the facile conversion of cyclopropanol to propionaldehyde[14-16] and in the base cleavage of 3-hydroxycyclobutanone[17].

The structural assignments for benzocyclobutenyl acetate and benzocyclobutenol are based on the nmr spectra shown in Figure I, Figure II and Figure III. The partial expanded nmr spectrum of these compounds is shown in Figure IV. The mass spectrum of benzocyclobutenyl acetate is shown in Figure V.

Scheme III: R = H or CH_3CO-



The upfield octet represents the methylene protons(H_A, H_M) on the four member ring (Scheme III). The proton <u>cis</u> to the OR groups (<u>trans</u> to the H_X) is slightly more deshielded by the OR group. Hence a slight downfield shift H_M with respect to H_A is seen. Each methylene proton is split by the vicinal methine proton (H_X) with coupling constants of 2.0 Hz and 4.4 Hz, respectively. This is a first order splitting

Figure I: Nmr Spectrum of Benzocyclobutenyl Acetate in CCl_4

Figure II : Nmr Spectrum of Benzocyclobutenol in CCl_4

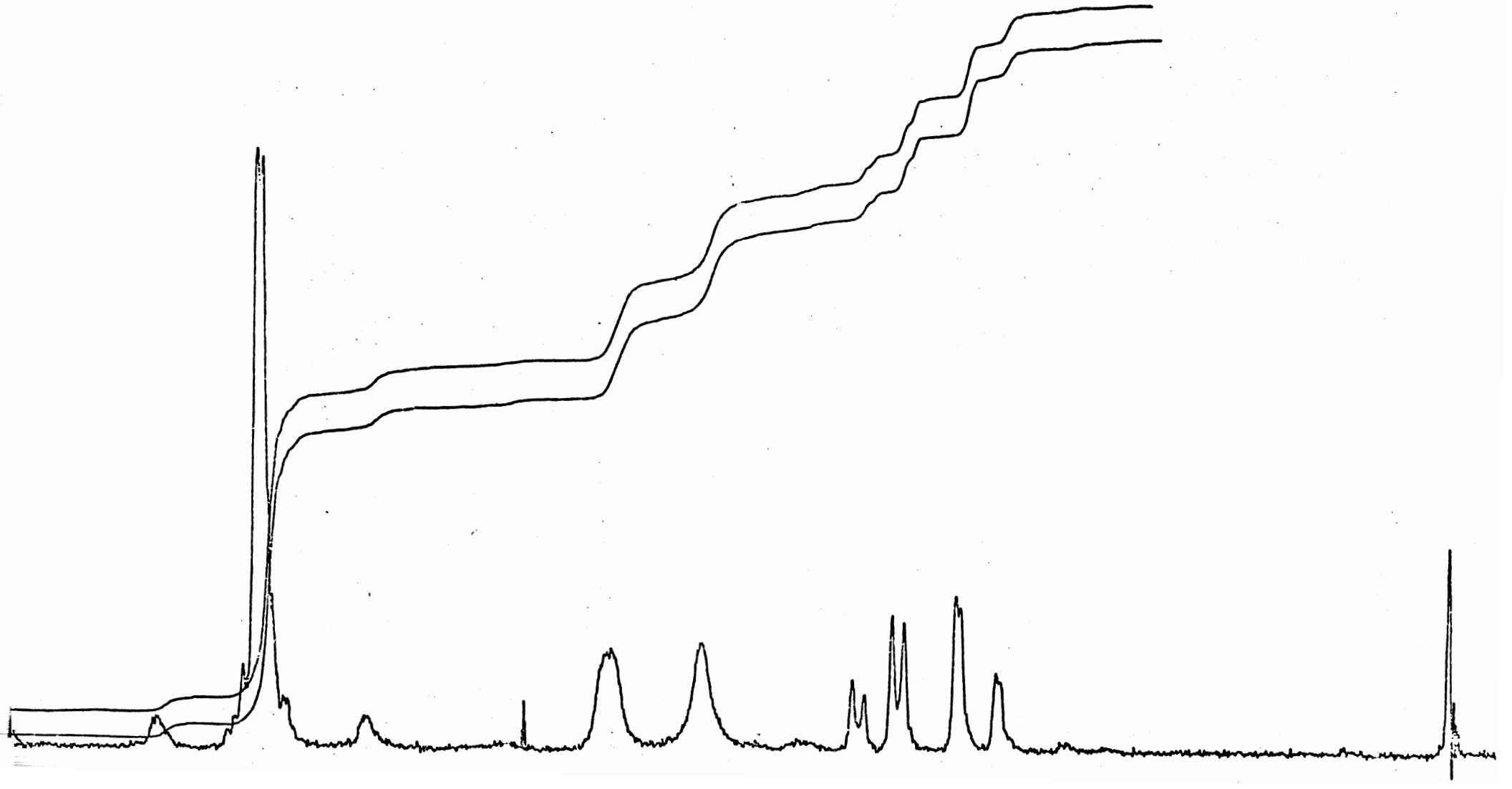


Figure III: Nmr Spectrum of Benzocyclobutenol in CCl_4 + D_2O

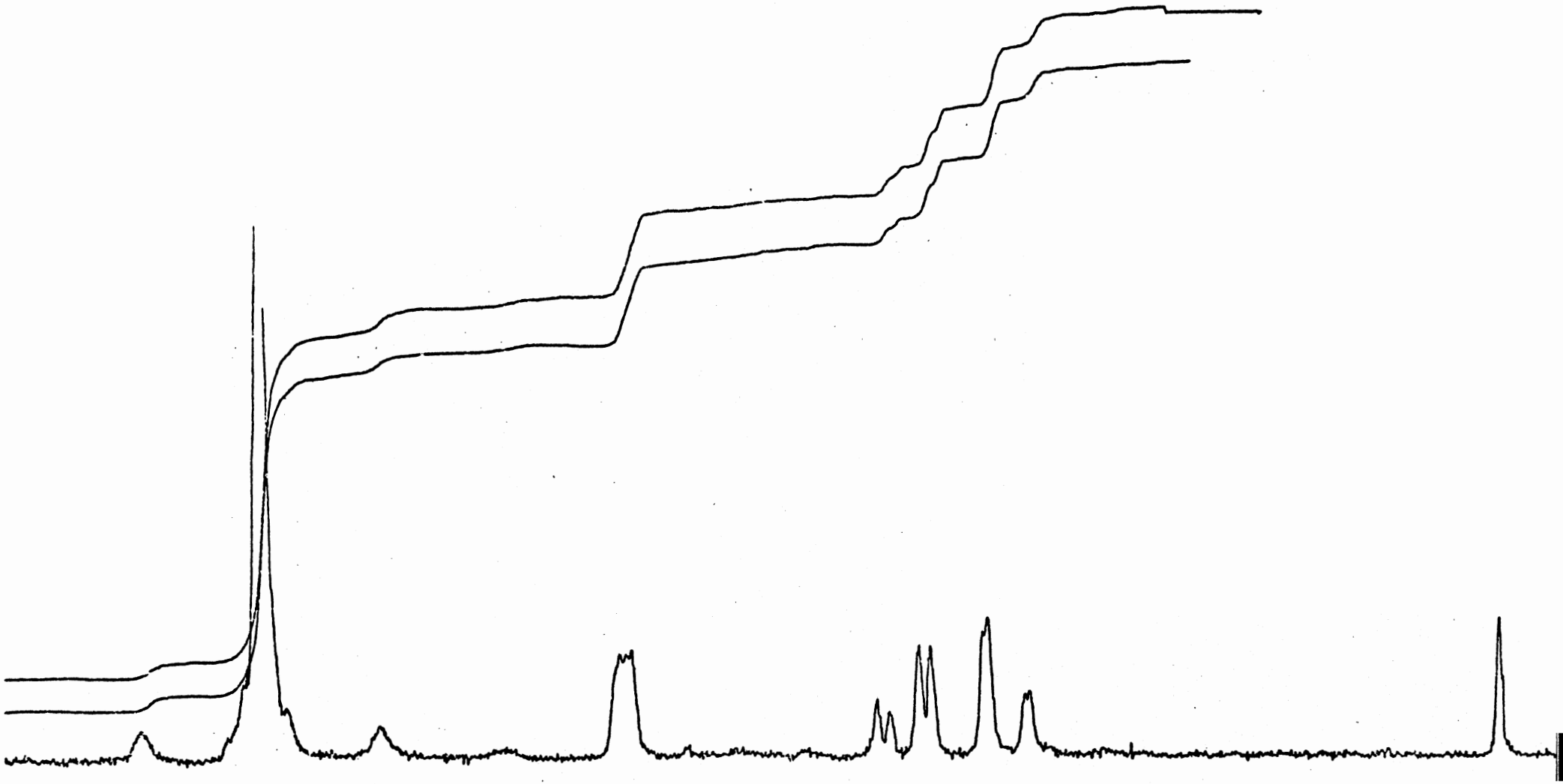


Figure IV : Nmr Spectrum of Benzocyclobutenol in CCl_4(Partial)

