THE REACTIONS OF SUBSTITUTED 5-HYDROXY-6-METHYL-BICYCLO[4.4.0.$0^{1,5}$]DECAN-9-ONES

Dissertation for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
JOHN DAVID YORDY
1974

This is to certify that the

thesis entitled

The Reaction of Substituted 5-Hydroxy

-6-methylbicyclo[4.4.0.$0^{1,5}$]decan-9-ones

presented by

John David Yordy

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Organic Chemistry

William H. Rauch

Major professor

Date September 14, 1974

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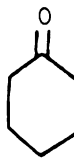

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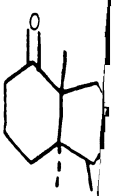


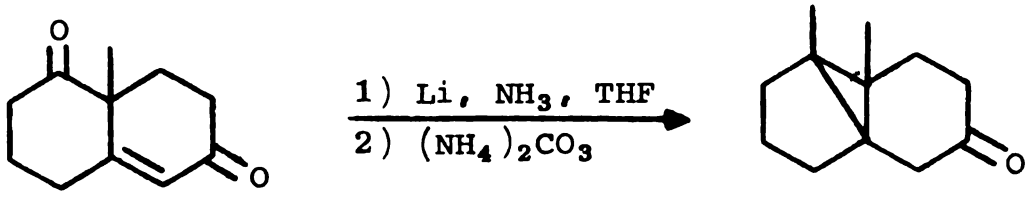
ABSTRACT

THE REACTIONS OF SUBSTITUTED
5-HYDROXY-6-METHYLBICYCLO[4.4.0.$0^{1,5}$]DECAN-9-ONES

By

John David Yordy

The bicyclo[4.4.0.$0^{1,5}$]decan-9-ones were prepared by lithium-ammonia reduction of the corresponding enediones as illustrated in Equation (1).

(1) 

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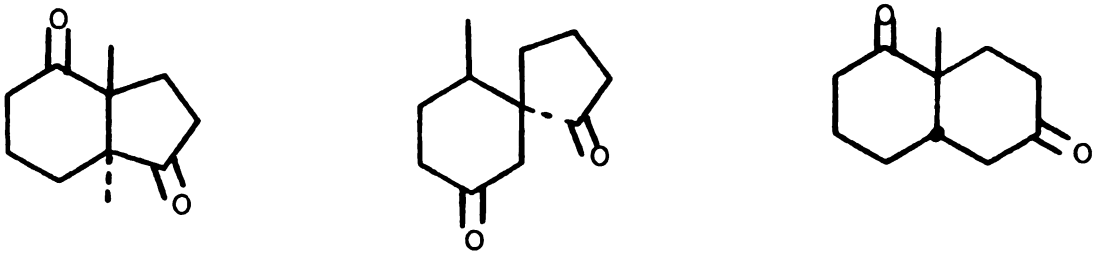
Cyclopropanols, such as 2, rearranged under the appropriate conditions of acid- or base-catalysis to give the synthetically versatile intermediates 3, 4, and 5 in good yield.



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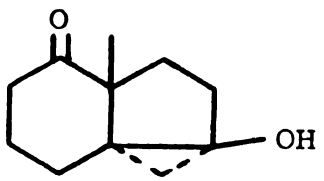
The formation of a hydrindandione from 2 has been shown to involve interaction of the carbonyl group with the cyclopropane ring, giving an isomeric cyclopropanol (6), which



6

is then cleaved to 5. Unexpectedly certain substituted bicyclo[4.4.0.$0^{1,5}$]decan-9-ones were found not to yield hydrindandiones. Moreover, only the trans- fused hydrindandione system has been obtained from those cyclopropanols which do undergo this type of rearrangement. The trans configuration was unequivocally demonstrated by X-ray analysis of a bromo derivative of 3.

These results are explained by conformational differences in the cyclopropanol systems which affect the carbonyl-cyclopropyl interactions necessary for rearrangements to the hydrindandione to occur.

A remarkable methyl substituent effect during the base-catalyzed rearrangement of 7 produced the twistane aldol 8 as the major product (Equation 2).

The unusual tricyclic methyl ethers 11 and 12 were formed during the acid treatment of 10 (Equation 3).

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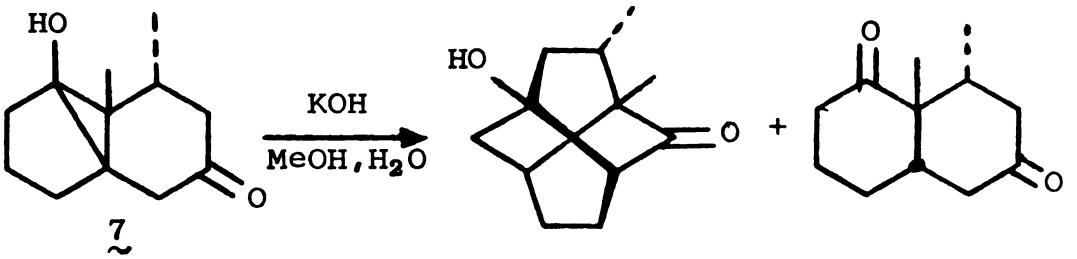

7

8 79% KOH, MeOH 9 21%

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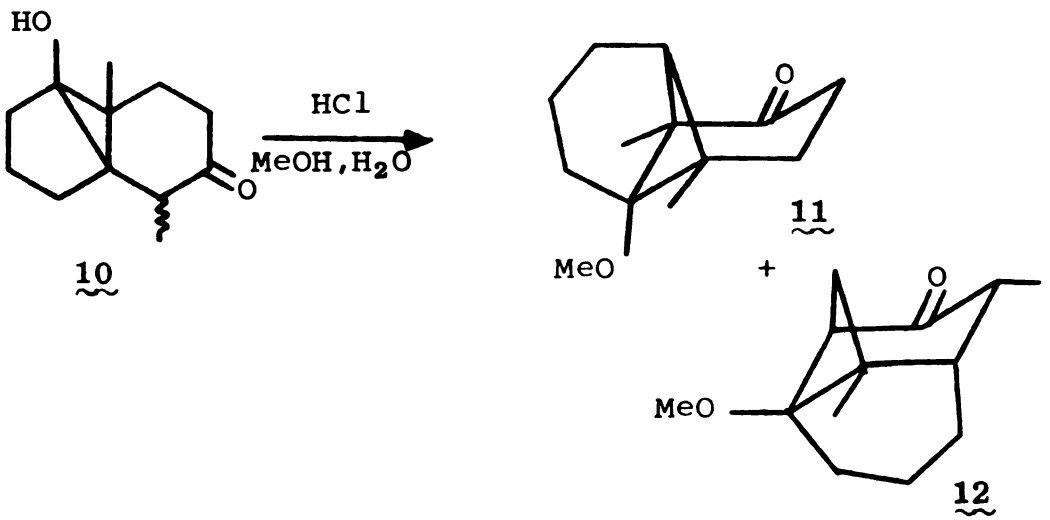

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THE REACTIONS OF SUBSTITUTED 5-HYDROXY-6-METHYLBICYCLO[4.4.0.$0^{1,5}$]DECAN-9-ONES

By

John David Yordy

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1974

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DEDICATION

This work is dedicated to the following:

Winifred, my wife, John, Eric, and Michael, our children, whose love and encouragement have made these years good and worthwhile;

Mr. and Mrs. John W. Yordy, my parents, and Mr. and Mrs. Clarence Hostetler, my parents-in-law, who have given the rich heritage of close and wonderful families.

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ACKNOWLEDGMENTS

The author is deeply grateful to Professor William Reusch for his friendship, counsel, and encouragement during the course of this work. He was always willing to listen, to ask probing questions, and to make suggestions. His guidance has contributed immeasurably to my professional development.

Appreciation is also extended to my colleagues for stimulating and informative discussions, and for their friendship and humor.

Finally, the author would like to thank the National Science Foundation, National Institutes of Health, and Michigan State University for financial support.

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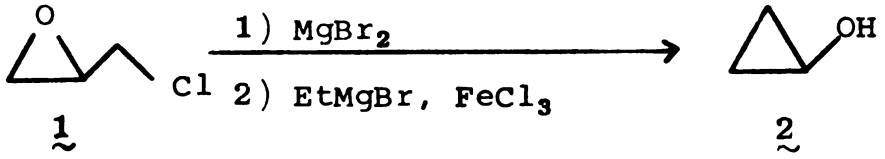
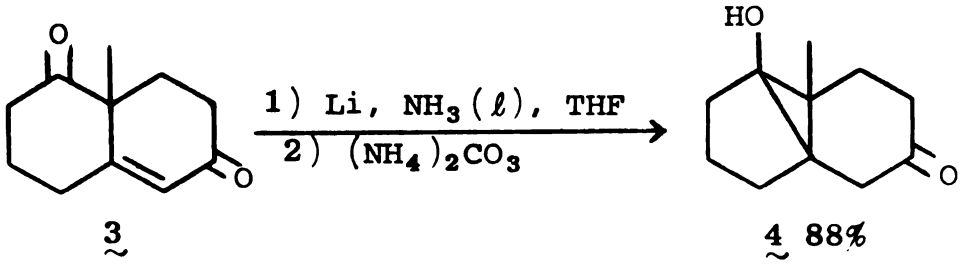
INTRODUCTION

While scattered references[1] to cyclopropanols appeared in the early literature, the authenticity of their molecular structures remained in doubt. It was not until Magrane and Cottle[2] accidentally synthesized cyclopropanol from epichlorohydrin in 1942, that the era of cyclopropanol chemistry really began (Equation 1).

(1) 

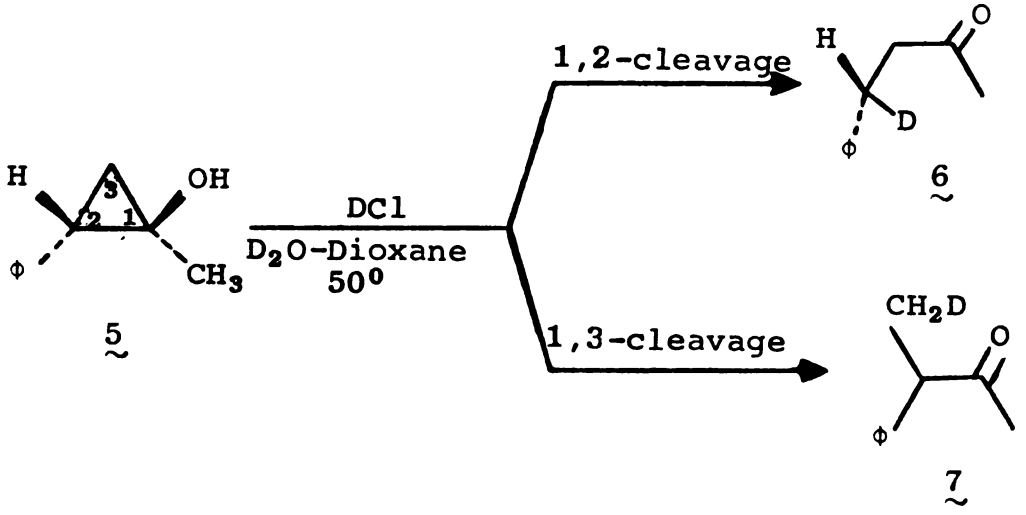
1 2

Since that time, many methods for the synthesis of cyclopropanols have been developed.[3,4] Synthetically useful cyclopropanols have been obtained in this laboratory by the lithium-ammonia reduction of substituted bicyclo[4.4.0]dec-6-ene-2,8-diones, as illustrated for Wieland Miescher ketone 3[5,6,7] (Equation 2).

(2) 

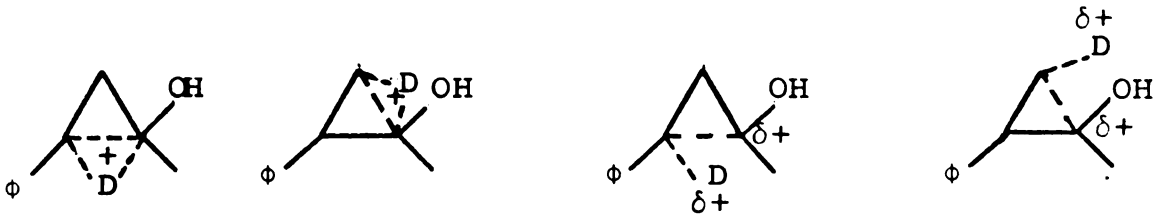
3 4 88%

The acid-catalyses of cyclopropanes may give rise to many ring opened or rearranged products. However, this is not the case with cyclopropanols since the hydroxyl group controls and facilitates ring opening by its ability to stabilize an adjacent positive charge. This selectivity is illustrated in Equation (3), protonation of cis-2-phenyl-1-methylcyclopropanol 5 leading to a 60:40 mixture of 4-phenyl-2-butanone 6 and 3-phenyl-2-butanone 7.[8]

(3) 

5 6 7

The product ratio observed here suggests that edge-protonated species, such as 8 and 9, may not be involved.



8 9 10 11

This conclusion is founded on the expectation that edge-protonated intermediate 8 would be more stable than 9, because the positive charge in 8 would be stabilized by the phenyl group. Intermediate 8 would, of course, lead exclusively to 6.[9]

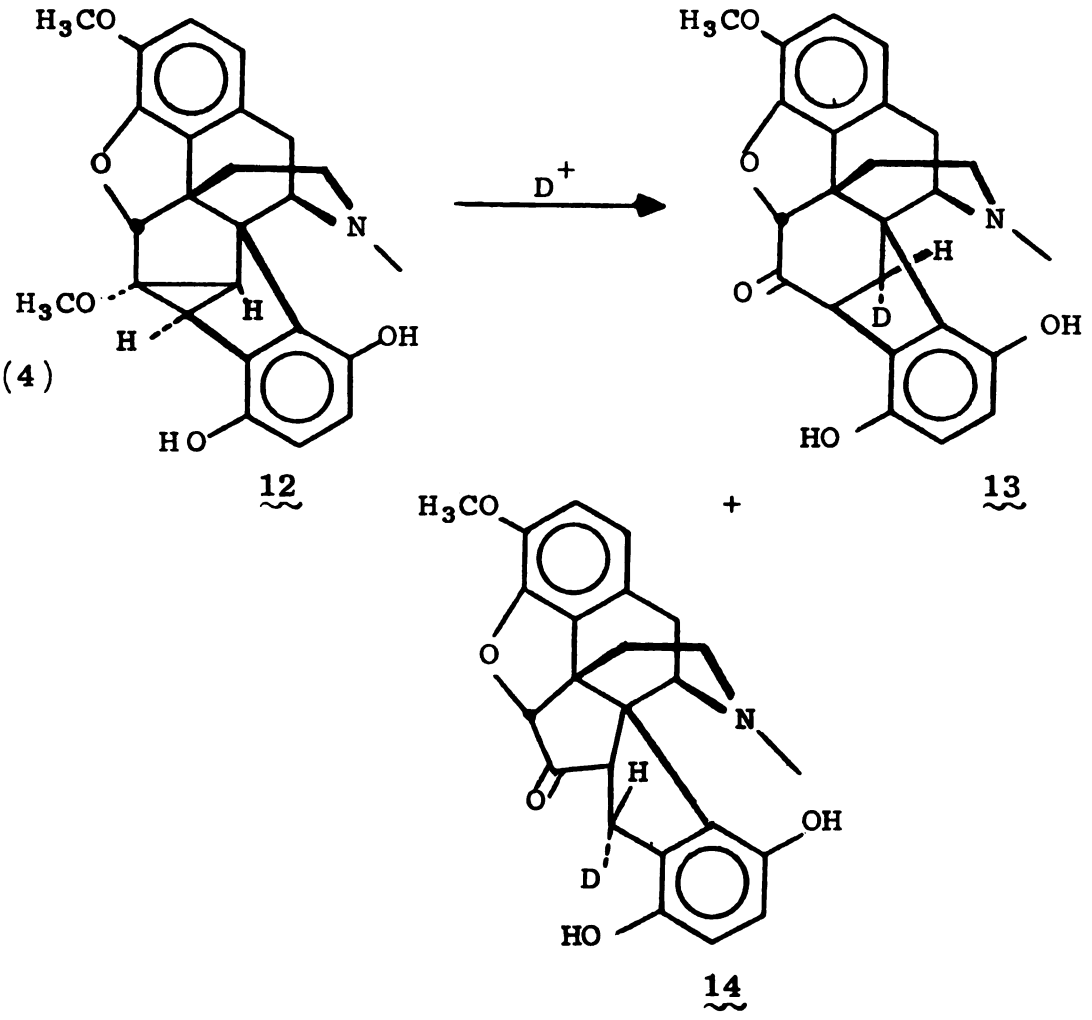
Stereochemical studies of acid-catalyzed cyclopropanol ring openings indicate that they generally proceed with retention of configuration. This is seen in Equation (3), where the treatment of optically active 5 with 1N deuterium chloride leads to 4-phenyl-2-butanone 6 with retention of configuration.[8]