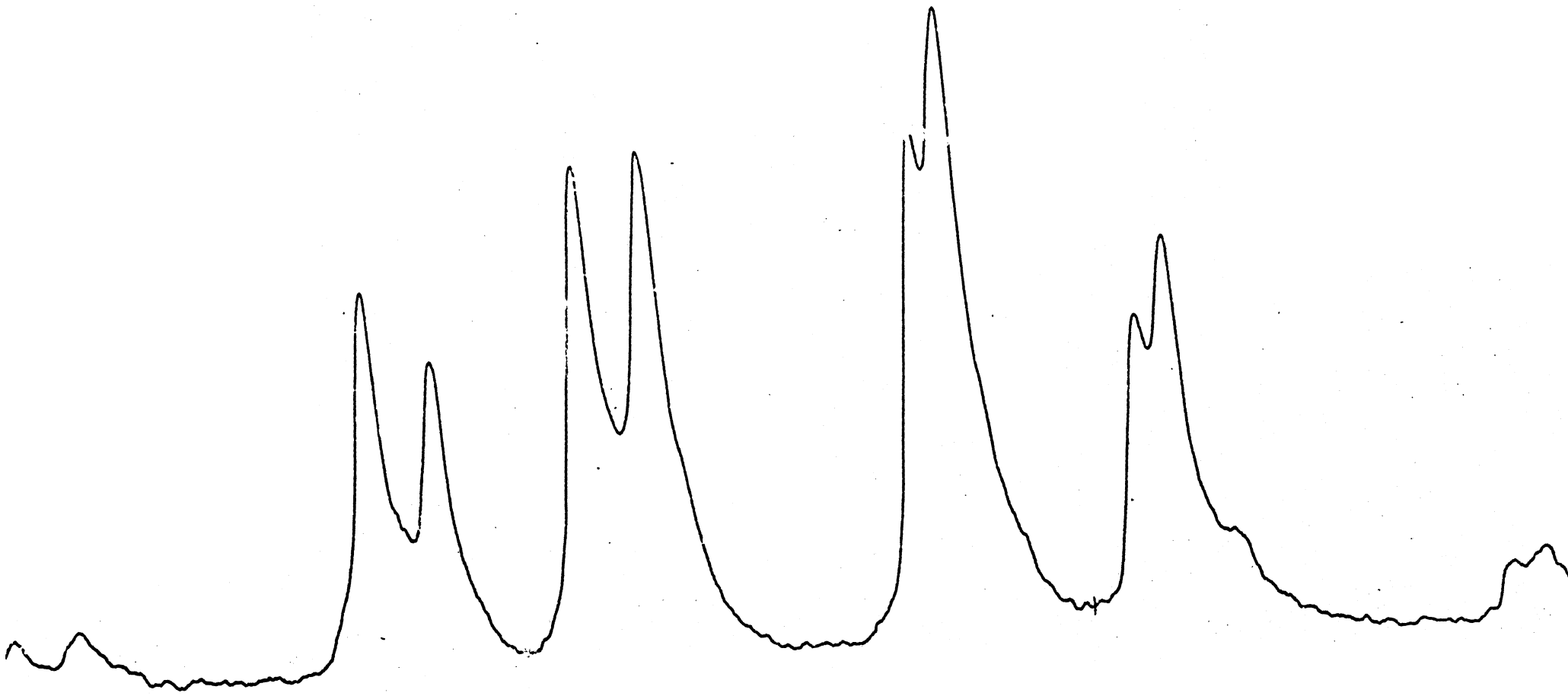
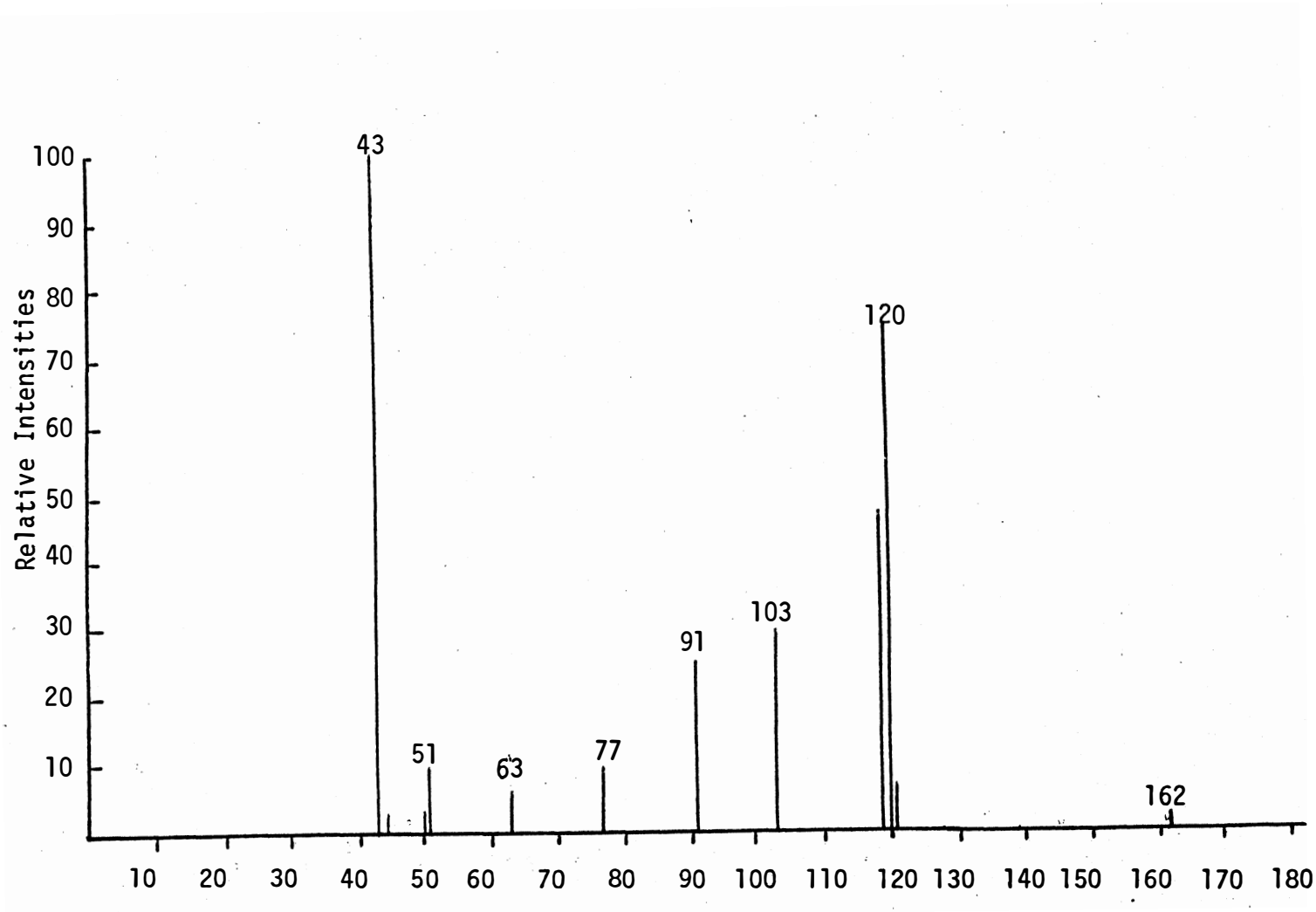
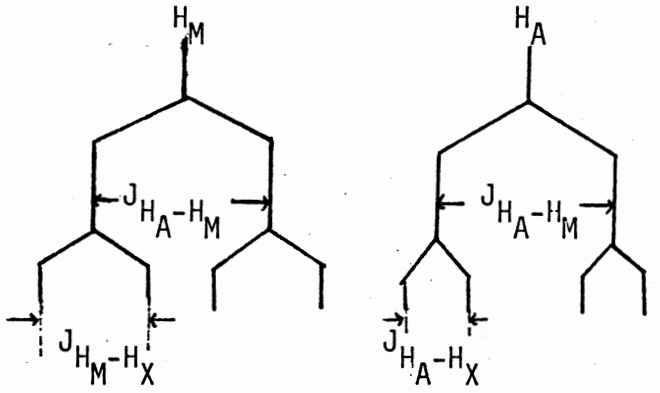


Figure V: Mass Spectrum of Benzocyclobutenyl Acetate

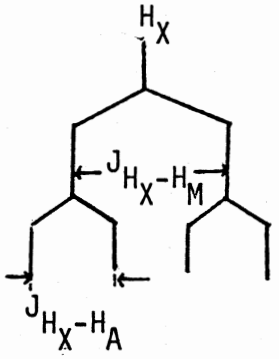


AMX system ($\Delta\nu/J > 7$)[18]. An idealized diagram is as follows:



$J_{H_A-H_M}$ = 14.4 Hz, $J_{H_X-H_A}$ = 2.0 Hz, $J_{H_X-H_M}$ = 4.4 Hz

The methine protons absorbed at low field and consist of a quartet. The splitting relative intensities can be diagrammed as follows:

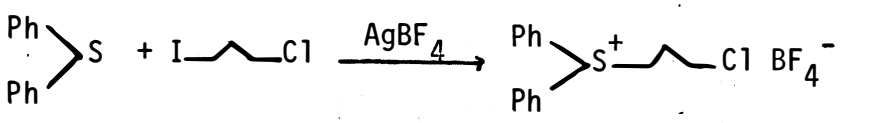


Karplus has described the theoetical dependence of the coupling constant for two hydrogens bonded to adjacent C atoms[16] on dihedral angle. Using Karplus' equation, $J_{HH'}$ = $A + B\cos\theta + C\cos 2\theta$ where constants A = 4.22 Hz, B = -0.5 Hz

and C = 4.5 Hz for sp^3 hybridization, we calculate the approximate dihedral angles between adjacent C-H bonds on the four-membered ring of the benzocyclobutenol $\theta^{cis} = 53^o$, $\theta^{trans} = 139^o$. Since the original Karplus equation is a zero-order approximation, and the vicinal coupling constants are assumed to depend only on the dihedral angle, the angles shown above have only a qualitative significance. Because the calculated bond angles are so distorted from their expected values all that can be said is that the ring is probably distorted and that cis protons give rise to small coupling constants and trans protons to large.