At least one exception to this general trend is known. The action of acid on photothebainehydroquinone 12 leads to 13 and 14, both resulting from cleavage of the cyclopropyl methyl ether with inversion of configuration (Equation 4).[10]

Base-catalyzed ring opening of cyclopropanols generally proceeds in a fashion corresponding to formation of the more stable carbanions (Equations 5 and 6).[8,11,12]

The stereochemistry of these ring opening reactions seems to depend upon the solvent and the nature of the

(4)



12 + 13 + 14

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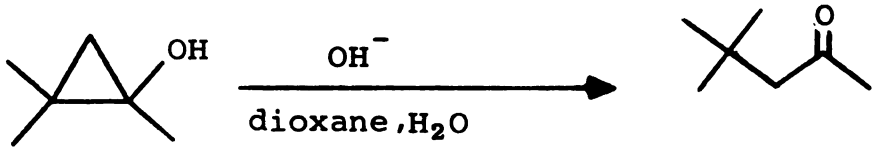

15 → 16

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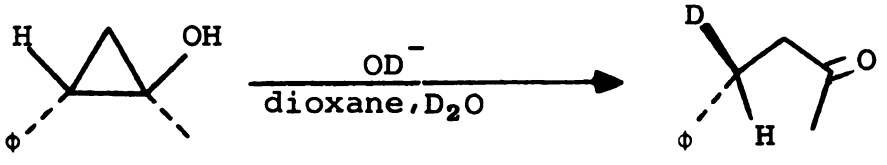
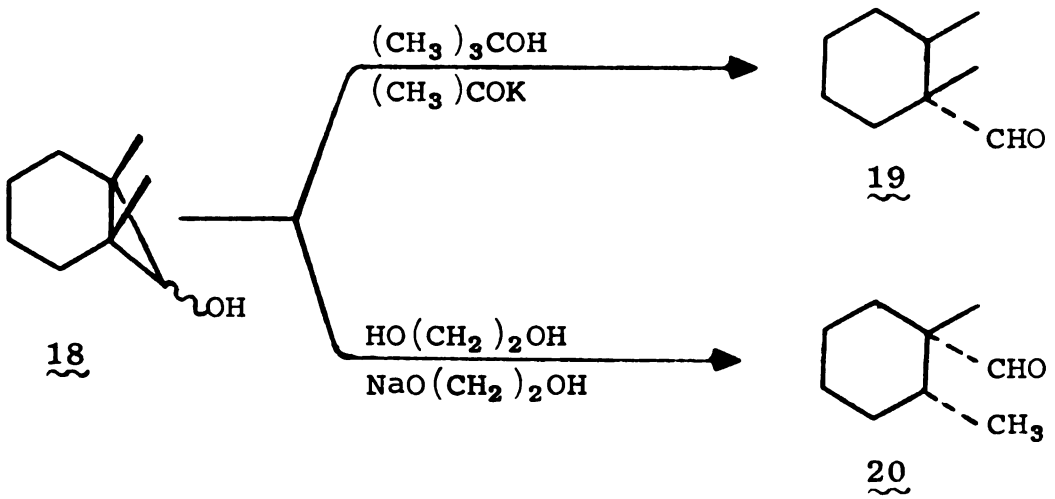


5 → 17

molecule being studied. Base catalyzed cleavage of 2-phenyl-1-methylcyclopropanol 5 in heavy water proceeded with inversion of configuration at the benzylic carbon (Equation 6).[8] On the other hand, Wharton and Bair[13] noted that both exo- and endo-7-hydroxy-1,6-dimethylbicyclo[4.4.0]heptane 18 opened with retention of configuration on treatment with potassium t-butoxide in t-butyl alcohol. However, the same system reacted with inversion of configuration, when an ethylene glycol solvent system was used (Equation 7).

(7)



These results are consistent with the observations and interpretations reported by Cram and coworkers[14] for electrophilic substitutions involving carbanion intermediates.

Recent studies by Wharton and Fritzberg[15] of the ring opening reactions of hemiketals derived from trans-2,3-di-t-butylcyclopropanone have disclosed that predominate retention of configuration occurred in both methanol-O-d and ethylene glycol-O-d_2 (Equation 8).

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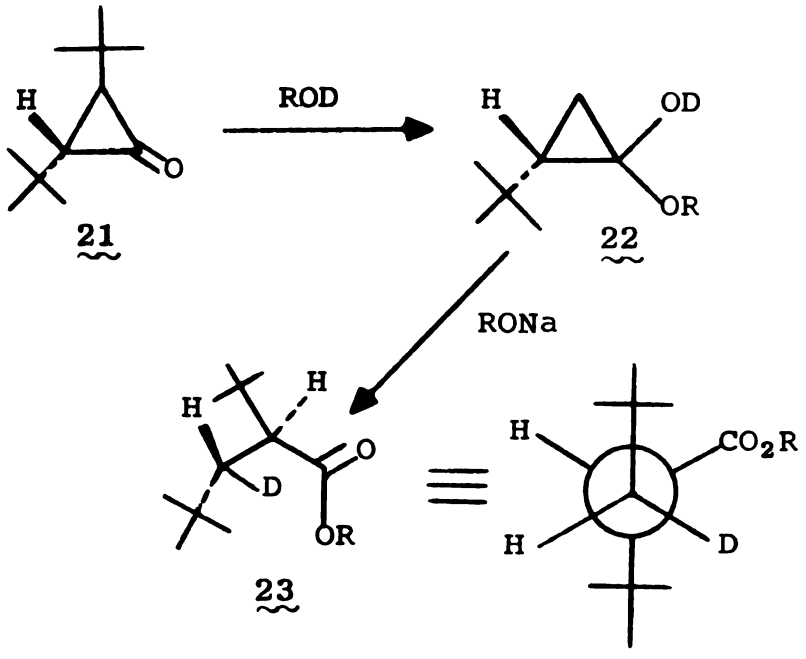
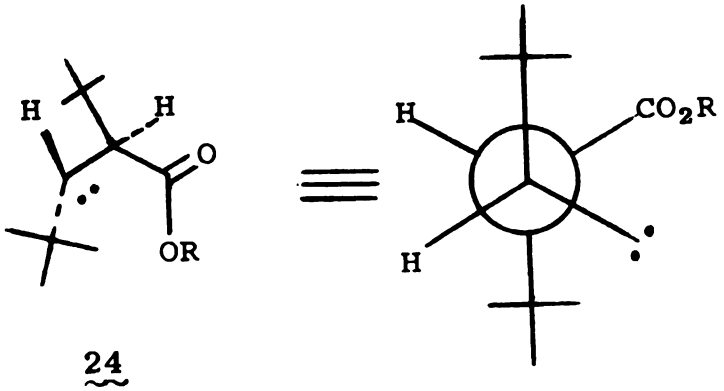


21 22 23

Cram's principles would have predicted inversion for the latter system. However, it is possible that the geometry of the substrate favors formation of the conformationally stable anion 24 which is protonated before inversion can occur.



24

Another exceptional result, reported by Nickon,[16] involved ring opening of the nortricyclic system 25 with

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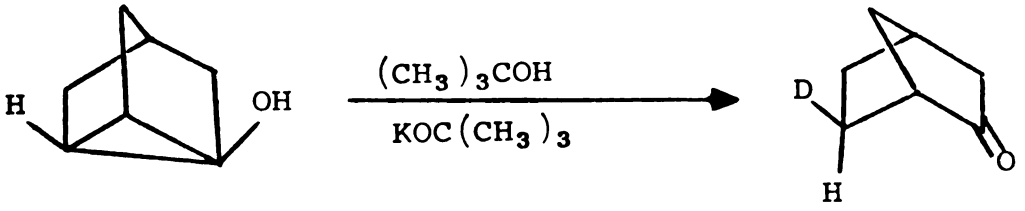
exclusive inversion of configuration in t-butanol solution (Equation 9), whereas retention would have been predicted by Cram's rules. Wharton[13] has suggested that this event

(9)

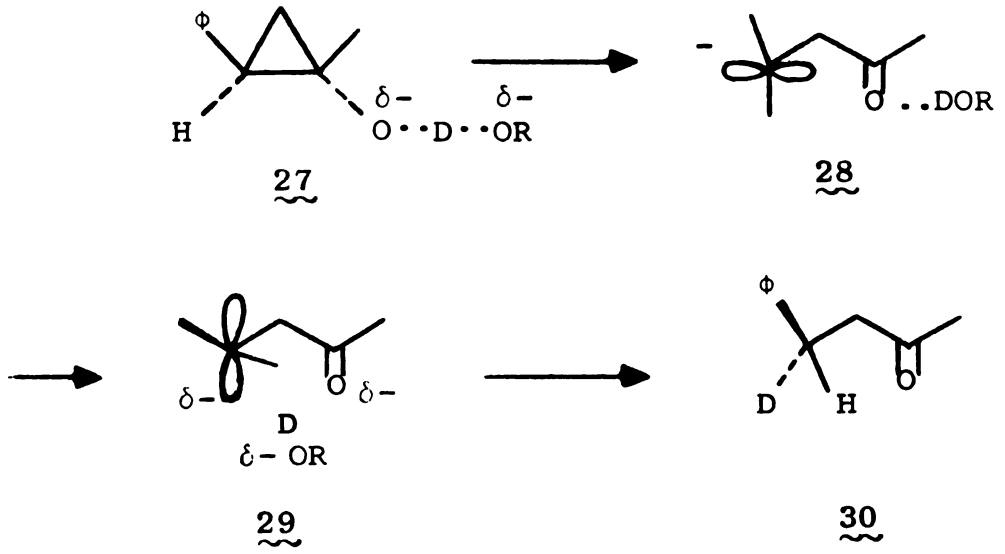


25 26

could be rationalized by a general and pervasive effect favoring exo attack in the norbornyl system.

Cram[17] has recently suggested a "rotation mechanism" as a means of accounting for the inversion of configuration observed with cyclopropanols such as trans-2-phenyl-1-methyl cyclopropanol (Equation 10).

(10)



27 28 29 30

During the past few years, cyclopropanols have been extensively used as synthetic intermediates. For example, compounds 31 and 34 undergo ring expansion to cyclobutanones on treatment with a variety of reagents (Equations 11 and 12).[18]

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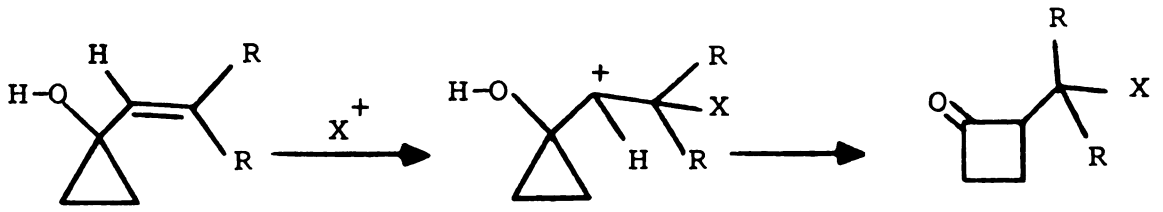
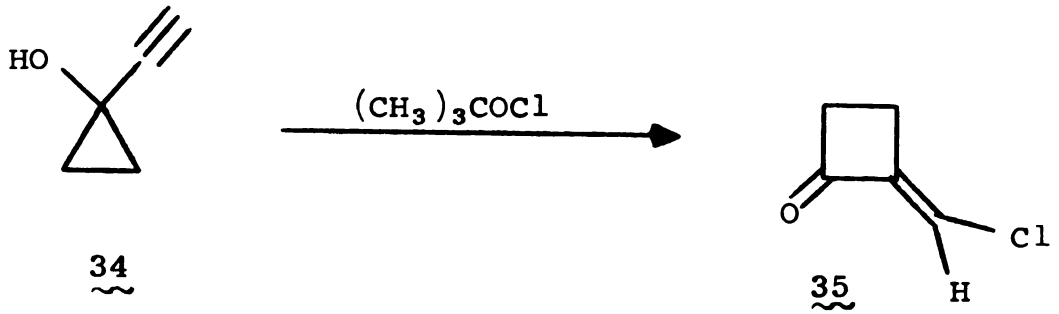


31 32 33

a. X = R = H
b. X = H; R = H or CH_3
c. X = OH; R = H or CH_3
d. X = $CH_2N(CH_2Ph)_2$; R = H

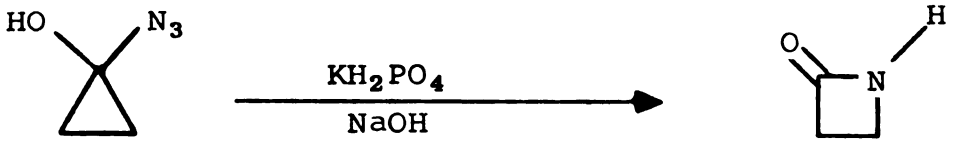
(12)



34 35

A related expansion of carbinol amines or azides provides a new route to β-lactams (Equation 13).[18]

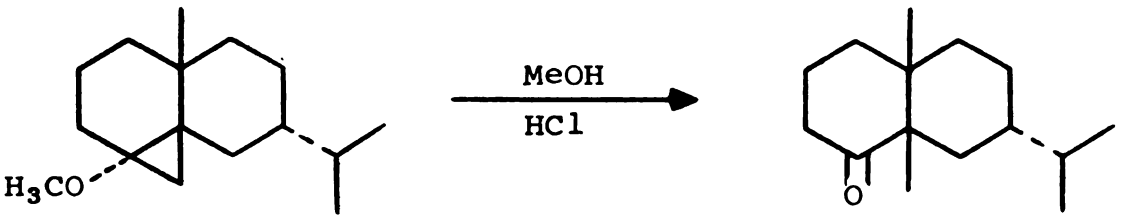
(13)



36 37

Cyclopropanol derivatives have also been used in the stereospecific introduction of quarternary methyl groups, as illustrated by the syntheses of 1-valverone (Equation 14)[19] and trans-1,6-dimethylbicyclo[4.4.0]decalone (Equation 15).[20]

(14)



38 39

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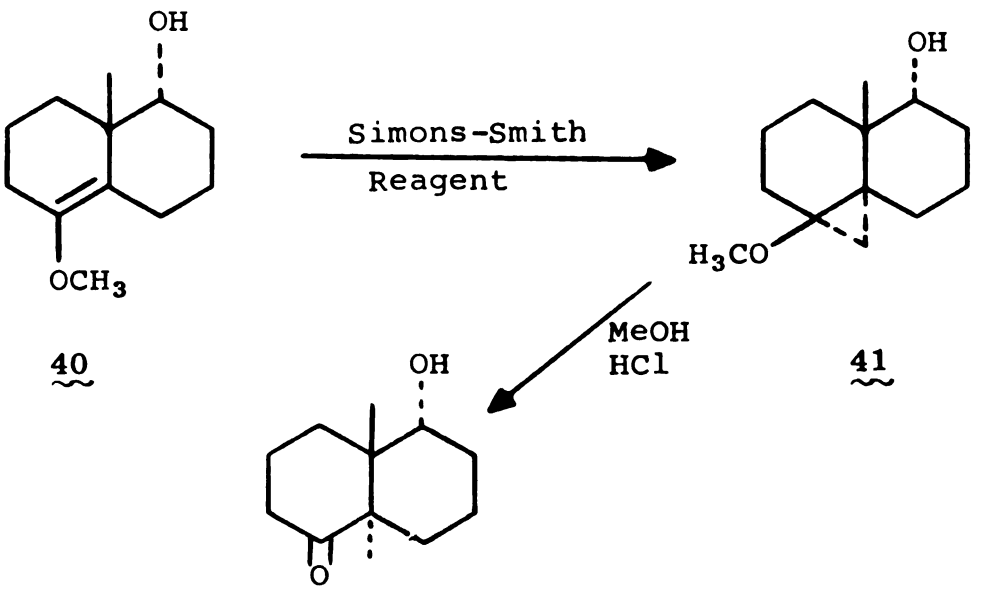
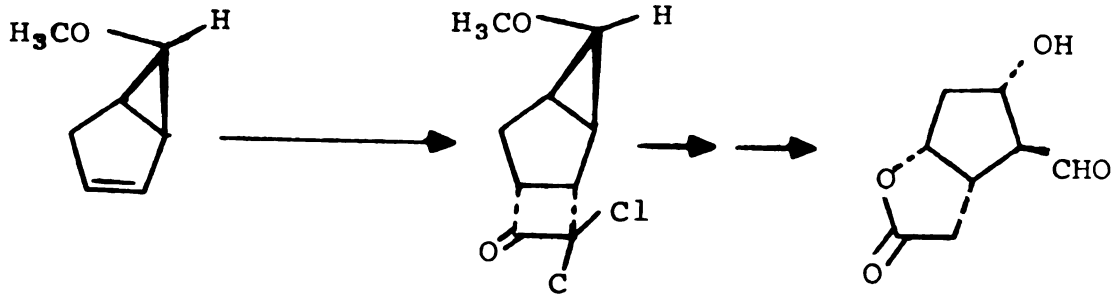


40 41 42

The cyclopropanol derivative 43 was effectively used by Corey and coworkers[21] in the preparation of the key intermediate 44 in the syntheses of prostaglandines E_2 and $F_{2\alpha}$ (Equation 16).[21]

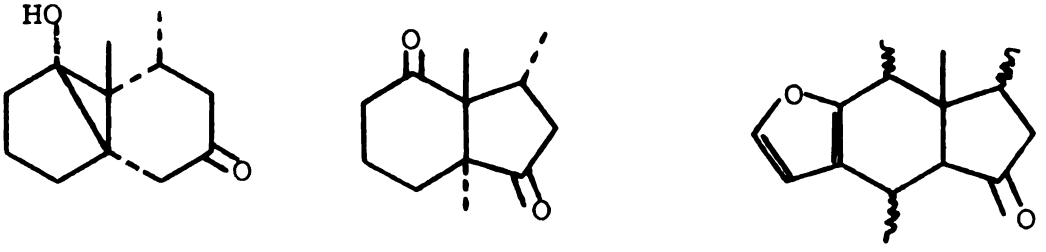
(16)



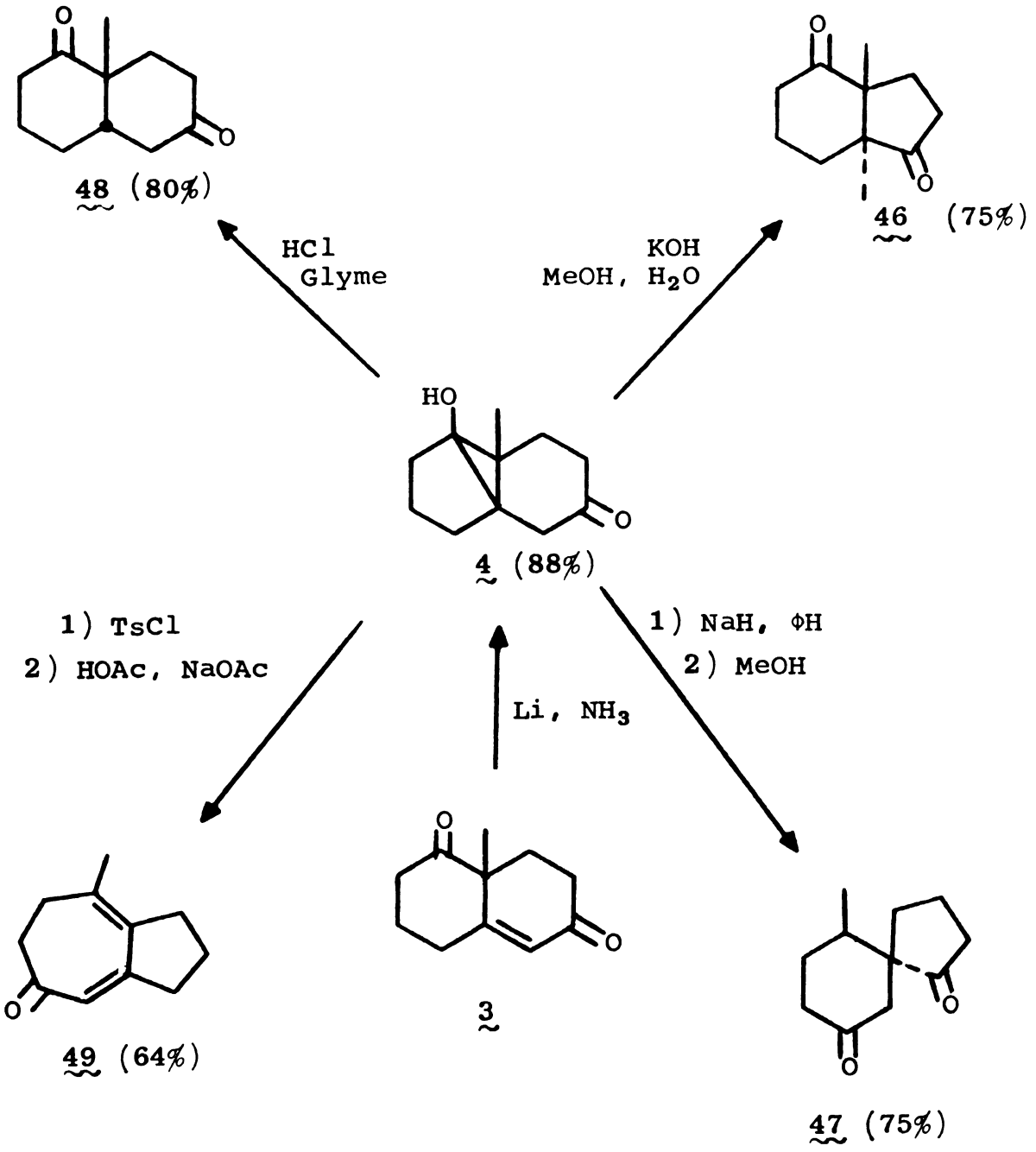
43 44 45

Cyclopropanol 4, which is easily prepared by lithium-ammonia reduction of the Wieland Miescher ketone 3, has been shown to be a versatile precursor of many synthetically useful ring systems (Scheme 1).[5,6,7]

In particular, the formation of the perhydroindanedione 46 suggested an attractive approach, via 50 and 51, to the unique sesquiterpene perguisone 52.[21a]



50 51 52


48 (80%)
HCl
Glyme
KOH
MeOH, H2O
46 (75%)
HO
4 (88%)
1) TsCl
2) HOAc, NaOAc
Li, NH3
1) NaH, ΦH
2) MeOH
49 (64%)
3
47 (75%)

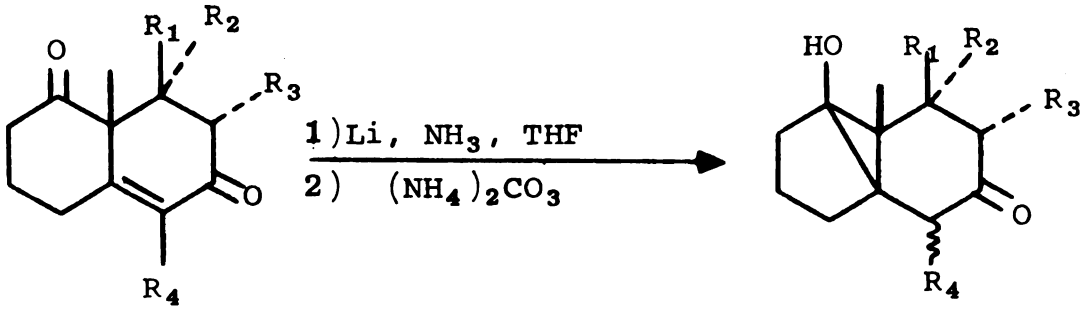
Scheme 1

However, cyclopropanol 50 failed to give 51 under conditions which produced 46 from cyclopropanol 45. This unexpected result led to an extensive study of the factors controlling the ring opening of substituted 5-hydroxytricyclo[4.4.0.$0^{1,5}$]-decan-9-ones.

RESULTS AND DISCUSSION

The cyclopropanols used in this study were prepared by the lithium-ammonia reduction of enediones 3 and 53-56:

(17)



3 ... $R_1 = R_2 = R_3 = R_4 = H$ 4

53 ... $R_1 = R_2 = R_3 = H$; $R_4 = CH_3$ ... 62

54 ... $R_2 = R_3 = R_4 = H$; $R_1 = CH_3$ ... 63

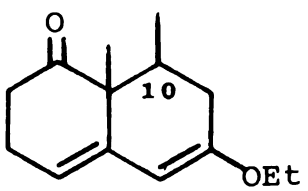
55 ... $R_1 = R_3 = R_4 = H$; $R_2 = CH_3$ ... 50

56 ... $R_1 = R_2 = R_4 = H$; $R_3 = CH_3$ ... 64

Except for 56, the syntheses of these bicyclo[4.4.0]dec-6-ene-2,8-diones are well documented.[22,23,24] However, enediones 54 and 55, prepared in equal amounts by the annulation of 2-methylcyclohexan-1,3-dione in the form of its monopyrrolidine enamine with 3-penten-2-one in formamide,[24b] could not be separated satisfactorily. From a study or models we noted that reactions which changed

either or both trigonal carbonyl centers to a tetrahedral configuration would introduce 1,3-diaxial interactions with the C-10 methyl of 55, but not with 54. Such interactions would be expected to result in a rate retardation, thus permitting the selective derivatization of 54 in the presence of 55.

The validity of this reasoning has been demonstrated by the selective formation of the dienol ether 57 from a mixture of 54 and 55. However, the conditions of this reaction proved extremely crucial and difficult to reproduce.



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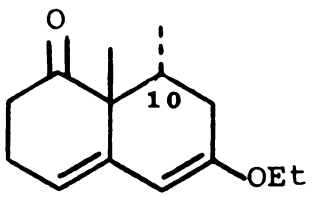
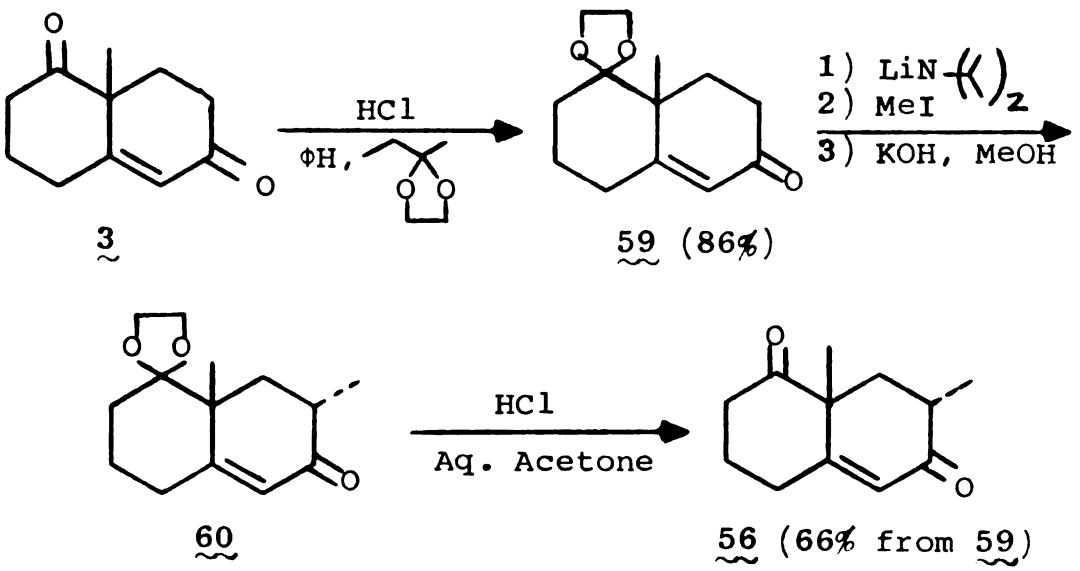


58

Thus failure to quench the reaction with triethyl amine at the optimum moment led to substantial amounts of 58. Hydrolysis of 57, after separation from starting materials, gave pure 54.

The preparation of 56 was accomplished as shown in Scheme II. Ketal 59 was prepared in 86% yield by a modification of the transfer ketalization procedure reported by Bauduin and Pietrasanta.[25] Formation of the kinetically favored conjugate base of 59 by the action of lithium diisopropyl amide in tetrahydrofuran, followed by addition of methyl iodide, led to α'-methyl epimers[26] Equilibration



3 59 (86%)

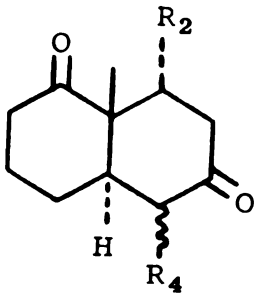
60 56 (66% from 59)

Scheme II

to the more stable isomer 60 was achieved by treatment with methanolic potassium hydroxide. This dimethyl ketal proved to be a crystalline solid (mp 109-110°) exhibiting a three proton singlet at δ1.40, a three proton doublet at δ1.12 (J = 6.0 Hz), and a one proton singlet at δ5.83 in the pmr. Deketalization of 60 with aqueous hydrochloric acid in acetone gave a white solid (56) having methyl and vinyl hydrogen signals in its pmr spectrum consistent with the proposed structure. The overall yield of 56 from 59 was 66%.