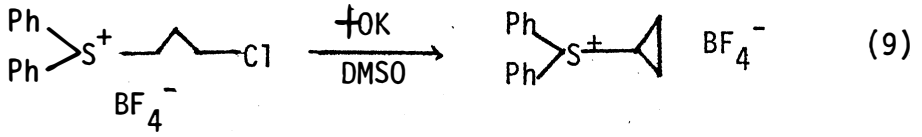
Synthesis of 2-Phenylcyclobutanol(26).

Alkylation of diphenyl sulfide(23) with a alkyl halide (24) and silver tetrafluoroborate led to the sulfonium salt (25) (eq 8). Ring closure of the 3-chloropropyldiphenylsulfonium fluoroborate(25) with potassium tert-butoxide in dimethyl sulfoxide and tetrahydrofuran (eq 9) gave the cyclopropyl diphenyl sulfonium fluoroborate(26)[21].



(8)

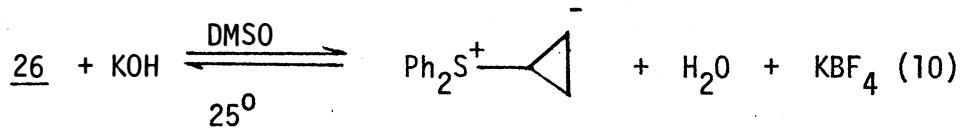
23 24 25



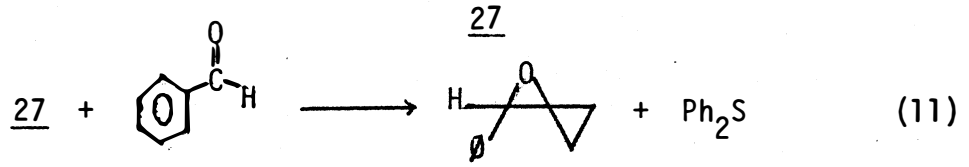
(9)

25 26

The condensation of benzaldehyde(28) with diphenylsulfonium cyclopropylid(27) followed by acid work-up leads directly to 2-phenylcyclobutanone(30) in 71% yield via intermediate oxaspiropentane(29)[22] (eq 10, 11, 12) in overall 50% yield based on nmr spectrum analysis.



(10)



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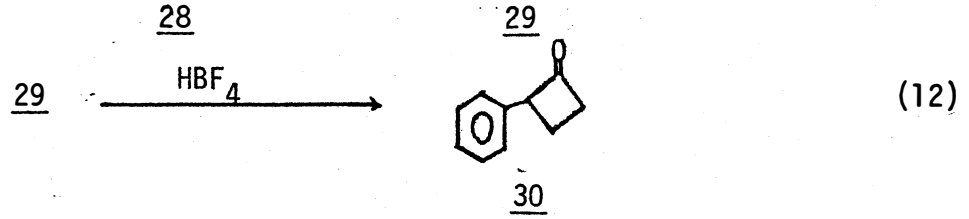
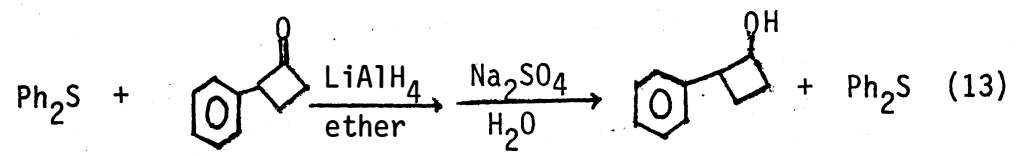


(12)

The phenylcyclobutanone was not well separated from the diphenylsulfide, either by fractional distillation ($80^{o}/0.2$ mmHg) or by column chromatography on silica gel (the eluent was 10% ether in hexane). Only 10% phenylcyclobutanone was

recovered after separation. Decomposition of the phenylcyclobutanone in the column was presumbly due to an impurity in the solvent or the silica gel. The percent ketone in the mixture can be calculated from integration of the nmr spectra (Figure VI).

Lithium aluminum hydride reduction of the ketone/sulfide mixture resulted in a mixture of 2-phenylbutanol and diphenylsulfide (eq 12)[23].



30 31

The nmr spectrum for the 2-phenylcyclobutanone is shown in Figure VI. The partial expanded nmr spectra of this compound is shown in Figure VII.

Scheme IV:

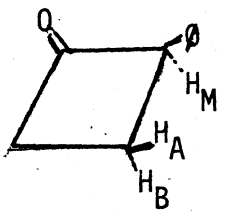


Figure VI : Nmr Spectrum of 2-Phenylcyclobutanone in CCl_4

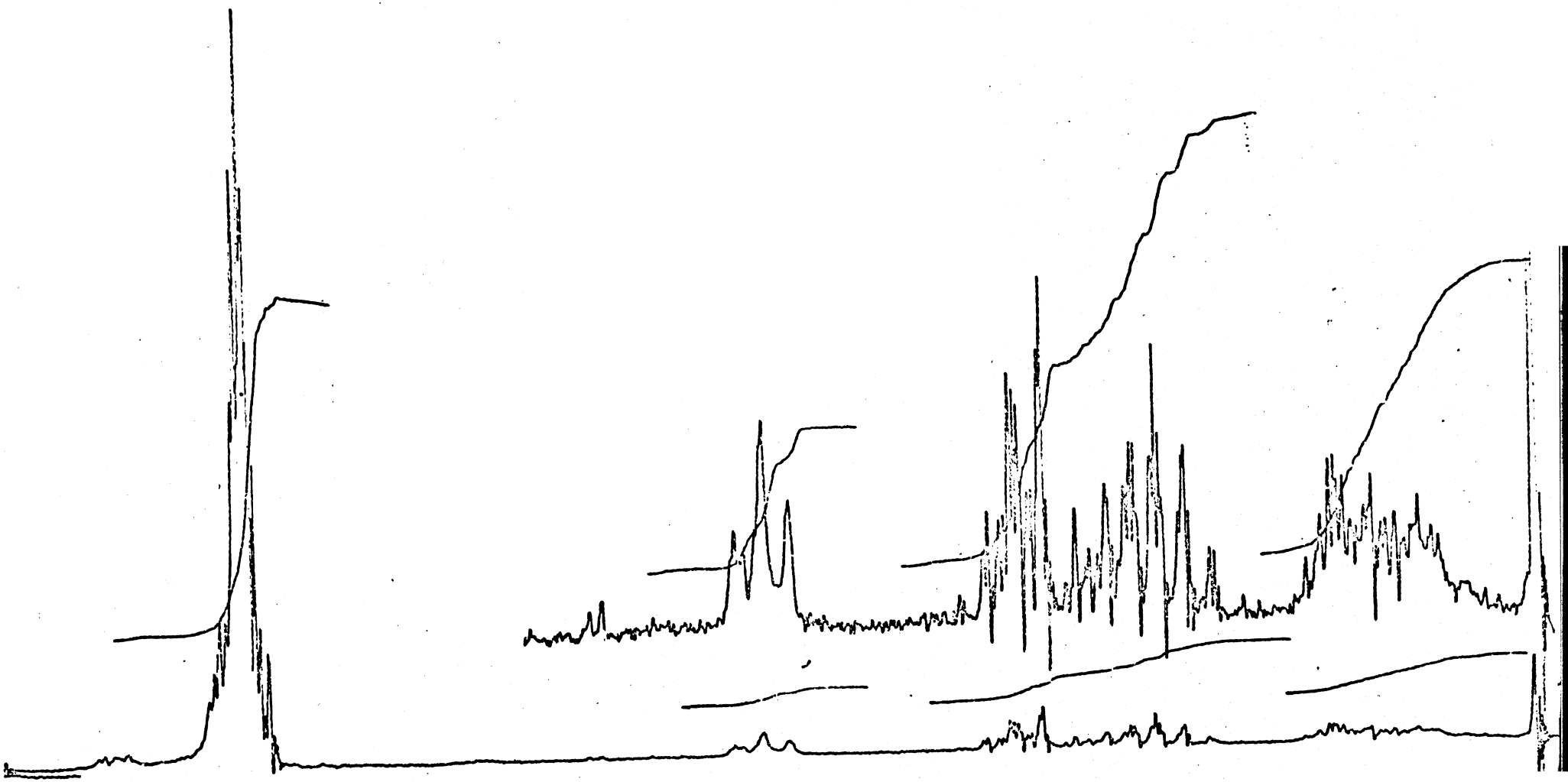
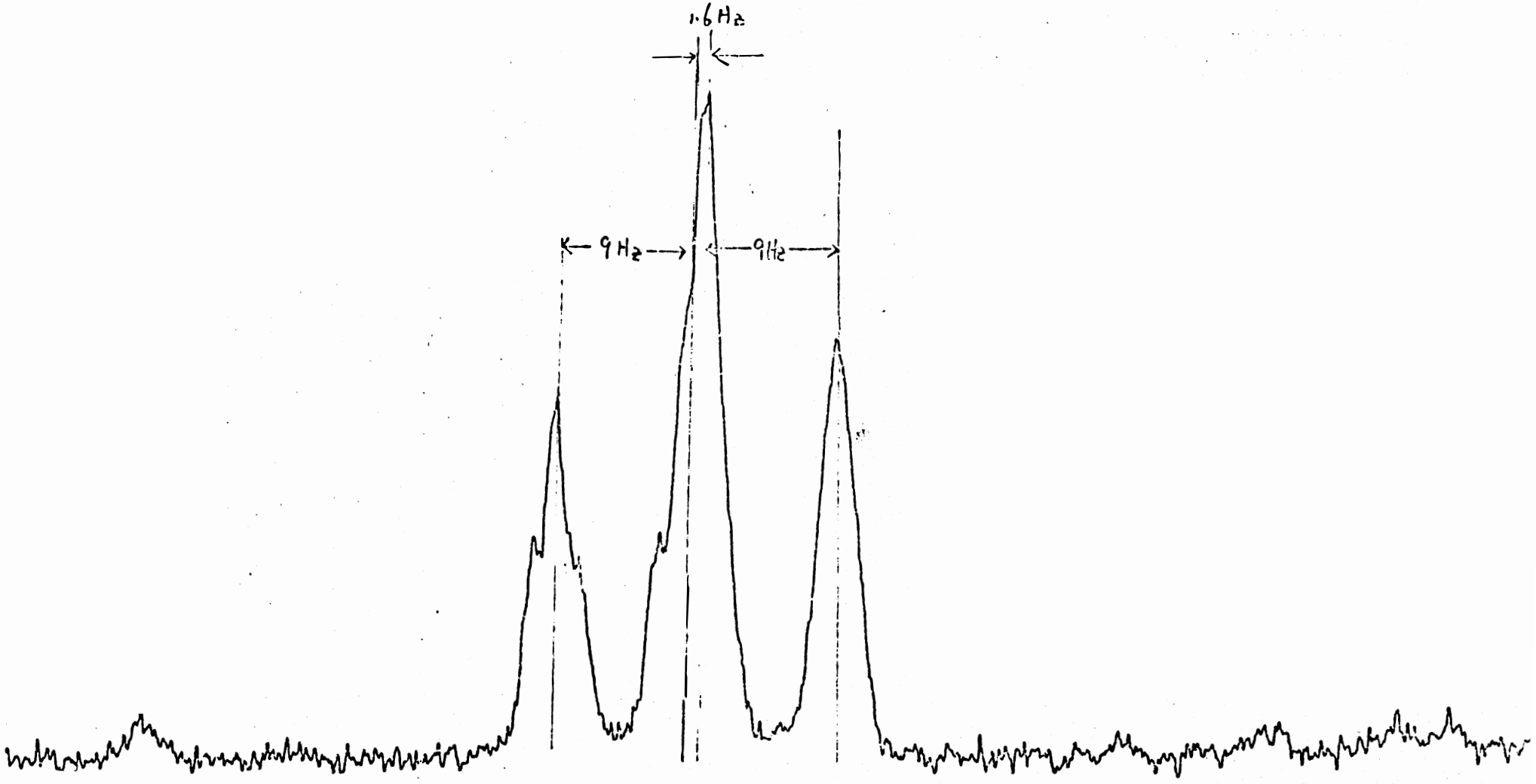
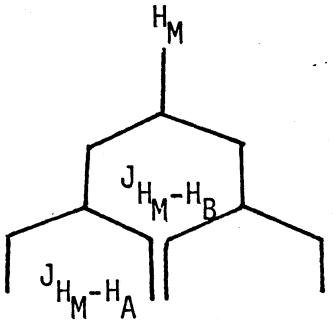


Figure VII : Nmr Partial Nmr Spectrum of 2-Phenylcyclobutanone in CCl_4



The methylene protons H_A and H_B (Scheme IV) in 2-phenylcyclobutanone are nonequivalent. The proton cis to the phenyl group (H_A) is more deshielded by the phenyl group than the proton trans to the phenyl group (H_B). Those protons absorbed at δ 1.70 and 2.84 as multiplets on the spectrum (Figure VI). The methine proton absorbed at δ 4.43 as a distorted quartet which is caused by coupling with methylene protons (H_A and H_B) with coupling constants of 9 Hz and 10.6 Hz, respectively. (The literature reported a triplet (finely split, J = 9 Hz))[22]. An idealized diagram is as follows:

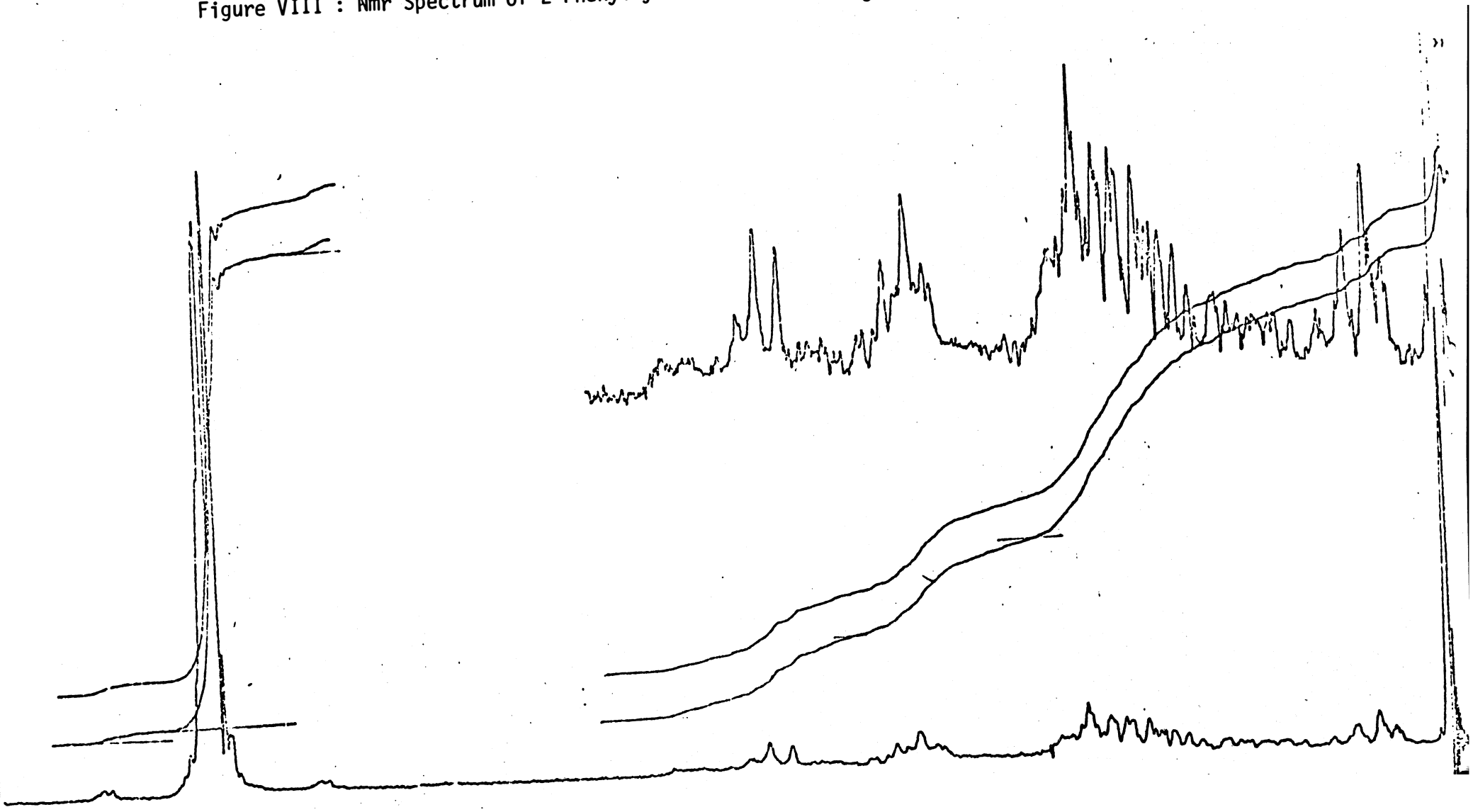


$$J_{H_M-H_B} = 10.6 \text{ Hz}, \quad J_{H_M-H_A} = 9 \text{ Hz}$$

The inner two peaks of the quartet coincide to make it look like a triplet. The correlection is made based on the spectrum and the Karplus' argument[18,19,20].