Reductive cyclization of the bicyclo[4.4.0]dec-6-ene-2,8-diones to cyclopropanols 4, 50, and 62-64 was carried out in liquid ammonia solution at -78°, using equivalent amounts of lithium metal. If no interaction between

non-adjacent functional groups had occurred, then the major products should have been the trans-decalindiones, formed by reduction of the enone systems. While trans-decalindiones have not been detected among the products from 3, 54, and 56, they are formed in the reduction of 53 and 55. In the case of 53, the trans-decalindione 65 was detected in

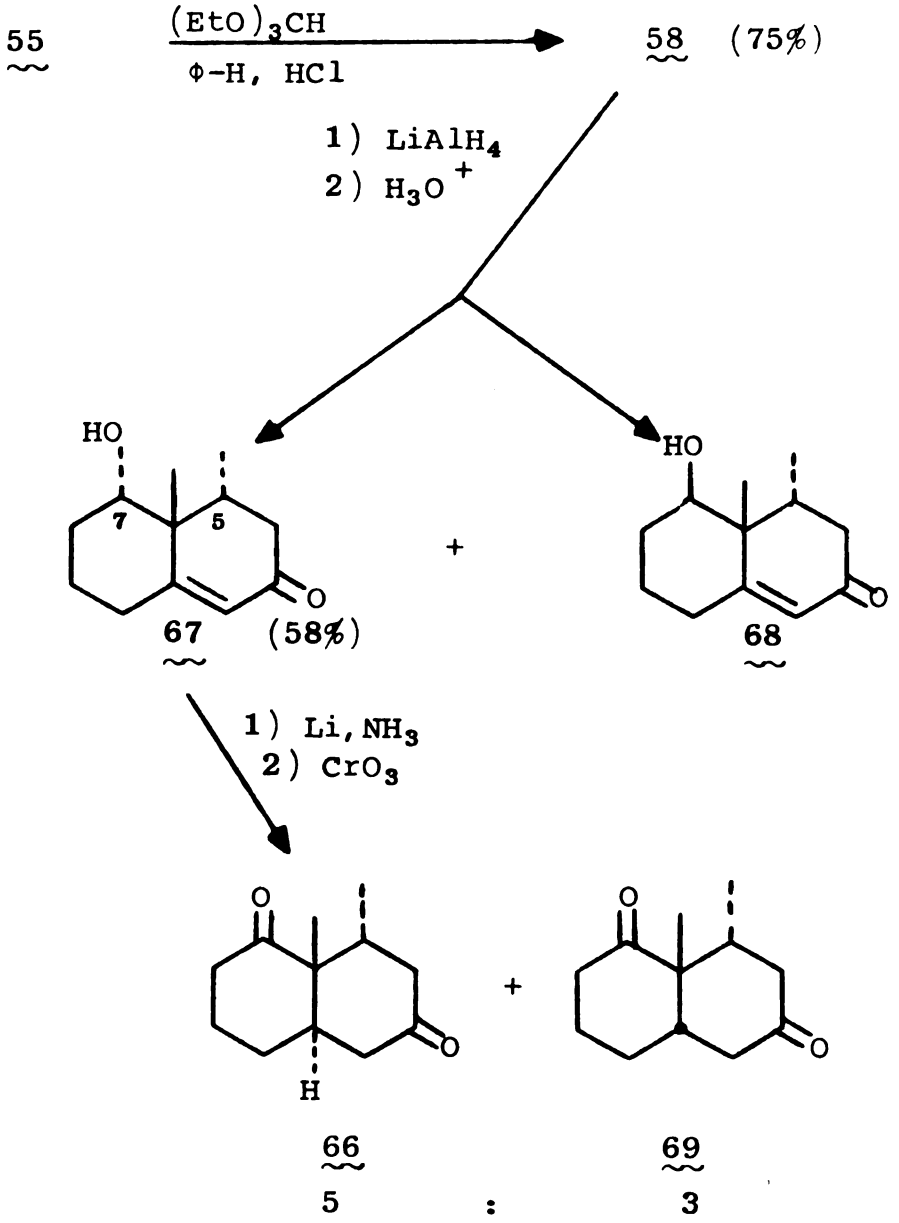


65 $R_2 = H$, $R_4 = CH_3$

66 $R_4 = H$, $R_2 = CH_3$

the mother liquor remaining after crystallization of the cyclopropanol 62. The trans-fusion of the decalin rings in 65 was suggested by the difference in the pmr line width at half-height of the angular methyl group and the TMS signal ($\Delta W_{h/2}$ = .61 cps),[27] and a comparison of its melting point (73-75°) with that given in the literature.[28]

The only crystalline material obtained in early applications of the dissolving metal reduction of 55 was a compound (mp 83-84°), displaying unconjugated carbonyl absorptions in the infrared. This product had different spectral properties from those of the isomeric cis-decalindione 69 and was identified as the trans- isomer 66 by an independent synthesis, as illustrated in Scheme III.


55
(EtO)3CH
Φ-H, HCl
58 (75%)
1) LiAlH4
2) H3O+
HO
7
5
O
67 (58%)
+
HO
O
68
1) Li, NH3
2) CrO3
O
O
H
+
O
O
66
69
5 : 3

Scheme III

Eventually cyclopropanol 50 and the trans-decalindione 66 co-crystallized from the reduction of 55.

The dienol ether 58 was obtained (75%) as a crystalline solid by the reaction of 55 with triethyl orthoformate.[29] Lithium aluminum hydride reduction of 58, followed by acid hydrolysis, gave epimeric alcohols from which the axial alcohol 67 crystallized in 58% yield. The equatorial alcohol was obtained from the mother liquor by preparative glpc. The stereochemical assignment of the hydroxyl group in these epimers was made by comparing the C-5 methyl and vinyl hydrogen chemical shifts in the pmr for each compound (Table I).

Table I. The C-5 methyl and vinyl hydrogen shifts for 67 and 68.

Compound	C-10 Methyl δ_{TMS}	Vinyl Hydrogen δ_{TMS}	Stereochemical Assignment of Hydroxyl Group
67	1.16	6.06	axial
68	1.05	5.83	equatorial

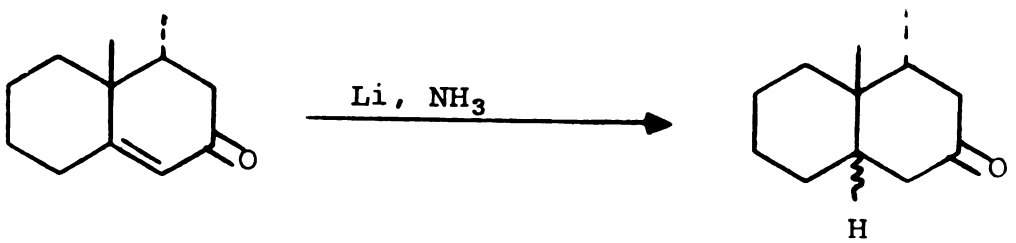
The downfield shift of these protons in compound 67 is consistent with the axial hydroxyl assignment.[30]

Lithium-ammonia reduction of 67 followed by oxidation with Collins reagent[31] gave isomeric decalindiones in a 38:62 ratio. The minor product, identical with the single

product obtained from catalytic hydrogenation of 55, was the cis isomer 69. The major product was the trans isomer 66.

This is one of a few cases in which a substantial amount of a cis-decalin is formed during dissolving metal reductions of enones. Such systems usually give the trans configurations with high stereoselectivity.[32,33] A similar result was expected for 67 since the structurally similar enone 70 (Equation 18) gave a trans/cis product ratio of 7:1[24b] and no cis-decalindione was detected in the reduction

(18)

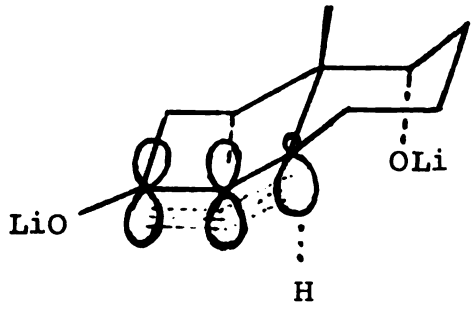


70

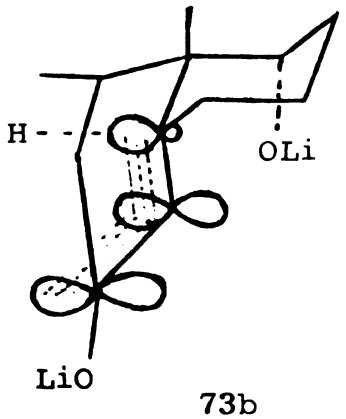
71 (trans, 71%)
72 (cis, 10%)

of 55. However, enone 67 differs from 54 and 70 by virtue of the axial hydroxyl group at C-2.

Stork[34] has suggested that overlap of the orbital on the β-carbon with the p-orbitals of the enolate anion must be maintained during reduction. A comparison of the trans and cis stereoelectronically allowed transition states 73a and 73b derived from 67 indicates that the C-2 hydroxyl and C-10 methyl interactions in 73a are relieved in 73b. Consequently the energies of the transition states are more



73a



73b

nearly equivalent and the trans/cis ratio much nearer unity than might otherwise be expected. Reduction of 68, the epimer having an equatorial hydroxyl at C-2, would be expected to give a much larger trans/cis product ratio.

Less circuitous routes to the trans fused 69, involving the protection of the unconjugated carbonyl followed by dissolving metal reduction of the enone system and removal of the blocking group, proved unsuccessful or gave poor yields.

The formation of cyclopropanols in these reductions indicates an interaction between the carbonyl and enone system at some stage in the course of the reaction. The exact nature of this has not been established. Two mechanisms have been considered: an electrophilic attack by the carbon carbon atom at the β-carbon of the enone radical or dianion,[35] and initial formation of a transannular delocalized radical anion. Formation of the trans-decalindiones 65 and 66 from 53 and 55 suggests that this interaction is sensitive to conformational changes induced by alkyl substituents.

Table II. The ultra violet spectra and half-wave potentials for bicyclo[4.4.0]dec-6-ene-2,8-diones and their corresponding derivatives.

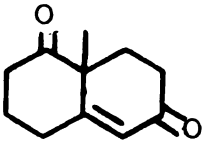
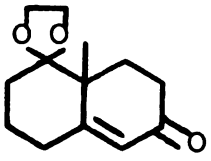
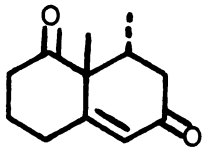
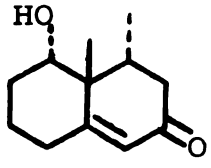
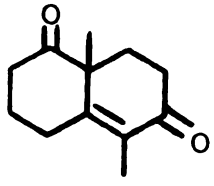
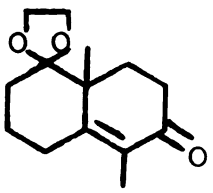
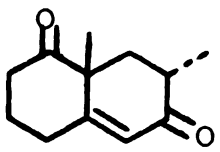
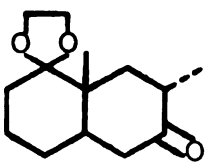
Compound		λ_{max}, nm	ϵ	Half-Wave Potential in Volts	
				Aceto-nitrile	DMF
3		243.3	12,100	-1.96	-1.93
59		242.0	13,130	-2.12	-2.03
55		246.9	10,550	-1.95	-1.90
67		242.2	13,680	-2.13	Undet.
53		251.7	11,900	-2.03	-1.95

Table II. Continued.

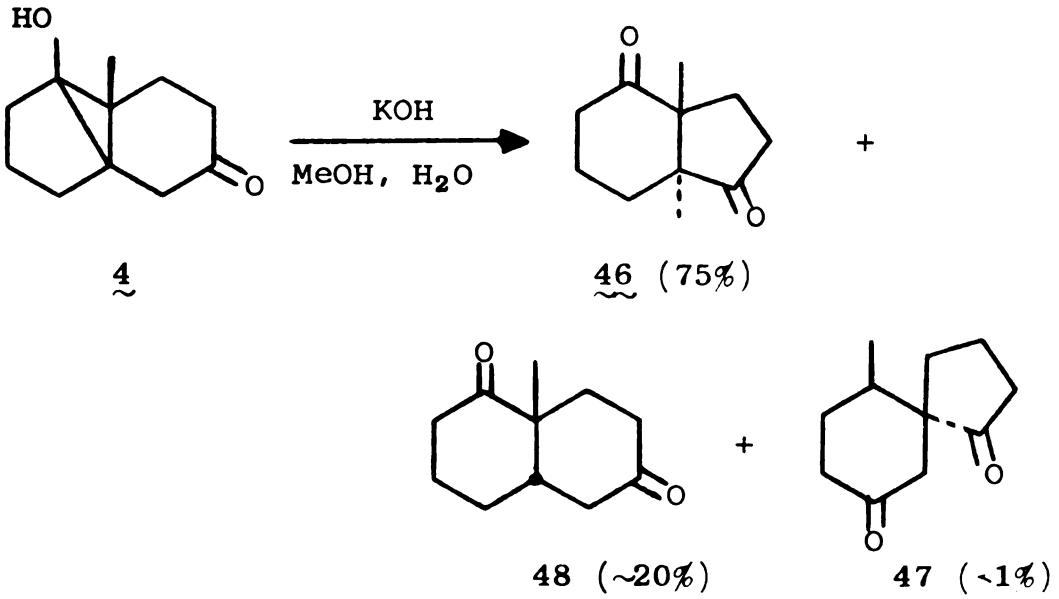
Compound		λ_{max}, nm	ϵ	Half-Wave Potential in Volts	
				Aceto-nitrile	DMF
74		251.1	14,070	-2.17	-2.11
56		243.3	11,400	-2.00	-1.95
60		241.2	12,450	-2.15	-2.11

A comparison of the π,π^* transitions of the enone systems in bicyclo[4.4.0]dec-6-ene-2,8-diones with the corresponding systems lacking the unconjugated carbonyl function indicates that some interaction exists in the unreduced systems (Table II). The unconjugated carbonyl group acts to decrease the energy required for the π,π^* transition of the enone systems. A comparison of the half-wave potentials for the same compounds indicates a similar trend.[36] The

unconjugated carbonyl group reduces the potential required for reduction. However, neither study permits an unambiguous prediction regarding the relative amounts of trans-decalindiones and cyclopropanol which may be formed during the lithium-ammonia reduction of the bicyclo[4.4.0]dec-6-ene-2,8-diones.

The course of ring opening reactions of these cyclopropanols depends on the particular reacting systems (Scheme I). For example, base-catalyzed ring opening of 4 with potassium hydroxide in a 1:1 methanol-water solution gives the trans-hydrindandione 46 in up to 75% yield, the cis-decalindione 48 (~20%), and only a trace of the spiro diketone 47 (Equation 19). The cis-decalindione 48 and the

(19)



4 46 (75%)

48 (~20%) 47 (~1%)

spiro diketone 47 were identified by comparison of their properties with those recorded for these compounds in the literature.[29,37]

Although both cis and trans ring fusions are possible for the perhydroindan system, 46 was assigned the trans configuration on the strength of its conversion to the known 2-deoxy derivative.[6] Confirmation of this configurational assignment was deemed essential because of the potential synthetic utility of this compound and because the stereospecificity of the rearrangement to 46 posed intriguing mechanistic problems.

The most unambiguous method of assigning the configuration of any complex molecule is to effect a structural analysis with three-dimensional X-ray diffraction data. To this end a bromo-derivative was prepared (84%) by the reaction of 46 with 2-pyrroledionehydrotribromide, PHT.[38,39] PHT selectively brominated the six-membered ring, suggesting that the α-methylene group in the five-membered ring is very hindered (such units can normally be brominated efficiently[37]). An axial configuration for the bromide was suggested by the observed downfield methyl shift[30] (Δ .31δ) in the pmr for the angular methyl adjacent to the six-membered carbonyl. However, the six-membered ring carbonyl stretching frequency shift[40] ($\Delta\nu$ = 20 cm^{-1}) indicated a pseudo equatorial bromine, possibly resulting from a distortion of the chair conformation of this ring.

Solution of the X-ray data[41] provided a stereoscopic view of the molecule (Figure 1), demonstrating that the methyl groups (C-10 and C-11) are trans and lie in a plane with C-8 and C-9. Another interesting structural feature

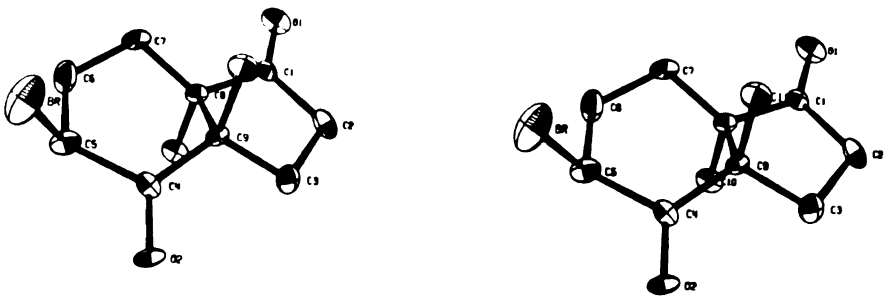
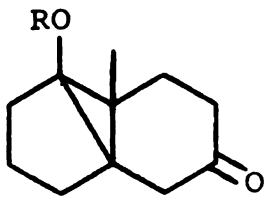
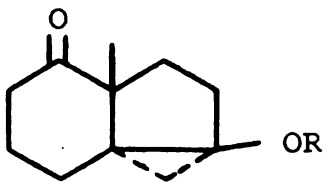


Figure 1. Stereodrawings illustrating the bromo-derivative of 46 as determined by X-ray analysis.

is found in the six-membered ring where C-5 is approximately coplanar with C-4, C-6, and C-8. This distortion of C-5, caused by the steric interaction of the axial bromine with the methyl at C-9, is not the result of crystal lattice forces, but is also present in solutions of this compound as demonstrated by the coupling constants of H-5 with H-6 and H-7 ($J_{5,6}$ = 4.0, $J_{5,7}$ = 6.8 H_3) in the pmr. These coupling constants are much larger than expected for an equatorial proton in a rigid six-membered ring, suggesting that the dihedral angles between the coupling hydrogens are considerably different from those expected in a chair conformation.

The trans-hydrindandione 46 is probably formed by ring opening of the isomeric cyclopropanol 75. This intermediate





4 .... R = H 75

76 .... R = Ac 77

has, in fact, been trapped as the acetate 77, along with the isomeric 76 by reacting one equivalent of a dialkyl amide base[26] in a solution of glyme or diglyme, hexamethylphosphoramide, and tetramethylethylenediamine followed by quenching with acetic anhydride. The two isomers are readily distinguished by the presence of the cyclopropyl hydrogens

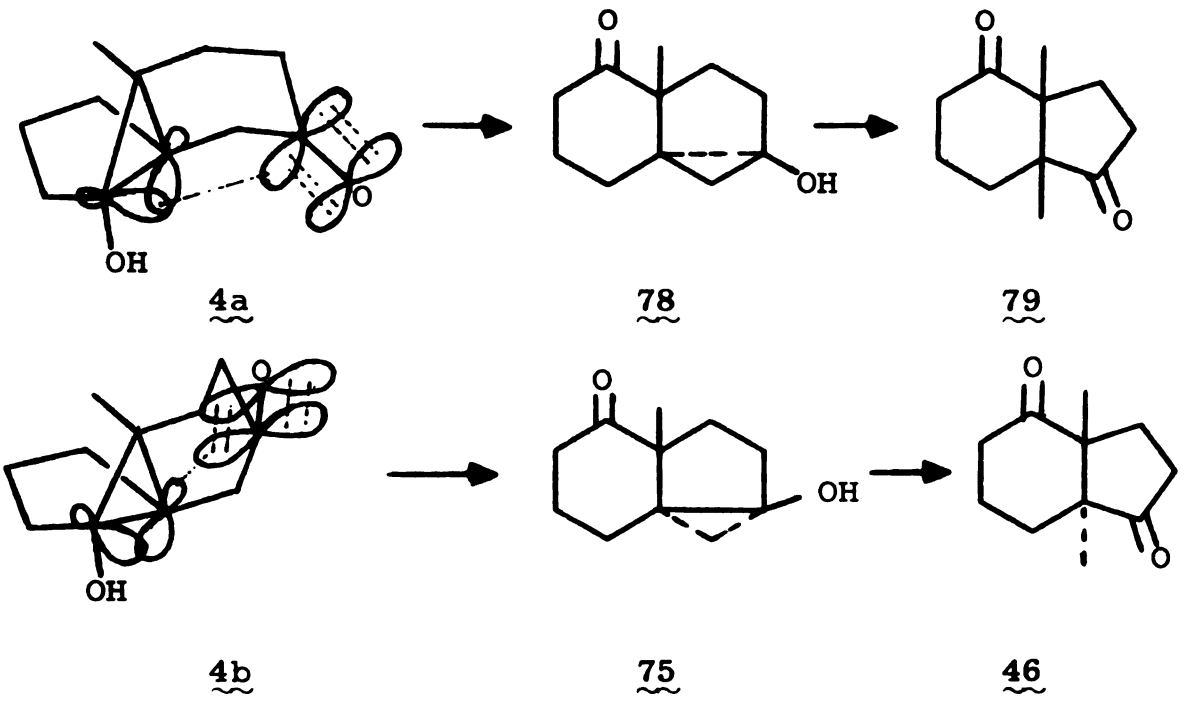
in 77. The ratio of 77 to 76 increased with time, as shown in Table III.

Table III. Ratio of cyclopropyl acetates 76 and 77.

Reaction Time, Hr.	Acetate 76	Acetate 77
3/4	4	1
1 1/2	4	3

The formation of a hydrindandione isomer from 4 apparently involves an interaction of the carbonyl group with the cyclopropane ring, causing a shift of the C-1 — C-5 bond to the C-5 — C-8 position, giving an isomeric cyclopropanol which is cleaved. The six-membered ring of 4 may assume one of two possible boat conformations relative to the three membered ring. As a result, two kinds of interactions, leading ultimately to isomeric hydrindandiones can be visualized (Scheme IV).

Since only the trans product 46 has been observed from these reactions, we may conclude either that the interaction leading to cis 79 does not occur, or that 79 is somehow lost or destroyed during these operations. This observation is consistent with other studies probing the spacial restrictions on homoconjugative interaction of cyclopropyl and carbonyl chromophores.[42] For example, the uv spectra of exo-tricyclo[3.2.1.$0^{2,4}$]octane-8-one 80 (λ_{max} 293 nm, ϵ22)



4a 78 79

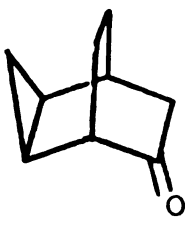
4b 75 46

Scheme IV.

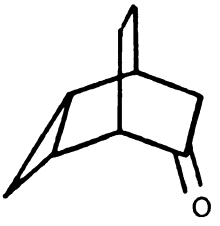
is almost identical to that of 7-norbornone (λ_{max} 290, ϵ14), whereas the absorption of the endo cyclopropyl ketone 81 (λ_{max} 276 nm, ϵ44) is much different.[43]

80 81

Circular dichroism characteristics of some n,π^* carbonyl transitions have been determined for the optically active β,γ-cyclopropyl ketones 82 and 83. The magnitude of the rotational strength was found to depend critically on the relative orientation of the cyclopropyl and carbonyl chromophores, the rotation of 82 being much more intense



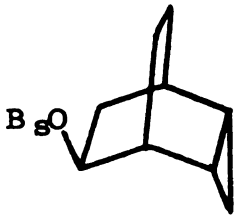
82



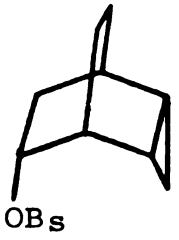
83

than that of 83.[44]

A similar geometric dependence is seen in the ionization of β-functionalized cyclopropyl derivatives. A preliminary report on the solvolysis of 84-87 has just appeared.[42] Three of these molecules ionize in a fashion similar to



84



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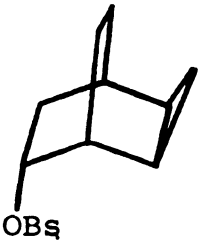
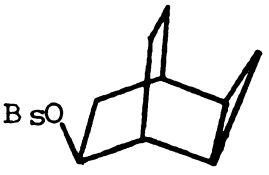


86



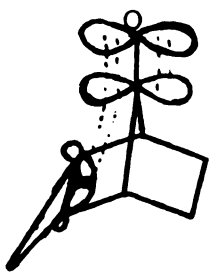
87

other bicyclo[2.2.2]octyl derivatives.[45] Only for isomer 87 is long-range cyclopropyl participation proposed.

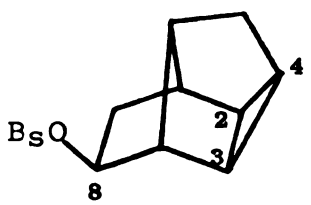
All of these examples bear one similarity. The p-orbital of the carbonyl function, or that of the developing carbonium ion, is orthogonal to the participating bond of the cyclopropyl ring in each case (81, 82, and 87).[46] This contrasts with the parallel orbital orientation preferred by the relatively stable cyclopropylcarbinyl cations.[47] This difference is probably due to the increased distance

over which the orbitals must interact for homoconjugation. The orthogonal orientation increases the effectiveness of orbital overlap.

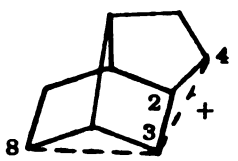
Two modes of orthogonal orbital overlap, leading to homoconjugation of a p-orbital and a cyclopropane ring, have been observed. The most effective is a symmetrical edge approach, leading to overlap as illustrated in 81a. However, it is clear that interaction with the corner of a



81a



88



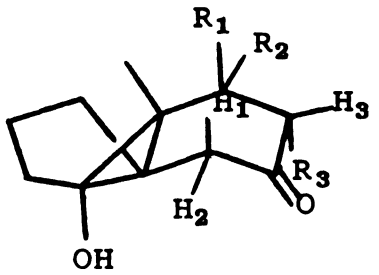
89

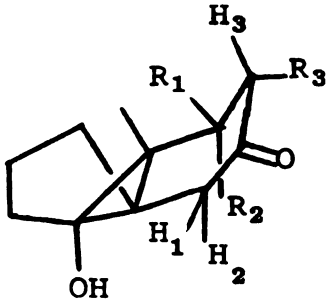
three-membered ring can also be significant.[48] Solvolysis of the exo brosylate 88 is characterized by complete scrambling between C-8 and C-4, suggesting the corner interaction intermediate 89. If edge interaction with the C-2 – C-3 bond were involved, deuterium scrambling between C-2 and C-3 should also have occurred. Absence of edge interaction is presumably due to the unsymmetrical orientation of the p-orbital relative to the edge bond.

These studies suggest that the cis-hydrindan 79 is not formed because the rate of corner interaction of 4b to give 75 (Scheme IV) is greater than the distorted edge interaction 4a leading to 78. The corner interaction results in

inversion of configuration at C-1 of 4b, since the carbonyl p-orbital is interacting with the back lobe of the C-1 — C-5 bond. Substituents on 4 which favor conformation 4a rather than 4b, or which cause subtle changes in the required cyclopropyl-carbonyl orientation and interaction are expected to hinder formation of the trans-hydrindandione.

This hypothesis can be evaluated by examining the products resulting from the ring openings of cyclopropanols substituted so as to favor either the six-membered ring conformation 4a or 4b. Of the four cyclopropanols with methyl substituents on the six-membered ring (50 and 62-64), the steteochemical uncertainty of the secondary methyl of 62 makes it a poor model. Likewise, the α-methyl of 64, although initially favoring 64b because this conformation minimizes the C-9 methyl non-bonding interactions, could epimerize under reaction conditions before ring opening occurs. The most appropriate models are 50 and 63, since there is little ambiguity regarding the conformations adopted by their respective six-membered rings and no possibility of epimerization exists. Cyclopropanol 63 should favor 63b and yield substantial amounts of a trans-hydrindandione while no cyclopropyl—carbonyl interaction will occur for 50, existing primarily as 50a. The rather severe non-bonded interactions for R_1 in 63a and R_2 in 50b makes these conformations thermodynamically less favored.





4a ... $R_1 = R_2 = R_3 = H$ ... 4b

64a ... $R_1 = R_2 = H$, $R_3 = CH_3$ 64b

63a ... $R_2 = R_3 = H$, $R_1 = CH_3$ 63b

50a ... $R_1 = R_3 = H$, $R_2 = CH_3$ 50b

Table IV tabulates the major products obtained from the base-catalyzed ring openings of cyclopropanols 4, 50, and 62-64. These results support the proposed correlation between the conformation of the six-membered ring and the appearance of a hydrindandione product. As predicted, 63 yields the trans-hydrindandione (97, 89%) as does 64 (102, 40%) although the product distribution from the latter suggests some epimerization may have occurred before ring cleavage. On the other hand, no bond rearrangement appears to have occurred for 62, but the stereochemical uncertainty of the secondary methyl makes a correlation of these results with conformation 4a or 4b impossible. In the case of cyclopropanol 50, where the axial methyl at C-10 strongly favors 50a, no hydrindandione is observed.

The major product obtained from the base-catalyzed rearrangment of 50 was the isomeric ketol 100 (Equation 20).[49]

Table IV. Products derived from the base and acid cleavage of cyclopropanols 4, 50, and 62-64 in MeOH solution.

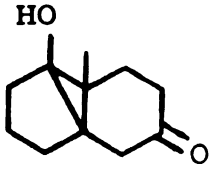
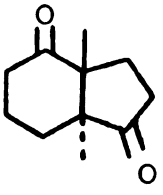
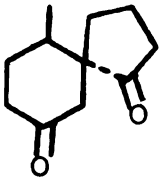
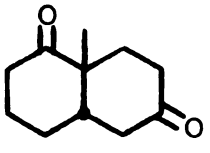
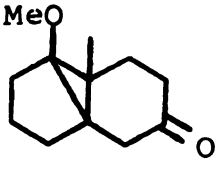
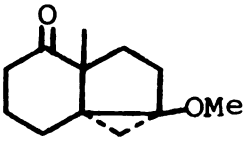
Cyclopropanol	Predicted Configuration	Products		% Yield
4 	4a & 4b	46 	a	13
			b	75
		47 	a	5
			b	1
		48 	a	15
			b	~20
		90 	a	20
		91 	a	44

Table IV. Continued.