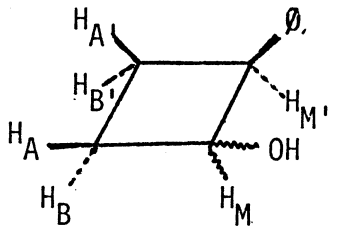
The nmr spectrum of 2-phenylcyclobutanol is shown in Figure VIII. The partial expanded nmr spectrum of this com-

Figure VIII : Nmr Spectrum of 2-Phenylcyclobutanol in $CDCl_3$



pound is shown in Figure IX.

Scheme V:



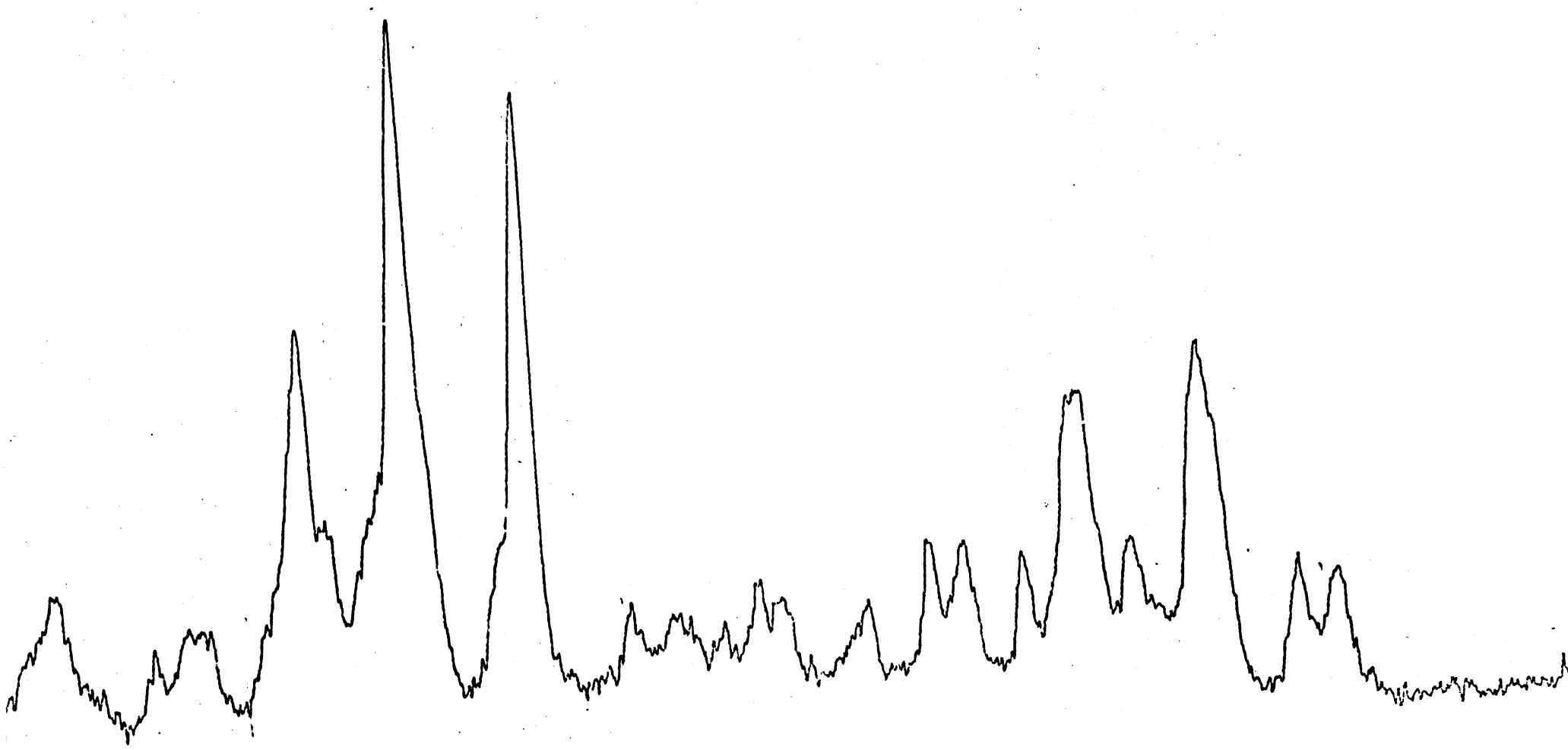
The methine proton $H_{M'}$ (Scheme V) absorbs at δ 3.8 - 4.2 as a triplet. Further information is necessary for assigning the coupling constants of the methine proton $H_{M'}$.

The peaks centered at δ 3.0 - 3.6 represent the methine proton H_M and appears as an octet. Since the four-membered ring on this compound is relatively flexible compared to the four-membered ring on the benzocyclobutenol, a small change in dihedral angle will markedly effect the coupling constant. The lack of information on coupling constants prevents an accurate assignment.

Tosylation of 2-Phenylcyclobutanol.

The 2-phenylbutanol reacts with tosylchloride in pyridine at 0^o to yield a white solid. The reaction can be

Figure IX : Partial Nmr Spectrum of 2-Phenylcyclobutanol in $CDCl_3$ + D_2O



followed by separation of pyridine hydrochloride as long needles. When no more precipitate appeared forming, the reation was judged to be complete. The crystals were re-crystallized from petroleum ether-chloroform to yield white crystals (mp 81 - 82^{o}). The elemental analysis for carbon and hydrogen gave results as follows:

Found	Theory
C: 67.41%	67.52%
H: 6.38%	6.00%

The nmr spectrum and mass spectrum are shown in Figure X and Figure XI respectively. Elemental analysis and nmr spectrum confirmed this compound.

Alkylation of Co(I) with Cyclopentyl Tosylate and Phenylethyl Tosylate.

The alkylation of cobaloxime(I) with cyclopentyl tosylate and phenylethyl tosylate both give air-stable orange compounds. The reaction of Co(I)oxime with phenylethyl tosylate did not go fast. After four hours there was 60% of starting material unreacted. It was found that the tosylate did not dissolve

Figure X : Nmr Spectrum of 2-Phenylcyclobutyl Tosylate in $CDCl_3$

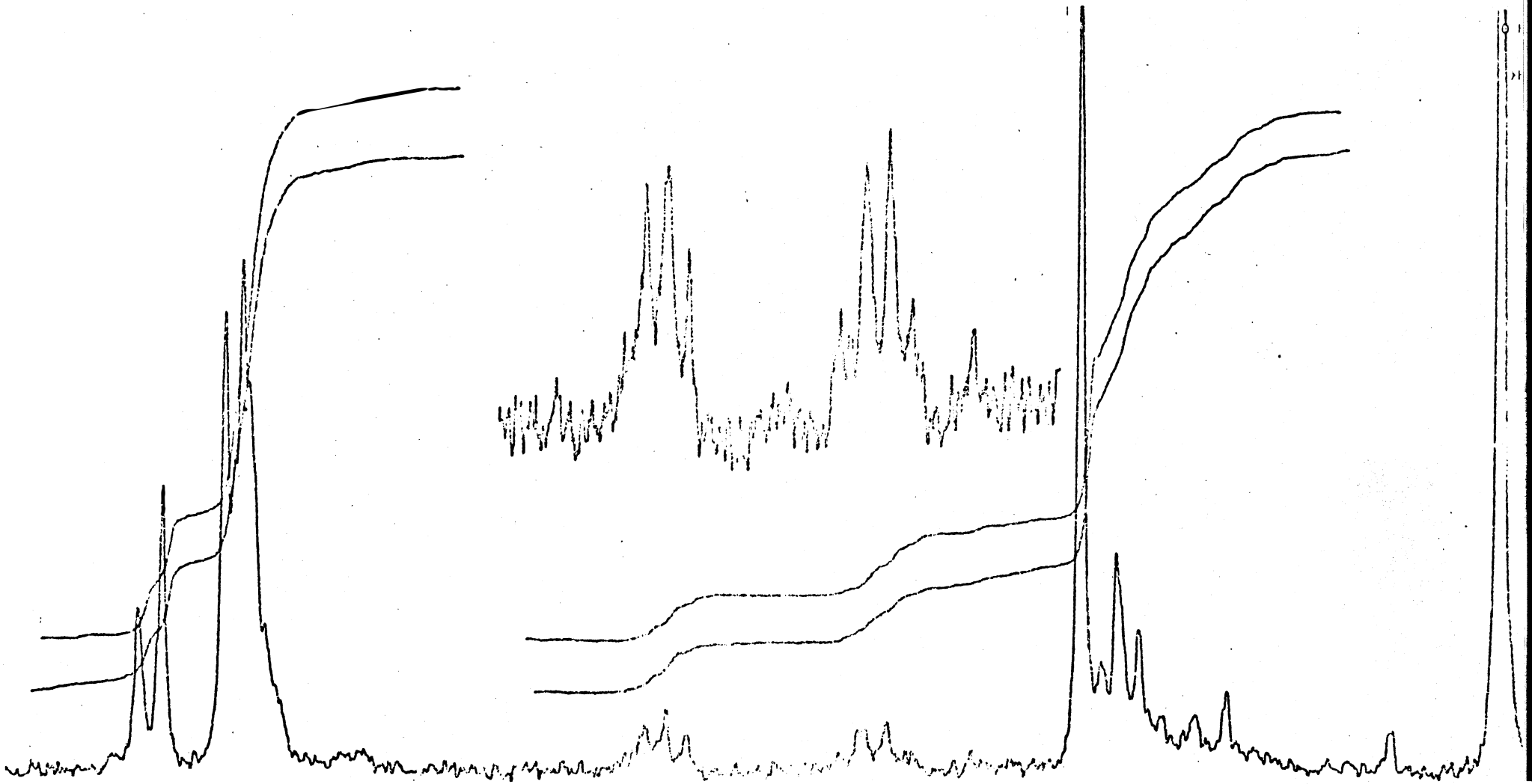
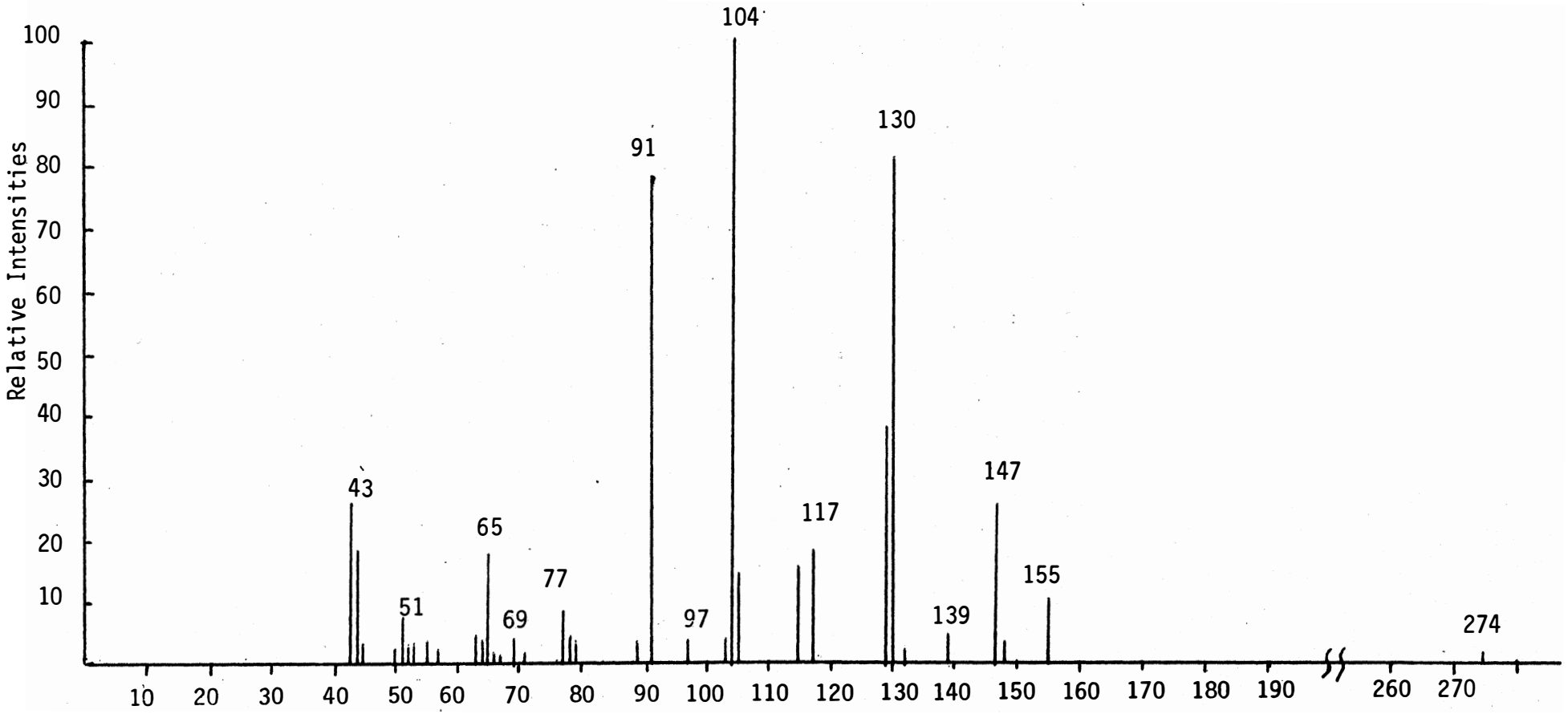
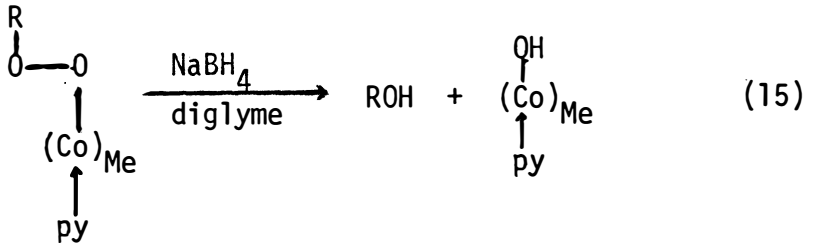


Figure XI : Mass Mass Spectrum of 2-Phenylcyclobutyl Tosylate



well, and is insoluble in water. Changing the solvent system and a longer reaction time might improve the reaction. However, neither of the two alkylcobalt product gave the peaks on the nmr spectrum which are expected for alkyl products. It is presumed that either the peaks of the alkyl protons are shifted to upfield to the methyl proton region of the cobaloxime or the oxygen inserted cobalt dimer was formed.

The first problem can perhaps be solved by adding a shift reagent or using a 100 MHz nmr spectrum. The later can be checked by treatment with sodium borohydride in diglyme. The oxygen insertion cobalt compound will be cleaved with sodium borohydride to give a alcohol and the normal alkyl cobalt compound will not (eq 15).



(15)

The alkylation of Co(I)(salen) (salen = bis(salicylaldehyde)ethylenediiminato)) with phenylethyl tosylate yields an orange brown solid after recrystallizing from petroleum ether-

chloroform. The nmr shows the alkylcobalt product with a distorted proton ratio indicating an impure product. The TLC shows two spots on a silica gel TLC plate (2 x 9 cm) with acetic acid - methanol - chloroform (1 : 1 : 1). Purification is necessary for this compound. Column chromatography is probably the best way to work out this problem.

Conclusion:

The alkylation of Co(I) with benzocyclobutenol and 2-phenylcyclobutyl tosylate was extremely slow. The low yields of products were probably due to the exposure to air and light during the work-up. The TLC indicated a high percentage of impurity which was presumed Co(II) complexes. The Co(II) (d^7) complexes are paramagnetism which will effect the nmr spectra to give a broad signal. This impurity has not been sufficiently separated from the products. Hence we could not get assignment of stereochemistry based on nmr spectra.

The purification of alkylcobalt(III) compounds was the most difficult part. Column chromatography is probably the best way to work out this problem. However, the Ugi hypothesis did not get answer under those conditions.

Experimental Section:

General.

Melting points were taken on a Thomas-Hoover melting point apparatus. Unless otherwise stated infrared spectra were determined in carbon tetrachloride solution on a Perkin-Elmer 337 IR spectrometer. Nmr spectra were determined in carbon tetrachloride solution on a Varian T-60 NMR spectrometer; chemical shifts given in δ with TMS as the internal standard. Coupling constants are given in hertz. Mass spectra were taken on a Du Pont 21-490 mass spectrometer. In experiments requiring dry solvents ether and tetrahydrofuran were distilled from $LiAlH_4$. Methylene chloride and dimethyl sulfoxide were distilled from calcium hydride. Apparatus for experiments requiring dry conditions was dried in an oven at 105^{o} for at least 12 hr. All the materials were used without further purification unless noted otherwise.

Benzendiazonium-2-carboxylate when dry detonates violently on being scraped or heated, and it is strongly recommeded that it be kept wet with solvent at all times. It

should be prepared and used in a hood behind a safety screen. A wet towel or sponge should be kept with in easy reach with which to deactivate any spilled material, which should then be disposed of by flooding with water[11].

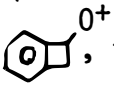
The solutions of cobaloxime(I) and cobalt(I)(salen) are oxygen and light sensitive, in all the work with these compounds they should be prevented from exposure to light and air. The $\{Co(salen)(C_5H_5N)_2\}\cdot Br$ for production of cobalt(I)(salen) and the standard reagents NaOH (10 M) solution and $NaBH_4$ solution (9.5 g in 100 ml of 3 M NaOH) were prepared by Dr. D. H. Buchanan.

Preparation of Benzenediazonium-2-carboxylate[11].