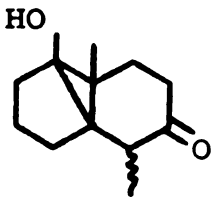
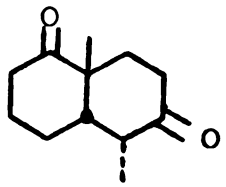
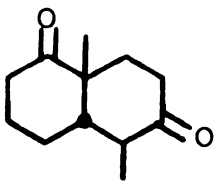
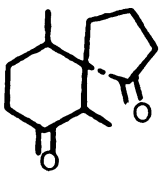
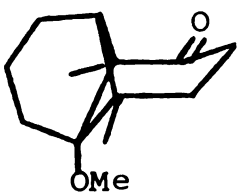
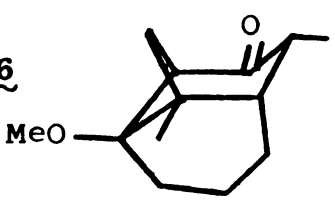
Cyclopropanol	Predicted Configuration	Products		% Yield
62 	4a	92 	a	21
			b	48
		93 	a	11
			b	24
		94 	a	3
			b	6
		95 	a	31
		96 	a	6

Table IV. Continued.

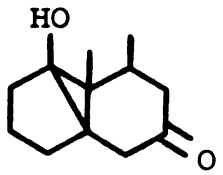
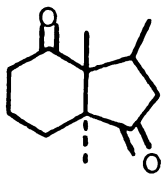
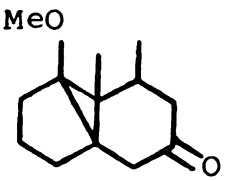
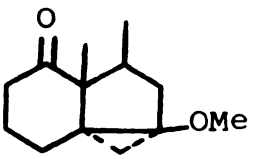
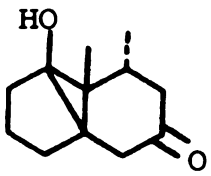
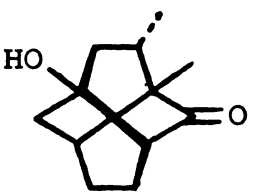
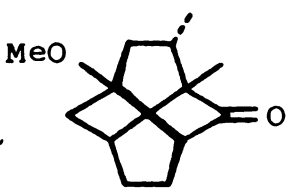
Cyclopropanol	Predicted Configuration	Products		% Yield
63 	4b	97 	a	11
			b	89%
		98 	a	27
		99 	a	57
50 	4a	100 	a	34[e]
			b	71[e]
		101 	a	7[e]

Table IV. Continued.

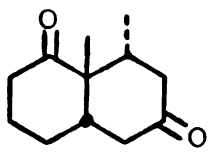
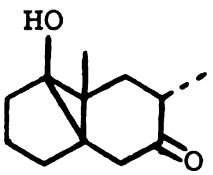
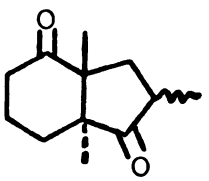
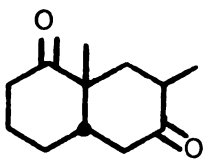
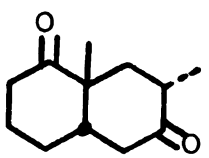
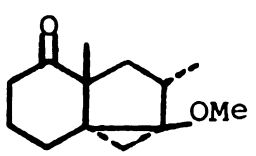
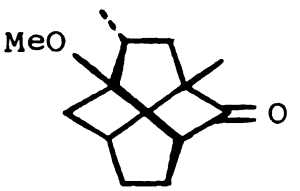
Cyclopropanol	Predicted Configuration	Products		% Yield
		69 	a	48[e]
			b	29[e]
64 	4b	102 	a	5
			b	40
		103 	a	19[d]
			b	35[d]
		104 	a	19[d]
			b	35[d]
		105 	a	32

Table IV. Continued.

Cyclopropanol	Predicted Configuration	Products	% Yield
106			c

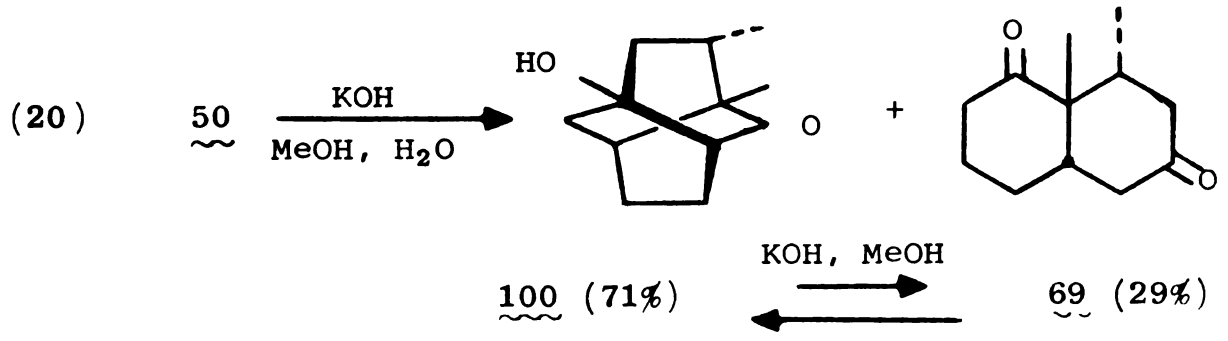
[a]Product from acid-catalysis.

[b]Product from base-catalysis.

[c]Although this twistane methyl ether was not observed, it was the major product obtained from the treatment of epimers 103 and 104 in absolute methanol with dry hydrochloric acid. See the Experimental Section.

[d]Combined yield of 103 and 104.

[e]The yields of these products, obtained from the treatment of a mixture of 50 and 66, have been adjusted to reflect their conversion from cyclopropanol 50.



A pure sample of 100, obtained by glpc, proved to be a crystalline solid (mp 106-107°). This compound was sensitive to moisture and decomposed in part to 69 on silica gel chromatography. Treatment of 100 with a benzene solution of p-toluenesulfonic acid yielded 69; however, hot methanolic KOH transformed either pure 100 or 69 into a 71:29 mixture of these isomers respectively.

A p-bromobenzensulfonate derivative (mp 124-125°), analyzed by means of a Picker FACS-1 four circle diffractometer, established the twistane conformation of 100 as shown in Figure 2.[50] Interestingly, the carbonyl bond angle (C-1 — C-2 — C-3) disclosed by this study is 108.9(4)°, indicating a degree of angle strain also reflected in the infrared stretching frequency of this function (1734 cm^{-1}). Torsion angles for the six-membered rings of the twistane skeleton approximate the twist-boat conformation.

Although several syntheses of twistane ring systems have been reported,[51-54] one of the most interesting new methods for preparing such compounds involves the intramolecular aldol condensation of cis-bicyclo[4.4.0]dec-3,9-dione

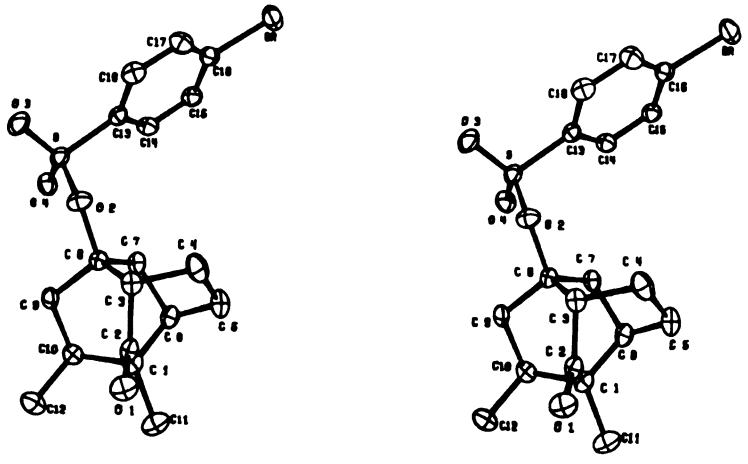
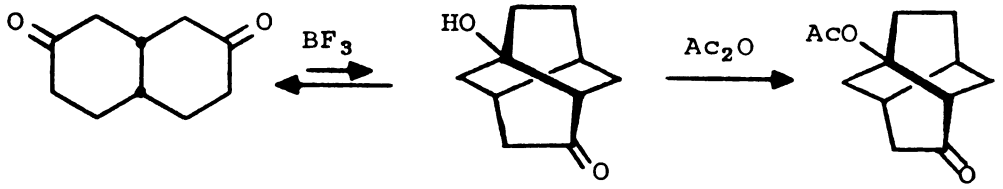


Figure 2. Stereodrawings illustrating the brosylate of 100 as determined by X-ray analysis.

discovered by Deslongchamps.[55a,b,c] Here an unfavorable aldol equilibrium was displaced by derivatization of the aldol hydroxy function (Equation 21). Subsequent reactions

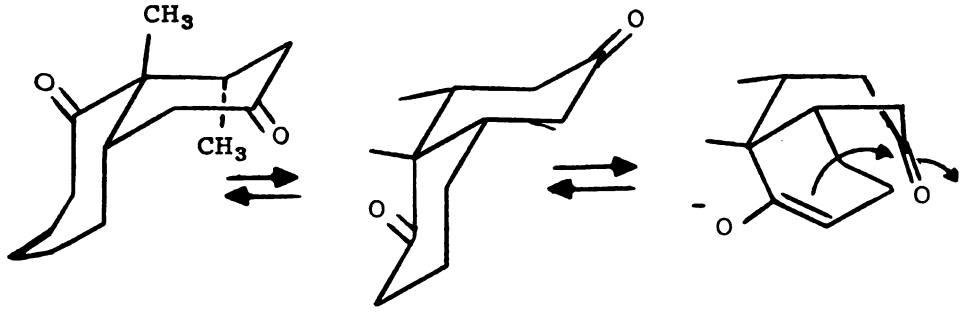
(21)



107 108 109

provided a variety of other twistane derivatives.

With the same alkaline conditions which induced conversion of 69 to 100, cis-decalindiones 48, 92, 93, 103, and 104, all having an equivalent arrangement of carbonyl functions, yielded no detectable quantities of the corresponding aldol isomers. We conclude, therefore, that the aldol cyclization of 69 and the unexpected stability of 100 are uniquely favored by the C-10 methyl substituent, probably because of extreme non-bonded interactions in at least one of the decalin conformations:

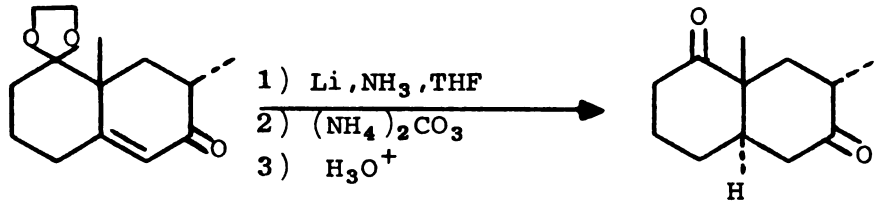


69a 69b 69c

The cis-decalin epimers 92 and 93 (Table IV) were formed in a 2:1 product ratio from cyclopropanol 62. This same ratio was obtained from pure 92, the sole product from the catalytic reduction of 53,[56] under the same alkaline conditions which induced conversion of 62 to 92 and 93.

Compounds 103 and 104, homogeneous by the glpc, were determined to be cis-fused by comparison of their properties, including the angular methyl widths at half-height, with the isomeric trans-decalindione 110, synthesized as shown in Equation (22).

(22)



60 110

The stereochemical assignments for the α-methyls of 103 and 104 were accomplished by a conformational analysis of 1-methyl-cis-bicyclo[4.4.0]decan-2,8-dione analogues. Since the 1-methyl-cis-decalindiones can exist in either of two chair conformations, 48a or 48b, the position of this equilibrium will be determined by substituents which stabilize one conformer relative to the other. Each conformation places the angular methyl in a unique environment which should be reflected by the observed pmr chemical shift and should be somewhat independent of other substituents if chair conformations are maintained.

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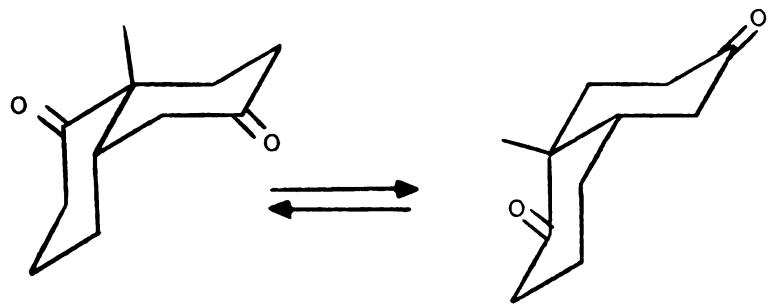


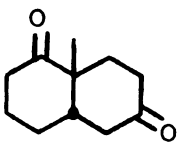
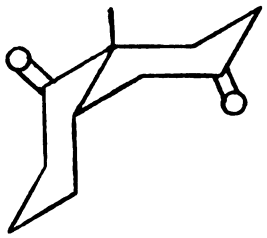
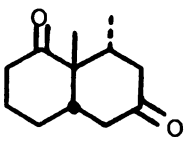
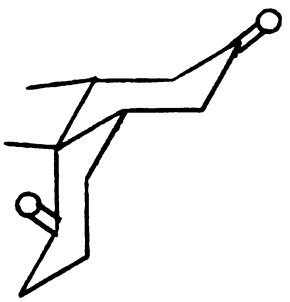
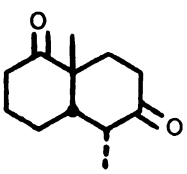
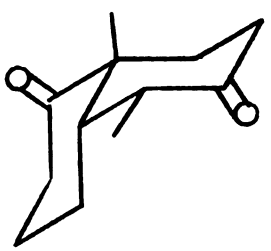
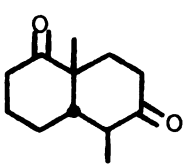
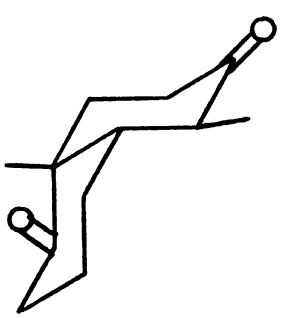
48a 48b

In Table V the chemical shifts of the angular methyls are tabulated for a series of cis-decalindiones and the preferred conformation is indicated. It is evident from these data that conformation 48a has a lower chemical shift value for the angular methyl (δ 1.31-1.37) than does 48b (δ 1.43-1.51). The stereochemistry was determined by correlating the chemical shift of the angular methyls for epimers 103 and 104 to the preferred conformation.

The products obtained from the acid treatment of cyclopropanols 4, 50, and 62-64 are also tabulated in Table IV. In addition to those products also observed in the base-catalyzed ring opening of these cyclopropanols, a number of methyl ethers were trapped. The formation of cyclopropyl methyl ethers 91, 99, and 105 from cyclopropanols 4, 63, and 64 is further support for a bond rearrangement occurring in only one conformation (4b) of the six-membered ring, since 50 and 62 did not give the corresponding methyl ethers. The stereochemistry of 91, and by analogy 99 and 105, was proven by a reaction sequence to be described later.

Tab

Table V. Conformation analysis of analogues of 1-methyl-*cis*-bicyclo[4.4.0]decan-2,8-dione.