A solution of 34.2 g (0.25 mole) of anthranilic acid and 0.3 g of trichloroacetic acid in 250 ml of tetrahydrofuran was prepared in a 600 ml beaker equipped with a thermometer and cooled in an ice-water bath. The solution was stirred magnetically, and 55 ml (48 g, 0.41 mole) of isoamylnitrite was added over a period of 1 - 2 minutes. A mildly exothermic reaction occured, and the reaction mixture was maintained at 18 - 25^{o} and stirred for a further

1 - 1.5 hours. A transient orange to brick-red precipitate appeared which was slowly converted to the tan product. When the reaction was completed, the mixture was cooled to 10^{o}, and the product collected by suction filtration on a plastic Buchnner funnel and washed on the funnel with cold dichloromethane until the washings were colorless (200 ml). (Caution: The filter cake should not be allowed to become dry.) The solvent-wet material was used in the next step.

Preparation of Benzocyclobutenyl Acetate[12].

The wet benzenediazonium-2-carboxylate was transfered immediately by washing from the funnel to a 500 ml round bottomed flask containing vinyl acetate (40 g, 0.47 mole) in 200 ml dichloromethane, then heated to reflux and stirred magnetically for 1.5 hr. The product was extracted into petroleum ether (30 - 60^{o}) and the ether evaporated to yield pure benzocyclobutyl acetate (10.72 g, 26.5%) as an oil. The mass spectrum shows the parent peak at m/e 162 and the peak m/e 119 indicated the fragment  , the peak at m/e 43 indicated the fragment $+\overset{O}{\overset{\|}{C}}CH_3$. The nmr spectrum shows peaks at δ1.7 (singlet, 3H), 2.8 - 3.63 (octet, 2H), 5.7 (quartet, 1H) and 7 (singlet, 4H)[12]. The ir spectrum shows strong peaks at

1050 - 1240 cm^{-1} indicating C-O stretching, at 1750 cm^{-1} indicating C=O stretching.

Preparation of Benzocyclobutenol[13].

Benzocyclobutenyl acetate (3.07 g, 0.02 mole) and 10% aqueous sodium carbonate (20 ml) were stirred rapidly for 10 hrs at room temperature. The product was extracted into 100 ml of ether, dried with Na_2SO_4 and the solvent evaporated. Crystallization of the residue from petroleum ether (30 - 60°) by putting it into the refrigerator overnight gave pure benzocyclobutenol (0.95 g, 30% yield) as white needles, mp 58 - 58.5° (lit[12] 58°). The ir spectrum shows a strong broad peak at 3600 - 3230 cm^{-1} indicating -OH stretching. The nmr spectrum shows peaks at δ 2.7 - 3.57 (octet, 2H), 4.47 (singlet, 1H) exchangeable proton, 5.0 (singlet, 1H) and 7.1 (singlet, 4H).

Preparation of 1-Chloro-3-iodopropane[21].

A solution of sodium iodide (197 g, 132 mole) in 500 ml

of acetone was stirred under nitrogen, and 1-bromo-3-chloropropane (197 g, 1.25 mole) was added rapidly. A light yellow precipitate formed and the reaction continued without evolution of heat. After 2 hrs the mixture was suction filtered and the precipitated sodium bromide washed with acetone. The acetone was evaporated, and ether (500 ml) was added to precipitate inorganic salts. The ether solution was evaporated and the resulting oil dried in vacuo (1.5 hr) to yield 217.6 g (85%) of 1-chloro-3-iodopropane. This oil was used without further purification. Nmr(CCl_4) δ 2.23 (quartet, J = 6.6 Hz, 2H), 3.30 (triplet, J = 6 Hz, 2H) and 3.62 (triplet, J = 6 Hz, 2H).

Preparation of 3-Chloropropyldiphenylsulfonium Fluoroborate[21].

A solution of diphenyl sulfide (60 g, 0.32 mole), 1-chloro-3-iodopropane (222 g, 1.09 mole), and 130 ml nitromethane was stirred at room temperature under nitrogen. The flask was shielded from light. Silver tetrafluoroborate (50.0 g, 0.26 mole) was added in one portion. After 16 hrs, 150 ml of methylene chloride was added and the mixture was filtered to facilitate removal of the suspended silver salts. The solid was washed with methylene chloride and the methylene

chloride portions were combined. The methylene chloride solution was evaporated until a solid appeared, then 500 ml of ether was added to precipitate the sulfonium salt. Initially an oil separated. Vigorous shaking of the mixture to extract out of the oily sulfonium salt layer the excess starting material induced crystallization. The crystals were collected, washed with ether (100 ml), and dried in vacuo. The yield was 75.6 g (84%): mp 105 - 107° (lit[21] 104 - 105°); nmr(CCl_4) δ 2.22 (broad, 2H), 3.74 (triplet, J = 6.5 Hz, 2H), 4.27 (triplet, J = 8 Hz, 2H), 7.5 - 8.1 (multiplet, 10H).

Preparation of Cyclopropyldiphenylsulfonium Fluoroborate[21].

A solution of 3-chloropropyldiphenylsulfonium fluoroborate (7.0 g, 0.02 mole) in 40 ml of tetrahydrofuran was stirred at 25° under nitrogen. A 1.1 M of potassium tert-butoxide in dimethyl sulfoxide (23 ml, 0.02 mole) was added dropwise. A deep amber color formed which disappeared rapidly. Near the endpoint of the addition, methylene chloride (35 ml) was added, and the mixture poured into a (1:1) v/v methylene chloride-water mixture (40 ml). The lower methylene chloride layer was removed and evaporated to yield an oil.

Addition 100 ml of ether and shaking gave crystals which were recrystallized from ether-ethanol to yield 2.83 g (82%) of a white crystalline solid, cyclopropyldiphenylsulfonium fluoroborate: mp 139 - 141° (lit[22] 139°); ir ($CHCl_3$) 3040, 1582, 1477, 1445, 1333, 1284, 912, 868, 829 cm^{-1}, also an extremely intense band from 1175 to 960 cm^{-1} due to the BF_4^- anion; nmr($CDCl_3$) δ 1.3 - 1.7 (multiplet, 4H), 3.44 - 3.95 (multiplet, 1H), 7.4 - 8.2 (multiplet, 10H).

Preparation of 2-Phenylcyclobutanone[22].

Under nitrogen, a solution of cyclopropyldiphenylsulfonium fluoroborate (2.78 g, 8.86 mmole) and 7 mmole of benzaldehyde in 30 ml of dimethylsulfoxide was prepared at room temperature. In one portion powdered potassium hydroxide (0.78 g, 14 mmole) was added and the solution stirred for one hour. The reaction mixture was then poured into cold aqueous 1 M tetrafluoroboric acid (25 ml) and extracted with 2 x 50 ml of ether. The ether was washed with water and then dried over anhydrous sodium sulfate. Evaporation of the solvent yielded a mixture of diphenyl sulfide and product 1.98 g (71% yield for ketone based on nmr spectrum)

which was distilled or filtered through a column of silica gel using hexane - ether mixtures: ir(CCl_4) 3077, 3040, 3008, 2967, 2941, 1786, 1605, 1495, 1449, 1387, 1773, 1155, 1120, 1057, 1040, 1020 cm^{-1}; nmr(CCl_4) δ 1.70 - 2.84 (very complex multiplet, 2H), 2.85 - 3.38 (complex multiplet, 2H), 4.43 (quartet, J = 9 Hz, J = 10.6 Hz, 1H), 7.20 (singlet, 5H). However, neither procedure gave ketone free of diphenylsulfide. The mixture was used directly used in the ne t step without further separation.

Preparation of 2-Phenylcyclobutanol[23].

Under nitrogen, lithium alumiun anhydride (0.25 g, 4 mmole) in 20 ml anhydrous ether was stirred in a 250 ml three-necked round bottom flask with an ice bath placed around the flask. A mixture of diphenyl sulfide and 2-phenyl-cyclobutanone (1.33 g, 68% wt. of ketone based on nmr) was added dropwise (over a period of 40 minutes). The ice was allowed to melt and stirring was continued for 1 hr. After refluxing 40 minutes, the solution was cooled and 1 ml saturated sodium sulfate was added and the mixture filtered. The solid was washed with 2 x 20 ml ether and the ether portions were combined. The ether was evaporated to yield a mixture

of diphenyl sulfide and 2-phenylcyclobutanol 1.10 g (80% yield for alcohol based on nmr) as a colorless oil: ir(CCl_4) 3320, 3040, 3000, 2960, 2940, 1605, 1495, 1225, 1105, 1023, 1000, 985, 943, 920, 694 cm^{-1}; nmr($CDCl_3$) τ 0.8 - 2.25 (multiplet, 4H), 2.9 - 3.4 (multiplet, 2H), 3.8 - 4.2 (triplet, 1H), 7.3 (singlet, 15H).

Preparation of 2-Phenylcyclobutyl Tosylate[25].

A mixture of diphenyl sulfide and 2-phenylcyclobutanol (1.08 g) in 15 ml of pyridine in an 125 ml glass-stoppered Erlenmeyer flask was cooled to 0^{o} and treated with tosyl-chloride (5 g, 0.02 mole). After solution was complete the flask was placed in a refrigerator for 24 hrs. The entire mixture was poured with stirring into 150 g of ice and water. The aqueous layer was extracted twice with 2 x 50 ml ether. The ether solution was washed with 2 x 50 ml cold 1 : 1 hydrochloric acid and then with 100 ml water, dried over anhydrous sodium sulfate and the ether evaporated to yield 1.41 g of an oil. Addition of 50 ml of petroleum ether and shaking induced crystallization. The crystals were collected and dried in vacuo to yield a white solid. These crystals were recrystallized from petroleum

ether-chloroform to yield 0.68 g (51%): mp 81 - 82°; ir (CCl_4) 3077, 3040, 3088, 2967, 1605, 1449, 1380, 1280, 1198, 1177, 1095, 1030, 934, 920, 849, 694, 660, 564, 548 cm^{-1}; nmr($CDCl_3$) δ 1.4 - 2.5 (multiplet, 7H), 3.3 -3.8 (quartet, 1H), 4.5 - 4.9 (triplet, 1H), 6.8 - 7.7 (multiplet, 9H); ms m/e(%) 274(1.4), 155(10), 147(26), 130(80), 117(18), 104 (100), 91(78), 65(17), 43(25).

Anal Calcd. for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00.
Found: C, 67.41; H, 6.38.

Preparation of Sodium Amalgan (Na(Hg)).

Sodium metal (3.0 g, 0.1305 mole) was cut in small chunks and crushed under the surface of 400 g (30 ml) of mercury in a 150 ml beaker in the hood. There was an exothermic reaction with light and smoke evolution. The amalgam was passed through a pin hole in a filter paper into a dry 50 ml Erlenmeyer flask and capped with a serum cap.

Na(Hg) (1 ml) was added to 25 ml of water, stirred magnetically and reacted with 50 ml standard HCl (0.184 M) in a 250 ml Erlenmeyer flask. After all reaction stopped,

phenolphthalein solution (2 drops) was added and the solution titrated with standard NaOH (0.202 M). A molarity of 4.72 was calculated for the Na(Hg).

Preparation of Pyridine (bis(salicylaldehyde)ethylenediiminato) cobalt(I)[26,27].

Under argon, a solution of 6.8 g (12 mM) of Co(salen)$(py)_2 \cdot Br$ in 160 ml of tetrahydrofuran (THF) was stirred and degassed in a 250 ml three-necked round bottom flask which was equipped with a serum cap, argon inlet and a side arm in which was placed 7 ml (33 mM) of Na(Hg) for 1 hour. Na(Hg) was decanted to the flask and magnetic stirring was continued for 3 hours to give deep green Co(I)(salen) solution.

Preparation of Phenylethylpyridine (bis(salicylaldehyde) ethylenediiminato) cobalt(III).

Under argon, the deep green Co(I)(salen) solution (80 ml, 6 mM) was added (via a cannula) to a capped droping funnel which was fitted with a 250 ml three-necked round bottom flask (wrapped with Al foil) in which was placed

1.66 g (6 mM) of phenylethyl tosylate. The solution was stirred magnetically for one hour. After injecting 5 ml of degassed pyridine, the reaction mixture was stirred for 10 min. Evaporation of the solvent by aspirator (20 mmHg) gave a dark brown, gummy solid which was crystalized from methanol-water, then recrystalized from chloroform-petroleum ether to give orange-brown crystals (1.81 g, 51%).

Nmr($CDCl_3$) δ 2.3 - 2.4 (doublet), 2.8 - 3.2 (multiplet), 4.2 - 4.4 (multiplet), and 6.9 - 7.5 (multiplet). This material is evidently impure.

Preparation of Pyridinephenylethylcobaloxime[28].

A 250 ml three-necked, round bottom flask (wrapped with Al foil) was fitted with an argon inlet, magnetic stirrer, serum cap and side arm in which was placed 8.4 g (35 mM) of phenylethyl tosylate. In the flask, methanol (85 ml) was degassed with argon for 1 hour. To this was added $CoCl_2 \cdot 6H_2O$ (7.14 g, 30 mM) and dimethylglyoxime (6.96 g, 60 mM). The pink slurry was stirred for 20 min. and 6 ml (60 mM) of standard NaOH solution was added *via* syringe (O_2 free). The dark brown mixture was stirred for 1 hour and an ice bath placed around the flask. Standard NaOH solution (3.0

ml), added via syringe was followed by 2 ml of degassed pyridine and 2.5 ml (6.25 mM) of standard $NaBH_4$ solution (all O_2 free). The solution was stirred at ice temperature for 20 min. To this, was added (from the side arm) 8.4 g (35 mM) of phenylethyl tosylate. The ice was allowed to melt and stirring was continued for 4 hours. The resulting slurry was poured into 200 ml of water containing 5 ml of pyridine and filtered. The precipitate was washed with 500 ml of water, then washed with ethyl ether to remove unreacted starting material and air dried. The alkylcobaloxime was recrystallized from about 200 ml hot methanol (dim light) to which 20 ml water was added after all the solid dissolved. Standing overnight in the refrigerator gave 3.46 g (25%) of dark orange crystals. Unreacted starting material (5.1 g) was recovered.

Nmr($CDCl_3$)δ 2.1 (singlet), 6.9 - 7.4 (multiplet), 8.5 - 8.8 (doublet).

Preparation of Pyridinecyclopentylcobaloxime.

In a similar fashion, a solution of cyclopentyl tosylate 8.7 g (35 mM) in 10 ml methanol (O_2 free) was added (via syringe) to a deep purple-green cobaloxime(I) solution. After 4 hours reactions standard work-up followed by recrystallization of the alkyl-

cobaloxime gave 7.14 g (47%).

Nmr($CDCl_3$) δ1.0 - 1.6 (broad singlet), 2.1 (singlet), 7.0 - 7.7 (multiplet) and 8.4 - 8.6 (doublet).

References:

1. G. N. Lewis, "Valence and The Structure of Atoms and Molecules", Chemical Catalog Company Inc., New York, 1932, P. 113.
2. A. Streitwieser, Jr., "Solvolytic Displacement Reactions", McGraw-Hill Book Co., New York, 1962, P. 94.
3. I. Ugi, D. Marquarding, H. Kusacek, G. Gokel and P. Gillespie, Angew. Chem. Intl. Ed., 9, 703(1970) and P. Gillespie, P. Hoffman, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Isolis and I. Ugi, ibid., 10, 687(1971).
4. P. D. Gillespie and I. Ugi, ibid., 10, 503(1971).
5. G. N. Schrauzer and E. Deutsch, J. Amer. Chem. Soc., 91, 3341(1969).
6. G. N. Schrauzer, Acc. Chem. Res., 1, 97(1968).
7. D. Dodd and M. D. Johnson, J. Organometal. Chem., 52, (1973).
8. G. N. Schrauzer, E. Deutsch, and R. J. Windgassen, J. Chem. Soc., 90, 2441(1968).
9. F. R. Jensen, V. Madan and D. H. Buchanan, J. Amer. Chem. Soc., 92, 1414(1970).
10. F. R. Jensen and D. H. Buchanan, Chem. Comm., 153(1973).
11. L. Friedman and F. Logallo, "Organic Synthesis", 48, John Wiley and Sons. Inc., New York, 1968, P. 12.

12. H. H. Wassernam, J. Amer. Chem. Soc., 87, 4002(1965).

13. M. P. Cava and K. Muth, J. Amer. Chem. Soc., 82, 652(1960).

14. J. K. Magrane and D. C. Cottle, ibid., 64, 484(1942).

15. G. W. Stahl and D. C. Cottle, ibid., 65, 1782(1943).

16. J. D. Roberts and B. C. Chambers, ibid., 73, 3176(1951).

17. E. Vogel and K. Hasse, Ann., 615, 22(1958).

18. R, M. Silverstein and G. C. Bassler, "Sepctrometric Identification of Organic Compounds" J. Wiley and Sons. Inc., New York, 1968, Chap. 4.

19. M. Karplus, J. Chem. Phys., 30, 11(1959).

20. M. Karplus, J. Amer. Chem. Soc., 85, 2870(1963).

21. B. M. Trost and M. J. Bogdanowicz, J. Amer. Chem. Soc., 95, 5298-5307(1973).

22. B. M. Trost and M. J. Bogdanowicz, J. Amer. Chem. Soc., 95, 5321-34(1973).

23. A. Burger and H. Helen, J. Org. Chem., 29, 2588(1964).

24. F. R. Jensen and R. C. Kiskis, J. Organometal. Chem., 49, C46(1973).

25. L. Fieser, M. Fieser, "Reagents for Org. Chem.", 1, John Wiley and Sons. Inc., New York, 1967, P. 1180.

26. G. Costa and G. Mestroni, Tet. Let., 783(1967).

27. G. Costa, G. Mestroni and G. Pellizer, J. Organometal. Chem., 11, 333-40(1968).

28. D. H. Buchanan, private communication.

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