Compound		δ, Angular Methyl	Preferred Conformation
48		1.37	
70		1.43	
92		1.33	
93		1.51	

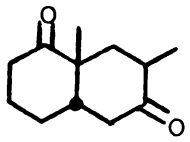
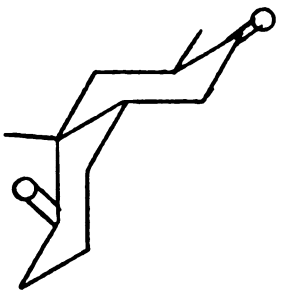
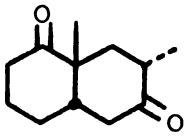
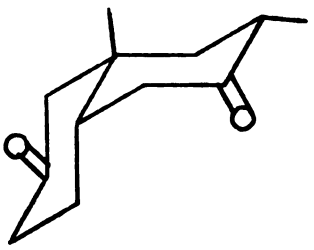
Tab

103

104

a
Co
ch

Table V. Continued

Compound	δ Angular Methyl	Preferred Conformation
103[a] 	1.47	
104[a] 	1.31	

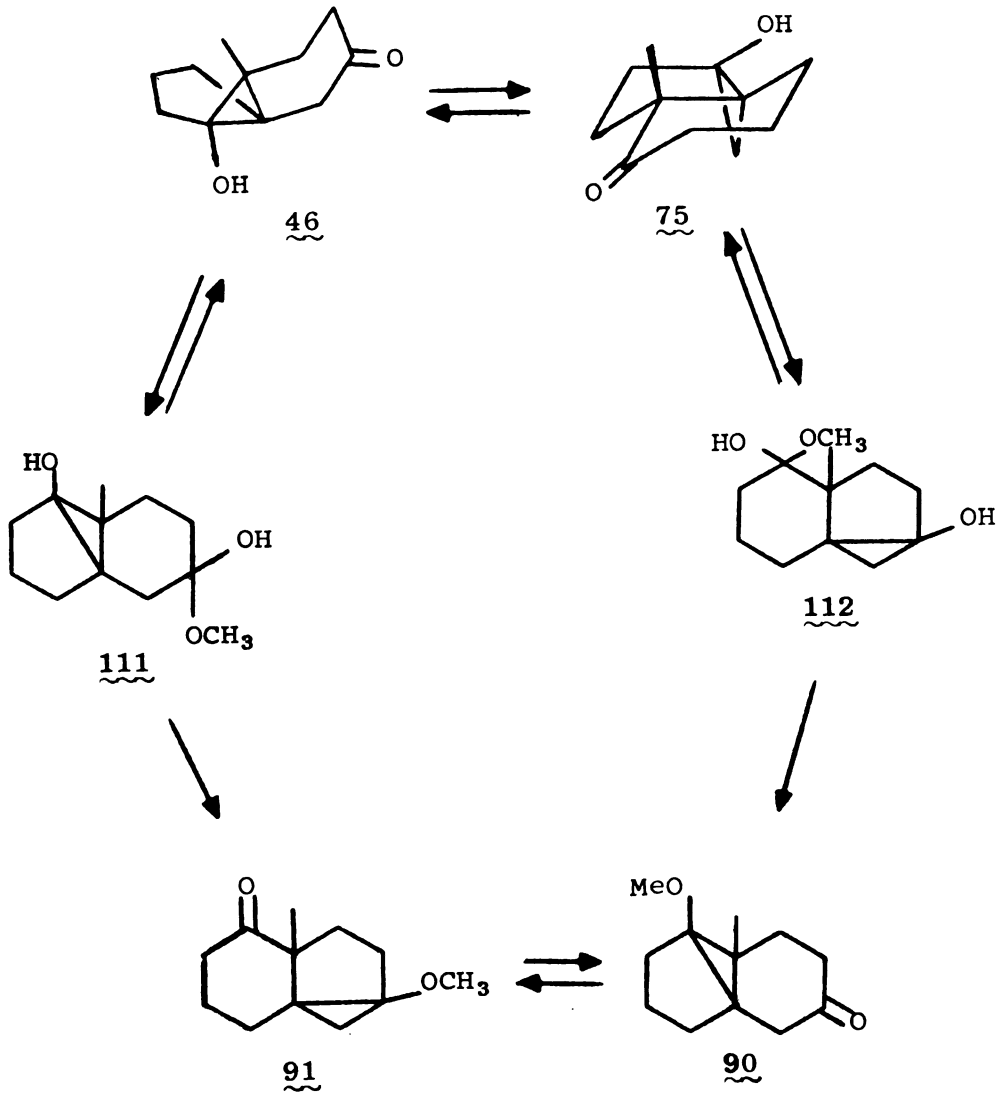
[a] Conformation and hence stereochemistry is suggested by the chemical shift of the angular methyl group.

Cyclopropyl methyl ethers 90 and 91 could arise from the isomeric cyclopropanols 4b and 75, probably via the corresponding hemiketals, as shown in Scheme V. Cyclopropyl methyl ethers 90 and 91 were not interconvertable by the mild acid conditions employed for their formation from 4b.

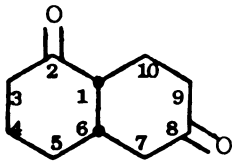
The twistane, copane, and tricyclo[4.4.0.$0^{2,9}$]decan methyl ethers were obtained from the corresponding cis-decalindiones by intramolecular aldol cycloizations, as illustrated for cis-bicyclo[4.4.0]dec-2,8-diones in Scheme VI. The yields of these trapped aldol derivatives markedly increased when the cis-decalindiones were treated with absolute methanol and dry hydrogen chloride. In this manner, for example, the twistane methyl ether 101 was obtained in 98% yield.

The chief diagnostic indicators used to differentiate these methyl ethers are present in the spectral data recorded in the Experimental Section. In particular, the mass spectrum of the twistane derivatives all displayed a base peak of m/e 110, whereas the copane derivative 95 and the tricyclo[4.4.0.$0^{2,9}$]decane methyl ether 96 showed base peak of m/e 193 and 151 respectively.

From the work reported and discussed in previous sections, it should be clear that the trans-hydrindandione 46 originates from 4b via an inversion of configuration at C-1. In contrast, the spiro diketone 47 is known to be formed from 4 with retention of configuration at C-6.[37] However,



Scheme V.



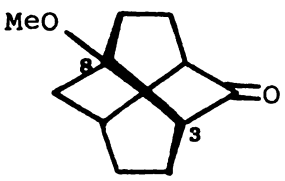
113

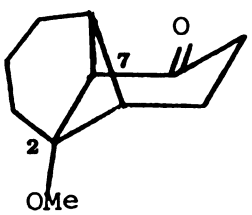
H^+,
CH_3OH

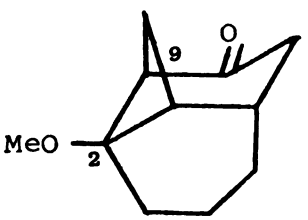
3,8-Bond Formation

2,9-Bond Formation

2,7-Bond Formation







114

Twistane Methyl Ether

115

Copane Methyl Ether

116

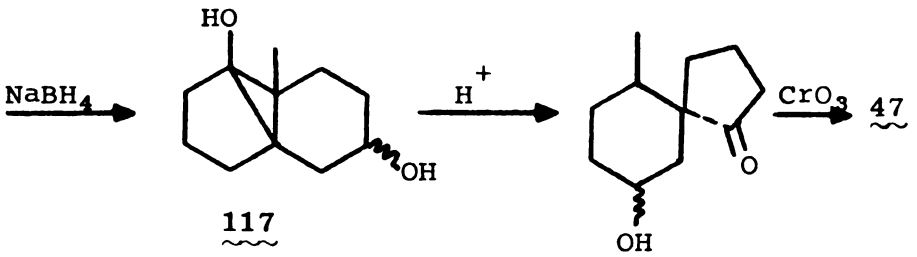
Tricyclo[4.4.0.$0^{2,9}$]-decane Methyl Ether

Scheme VI.

it remains an open question whether the cis-decalindione 48 is formed from cyclopropanol 4 with inversion of configuration at C-1 or from cyclopropanol 76 by retention of configuration at the same carbon.

One approach to answering this question is to determine the products obtained from similar ring opening reactions using derivatives of cyclopropanols 4 and 75 in which the carbonyl function has been protected or removed, thus preventing interconversion of one cyclopropanol to the other.

To this end, reduction of 4 followed by acid treatment of the crude diol 117 gave the known epimers 118 and 119,[37] oxidation of which yielded 47, identical to an authentic sample[37] (Equation 23). The stereospecificity of several

(23) 

118 = equatorial OH
119 = axial OH

reducing reagents in methanol at different temperatures can be determined from the ratios of 118:119 which are obtained (Table VI).

However, base cleavage of 117 followed by oxidation gave two products, the spiro diketone 47 and the cis- decalindione 48 in a 58:42 ratio respectively. This important

result demonstrates unequivocally that base catalyzed cleavage to the spiro diketone 47 occurs with retention of configuration, whereas inversion of configuration was the "modus operandi" leading to the cis-decalindione 48.

Table VI. Stereospecificity of reducing agents for the reduction of cyclopropanol 4.

Reagent	Temperature (°C)	Ratio of 118:119
$NaBH_3CN$[58,59]	0	71:21
$NaBH_4$	-44	93: 6

In a similar manner, the carbonyl function of cyclopropyl methyl ether 91 was protected as the alcohol. Cleavage with either boron tribromide in methylene chloride, or dry hydrogen chloride in absolute methanol, followed by oxidation, gave a single product, the trans-hydrindandione 46.

In the case of cyclopropyl acetate 77, protection of the carbonyl was not necessary. Thus saponification of 77 in methanolic potassium hydroxide gave 46, with no detectable amounts of spiro diketone 47 or cis-decalindione 48 being formed.

These results suggest that the cis-decalindione 48 originates only from the unrearranged cyclopropanol 4 by acid- or base-catalyzed ring opening with inversion of configuration.

EXPERIMENTAL

General

All reactions have been conducted under nitrogen or argon and stirred with magnetic devices unless otherwise noted. Organic extracts were dried over anhydrous sodium or magnesium sulfate before they were concentrated or distilled.

Infrared spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer using sodium chloride cells. Proton magnetic resonance (pmr) spectra were obtained with either a Varian T-60 or a Varian HA-100 high resolution spectrometer; tetramethylsilane was used as an internal standard in most cases. Ultraviolet spectra were obtained on a Unicam SP-800 or a Cary 17 spectrometer. Mass spectra were obtained with a Hitachi RMU-6 mass spectrometer or a LKB gas chromatograph-mass spectrometer.

Melting points were taken on either the Hoover-Thomas apparatus (capillary tubes) or on a hot-stage microscope and are uncorrected.

Gas-liquid partition chromatographic analyses (glpc) were conducted with either a Varian 1200 flame ionization gas chromatograph or an Aerograph A-90P3 thermal conductivity instrument.

Micro-analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

1-Methylbicyclo[4.4.0]dec-6-ene-2,8-dione 2-Ethylene Ketal (59)

A solution of 5.05 g (28.4 mmol) of W. M. ketone (3) in 200 ml of dry benzene and 2 ml of butan-2-one 2-ethylene ketal was acidified with dry hydrogen chloride to a pH <1.[25] The reaction was monitored by glpc. After 3 days, 3 ml more of butan-2-one 2-ethylene ketal were added. This solution was stirred for an additional 3 days, and then washed sequentially with saturated sodium bicarbonate, 10% sodium hydroxide solution, and water. The organic phase was dried and the solvent removed at reduced pressure to yield 6.23 g of crude product. Crystallization from 3 ml of ether gave 4.20 g of white crystals. Chromatography of the mother liquor on 20 g of neutral alumina (activity III) provided an additional 0.92 g for a total yield of 5.12 g (86%). An analytical sample had mp 69-70° (lit.[57] 66-67°): ir 1668, 1622, 1328, 1170 cm^{-1}; pmr ($CDCl_3$) δ1.36(s, 3H), 1.50-2.70 (m, 10H), 3.98(s, 4H), 5.79(s, 1H).

trans-1,9-Dimethylbicyclo[4.4.0]dec-6-ene-2,8-dione 2-Ethylene Ketal (60)

To a solution of 0.65 ml (4.96 mmol) of diisopropyl amine in 5 ml of THF at 0° was added 2.08 ml (5.00 mmol) of 2.4M n-butyl lithium. After the solution was stirred for

10 min, 1.00 g (4.51 mmol) of 1-methylbicyclo[4.4.0]dec-6-ene-2,8-dione 2-ethylene ketal (59) in 3 ml of THF was added. This enolate anion solution was warmed to room temperature and stirred for 15 min, following which 0.314 ml (5.00 mmol) of methyl iodide was added and this solution was stirred an additional 1 1/2 hr. The reaction mixture was diluted with benzene and washed with water and saturated sodium chloride solution. Evaporation of the organic phase gave an oil which was shown by glpc analysis (20% SE 30, 185°) to consist of two products. The oil was dissolved in a 30:1 methanol-water solution, 1.0 g of KOH was added, and the solution stirred overnight. After dilution with water and extraction with benzene, the combined organic phases were washed with water, saturated sodium chloride solution, and then dried and evaporated. The resulting oil was diluted with ether and cooled to give 0.795 g (75%) of crystalline ketal (60). An analytical sample, obtained by recrystallization from ether-ethyl acetate, had mp 109-110°: ir(CCl_4) 1673, 1622, 1369, 1112, 1053 cm^{-1}; pmr ($CDCl_3$) δ1.12(d, J = 6.0 hz, 3H), 1.40(s, 3H), 1.52-2.95(m, 9H), 4.00(s, 4H), 5.83(s, 1H); mass spectrum (70 eV) m/e (rel intensity) 236(4), 99(100), 55(10).

Anal. Calcd. for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53

Found: C, 71.02; H, 8.65.

trans-1,9-Dimethylbicyclo[4.4.0]dec-6-ene-2,8-dione (56)

A crude sample of ketal 60, prepared as previously

described from 6.20 g (23.6 mmol) of ketal 59, was dissolved in 250 ml of acetone which contained 2 ml of water and 5 ml of concentrated hydrochloric acid solution. After stirring the solution for several days, most of the acetone was removed at reduced pressure, and the residue was diluted with water and extracted with benzene. The organic phase was washed sequentially with water, saturated sodium bicarbonate solution, and saturated sodium chloride solution. Evaporation of the solvent left an oil residue which was dissolved in ether and cooled to induce crystallization (first crop 1.90 g, second crop of 1.62 g) for a combined yield of 3.52 g (66%) 56. An analytical sample, obtained by recrystallization from ether, had mp 98-100°: ir(CCl_4) 1715, 1672, 1624, 1452, 872 cm^{-1}; pmr($CDCl_3$) δ1.17 (d, J = 6.5 Hz, 3H), 1.52(s, 3H), 1.58-3.10(m, 9H), 6.84(s, 1H); mass spectrum (70 eV) m/e (rel intensity) 192(27), 177(11), 174(40), 164(10), 150(17), 137(100), 121(45), 108(40), 93(51), 55(77).

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39

Found: C, 75.01; H, 8.42.

Lithium-Ammonia Reduction of Substituted Bicyclo[4.4.0]dec-6-ene-2,8-diones 3, 53, 54, 55, and 56

The general method for the preparation of cyclopropanols from their corresponding enediones is illustrated by the reduction of Wieland Miescher ketone 3.

(a) (1R*,5α,6β)-5-Hydroxy-6-methyltricyclo[4.4.0.0^{1,5}]-decan-9-one (4)

A solution of 1.34 g (193 mmol) of lithium in 500 ml of liquid ammonia, freshly distilled from sodium, and 25 ml of tetrahydrofuran was prepared in a three-necked flask equipped with an overhead stirrer and a dry-ice condenser. To this solution was added dropwise (80 min) 17.1 g (96 mmol) of Wieland Miescher ketone (3)[22a,b] in 125 ml of tetrahydrofuran. After addition the mixture was stirred for 20 min at -78°, following which it was decomposed by the addition of a large excess of anhydrous ammonium carbonate. The liquid ammonia was evaporated by placing the flask, through which a stream of nitrogen flowed, in a water bath. The slurry which remained was treated with water and ether, transferred to a separatory funnel, extracted with ether, and finally the organic extracts were washed with water and dried. Removal of the solvent at reduced pressure left an oil which crystallized to give 16.0 g of a white solid. Recrystallization from ether gave 15.1 g (87%) of pure cyclopropanol 4. Cyclopropanol 4 can be sublimed at 92° and 0.05 torr without decomposition. An analytical sample, obtained by several recrystallizations from ether, had mp 98-100°: ir(CCl_4) 1710, 1150 cm^{-1}; pmr($CDCl_3$) δ1.08(s, 3H), 1.60-2.48(m, 12H), 3.12(bs, 1H); mass spectrum (70 eV) m/e (rel intensity) 180(100), 165(47), 152(15), 137(73), 124(57), 109(43), 97(46), 81(49), 67(37), 55(90).

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.33; H, 8.88

Found: C, 73.21; H, 8.78.

(b) (1R*,5α,6β,10)-5-Hydroxyl-6,10-dimethyltricyclo-[4.4.0.0^{1,5}]decan-9-one (62)

Lithium-ammonia reduction of 7.00 g (36.4 mmol) of 1,7-dimethylbicyclo[4.4.0]dec-6-ene-2,8-dione 53, conducted as previously described, yielded 8.30 g of an oil containing some THF. Crystallization from ether gave 3.20 g (46%) of white crystals. Several recrystallizations from ether-hexane gave an analytical sample, mp 115-118^0 (lit.[37] 96-102^0): ir(CCl_4) 3570, 1695 cm^{-1}.

In addition to cyclopropanol 62, the mother liquor contained ~28% of the trans-decalindione 65 which could be readily separated from 62 by preparative glpc (4% QF-1, 180^0). An analytical sample had mp 73-75^0: ir(CCl_4) 1710, 1450 cm^{-1}; pmr($CDCl_3$) δ0.62(d,J = 7H_3, 3H), 0.94 [s, 3H; $\Delta W_{h/2}$ = 0.61 cps (sweep width 50 Hz)], 1.05-2.40(m, 12H); mass spectrum (70 eV) m/e (rel intensity) 194(53, 127(100), 68(95).

(c) (1R*,5α,6β,8α)-5-Hydroxy-6,8-dimethyltricyclo-[4.4.0.0^{1,5}]decan-9-one (64)

Lithium-ammonia reduction of 1.50 g (7.82 mmol) of trans-1,9-dimethylbicyclo[4.4.0]decan-2,8-dione 56 yielded 1.53 g of an oil which did not crystallize under various conditions. The pmr spectrum indicated only one product,

although glpc analysis indicated a trace of enedione 56 was also present. Cyclopropanol 64 had the following properties: ir(film) 3350, 1705 cm^{-1}; pmr($CDCl_3$) δ0.99(d, J = 6.5H_3, 3H), 1.10(s, 3H), 1.15-2.90(m, 11H), 3.96(bs, 1H); mass spectrum (70 eV) m/e (rel intensity) 194(84, 179(59), 174(31), 166(25), 151(96), 137(70), 124(80), 123(80), 109(65), 95(100), 81(65), 69(75), 55(85).

(d) (1R*,5α,6β,7α)-5-Hydroxy-6,7-dimethyltricyclo-[4.4.0.$0^{1,5}$]decan-9-one 50

Lithium-ammonia reduction of 10.0 g (52.1 mmol) of trans-1,10-dimethylbicyclo[4.4.0]dec-6-ene-2,8-dione 55, conducted as previously described, yielded 10.4 g of an oil. Crystallization at -78° yielded 6.4 g of crystalline material consisting of a 3:1 mixture of 50 and (1β,6α,10α)-1,10-dimethylbicyclo[4.4.0]decan-2,8-dione 66. Recrystallizations did not alter this ratio; however, a careful Kugelwöhr distillation substantially increased the purity of 50: ir(CCl_4) 3475, 1706 cm^{-1}; pmr($CDCl_3$) δ1.06(s, 3H), 1.15(d, J = 6.5 Hz, 3H), 1.40-2.75(m, 11H), 3.52 (bs,1H); mass spectrum (70 eV) m/e (rel intensity) 194(32), 179(18), 176(22), 161(27), 151(26), 135(60), 123(42), 109(42), 95(40), 69(72), 55(70), 41(100).

An analytical sample of the minor product 66, prepared by recrystallization from ether, had mp 82.5-83.5° and spectral properties identical to those recorded for the major product obtained from the dissolving metal reduction

and subsequent oxidation of (5α,6β,7α)-7-hydroxy-5,6-dimethylbicyclo[4.4.0]dec-1-ene-3-one 67.

(e) (1R*,5β,6α,7α)-5-Hydroxy-6,7-dimethyltricyclo-[4.4.0.0^{1,5}]decan-9-one (63)

Lithium-ammonia reduction of 258 mg (1.34 mmol) of cis-1,10-dimethylbicyclo[4.4.0]dec-6-ene-2,8-dione 54 gave 292 mg of an oil which did not crystallize under various conditions even though the pmr spectrum suggested a single product predominated. This oil had the following properties: ir(film) 3450, 1700 cm^{-1}; pmr($CDCl_3$) δ0.91(s, 3H), 1.01(d, J = 6.5 Hz, 3H), 1.12-2.80(m, 11H), 3.47(bs, 1H); mass spectrum (70 eV) m/e (rel intensity 194(23), 179(25), 176(32), 160(27), 151(31), 145(40), 133(46), 124(49), 74(75), 59(100).

8-Ethoxy-trans-1,10-Dimethylbicyclo[4.4.0]dec-5,7-diene-2-one (58)

To a solution of 1.00 g (5.20 mmol) of trans-1,10-dimethylbicyclo[4.4.0]dec-6-ene-2,8-dione 55 in 40 ml of benzene were added 0.2 ml of ethanol and 2 ml of redistilled ethyl orthoformate. Dry hydrogen chloride was then introduced until a pH <1 was obtained. The reaction mixture was stirred for 2 hr at room temperature, and then sequentially washed with saturated sodium bicarbonate, water, and saturated sodium chloride solution. Evaporation of the solvent gave 1.170 g of crude product which slowly solidified to a yellow solid on cooling. Crystallization from an ether-hexane

solution gave 0.792 g of white crystals. The mother liquors were chromatographed on 20 g of Woelm neutral alumina (activity III). Elution with 10-30% ethyl acetate in hexane gave an additional 0.128 g of the dienolether 58 for a combined yield of 0.857 g (75%). Recrystallization from ether-pentane gave an analytical sample: mp 95-96°; ir(CCl_4) 1710, 1650, 1625, 1380, 1355, and 1170 cm^{-1}; pmr($CDCl_3$) δ0.97(d, 3H, J = 7.0 Hz), 1.17(s, 3H), 1.31(t, 3H, J = 7.0 Hz), 1.42-2.95(m, 7H), 3.79(1, 2H, J = 7.0 Hz), 5.24 (s, 1H), 5.66(dd, 1H, J = 3.0 Hz, J' = 3.0 Hz); mass spectrum (70 eV) m/e (rel intensity) 220(100), 205(9), 192(41), 177(58), 163(44), 149(30), 135(58), 121(17), 91(30), 77(20).

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 76.32; H, 9.15

Found: C, 76,34; H, 9.14.

Reduction and Hydrolysis of 8-Ethoxy-trans-1,10-dimethyl-bicyclo[4.4.0] dec -5,7-diene-2-one (58)

A solution of 500 mg (2.27 mmol) of dienol ether 58 in 10 ml of dry THF was added to a suspension of 200 mg of lithium aluminum hydride in 50 ml of dry THF and the mixture was refluxed under a nitrogen atmosphere overnight. The reaction mixture was then cautiously decomposed with water and the solvent was removed at reduced pressure. The residue was dissolved in 100 ml of acetone and 3 ml of water, acidified to pH <1 with hydrochloric acid, and stirred at room temperature for 1/2 hr. Most of the acetone was evaporated at reduced pressure, ether was added and the organic phase was washed with water and saturated sodium bicarbonate

solution, then dried over magnesium sulfate. Evaporation at reduced pressure gave a semi-crystalline solid. Careful crystallization from ether yielded 250 mg (58%) of (5α,6β,7α)-7-hydroxy-5,6-dimethylbicyclo[4.4.0]dec-1-ene-3-one 67, mp 122-123°: ir CCl_4 3600, 3380, 1572, 1620, 1040 cm^{-1}; pmr($CDCl_3$) δ1.16(d, 3H, J = 7.0 Hz), 1.21(S, 3H), 1.45-3.20 (m, 9H), 4.14(m, 1H), 6.06(S, 1H); mass spectrum (70 eV) m/e (rel intensity) 194(48), 176(16), 161(100), 138(41), 123(61).

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34
Found: C, 74.18; H, 9.41.

Glpc analysis (4% QF-1, 190°) indicated that, in addition to 67, the mother liquor contained ~ 50% of the (5β,6α,7α)-7-hydroxy-5,6-dimethylbicyclo[4.4.0]dec-1-ene-3-one (68), which was isolated by preparative glpc as a crystalline solid, mp 117-119°: ir(CCl_4) 3600, 3390, 1668, 1612, 1036 cm^{-1}; pmr($CDCl_3$) δ 1.05(d, 3H, J = 7.0 Hz), 1.29 (s, 3H), 1.41-3.01(m, 9H), 3.85(m, 1H), 5.83(s, 1H); mass spectrum (70 eV) m/e (rel intensity) 194(33), 176(23), 161(100), 138(36), 123(51), 91(51), 41(64).

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34
Found: C, 74.01; H, 9.34.

Lithium-Ammonia Reduction and Oxidation of (5α,6β,7α)-7-Hydroxy-5,6-dimethylbicyclo[4.4.0] dec -1-ene-3-one (67)

To a solution of 130 mg (0.67 mmol) of 67 in 75 ml of liquid ammonia and 25 ml of dry THF at -33° was added small amounts of lithium metal until a blue color persisted. The

reaction mixture was then stirred for 15 min, quenched with ammonium chloride, and the ammonia was evaporated to give a residue which was dissolved in water and extracted with ether. The ether extract was dried and the solvent was evaporated to give an oil, which was dissolved in 2 ml of methylene chloride and oxidized by freshly prepared Collins reagent.[31] A black, tarry deposit separated immediately. The reaction was stirred for an additional 15 minutes at room temperature. The solution was then decanted from the residue which was washed with 40 ml of ether. The combined organic solutions were washed with three portions of 5% sodium hydroxide solution, 5% aqueous hydrochloric acid, water, and saturated sodium bicarbonate solution. Evaporation of the solvent gave 105 mg of an oil consisting of two components in a 62:38 ratio. These were isolated with difficulty by the repeated passage of impure fractions through a 4% QF-1 column at 170°. The major component was the trans-decalin 66, mp 82.5-83.5: ir(CCl_4) 1710, 1440, 1410 cm^{-1}; pmr($CDCl_3$) δ 0.92(d, 3H, J = 7.0 Hz), 1.36(s, 3H), 1.46-3.00(m, 12H); mass spectrum (70 eV) m/e (rel intensity) 194(54), 179(13), 161(33), 123(53), 111(49), 95(39), 69(100), 55(61), 41(81).

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34

Found: C, 74.10; H, 9.44.

The minor component was the cis-decalin 69, recovered as an oil and shown by glpc and ir analysis to be identical

to the single product obtained from catalytic hydrogenation of trans-1,10-dimethylbicyclo[4.4.0] dec -6-ene-2,8-dione 55.

(1α,6α,10β)-1,10-Dimethylbicyclo[4.4.0]decan-2,8-dione (69)

A solution of 100 mg (0.52 mmol) of trans-1,10-dimethylbicyclo[4.4.0] dec -6-ene-2,8-dione 55 in 1 ml of ethanol was added to a pre-hydrogenated suspension of 10 mg of 10% palladium on charcoal in 5 ml of ethanol, and the resulting mixture was shaken in a Parr hydrogenator (50 psi, room temperature). Hydrogen uptake ceased after 25 min; the suspension was then filtered and the catalyst washed with hot ethanol.[29] Chromatography of the crude organic product on silica gel gave 95 mg (94%) of (1α,6α,10β)-1,10-dimethylbicyclo[4.4.0]decan-2,8-dione 69 as an oil: ir(CCl_4) 1720, 1705, 1085 cm^{-1}; nmr ($CDCl_3$) δ 1.23(d, J = 6.0 Hz, 3H), 1.43(S, 3H), 1.52-3.20(m, 12H); mass spectrum (70 eV) m/e (rel intensity) 194(35), 179(3), 161(10), 123(20), 110(91), 95(28), 81(29), 69(75), 55(47), 41(100).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34

Found: C, 74.11; H, 9.20.

(1β,6α,9α)-1,9-Dimethylbicyclo[4.4.0]decan-2,8-dione (110)

Lithium was added in small pieces to a solution of 150 mg (0.64 mmol) of trans-1,9-dimethylbicyclo[4.4.0]dec-6-ene-2,8-dione 2-ethylene ketal 60 in 20 ml of THF and 75 ml of liquid ammonia until a blue color persisted. This solution was then stirred at reflux for 1 hr, following

which the reaction was quenched with excess ammonium chloride. The ammonia was evaporated by placing the flask in a cold water bath, and the residue was taken up in ether and washed with water. Several drops of concentrated H_2SO_4 were added to the etherial solution which was then stirred overnight. The solution was sequentially washed with water and saturated sodium bicarbonate solution, then dried and evaporated. An analytical sample was crystallized from ether, mp 58-61°: ir(CCl_4) 1708, 1445, 1165 cm^{-1}; pmr($CDCl_3$) δ 1.07(d, J = 6.5 Hz, 3H), 1.40[s, 3H; d, J = 0.59 cps (sweep width 50 Hz) and $\Delta W_{h/2}$ = 0.95 cps], 1.50-3.92(m, 12H); mass spectrum (70 eV) m/e (rel intensity) 194(100), 179(10), 166(15), 161(13), 95(65), 41(95).

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34

Found: C, 74.32; H, 9.16.

Base-Catalyzed Reactions of Substituted Tricyclo[4.4.0.$0^{1,5}$]-decan-9-ones

The general method for effecting base-catalyzed rearrangements of tricyclo[4.4.0.$0^{1,5}$]decan-9-ones is illustrated by the reaction of cyclopropanol 4 with KOH in aqueous methanol.

(a) trans-1,6-Dimethylbicyclo[4.3.0]nona-2,7-dione (46)

To 8 ml of a deoxygenated 50:50 methanol-water mixture at 0° was added 1.02 g (5.67 mmol) of (1R*,5α,6β)-5-hydroxy-6-methyltricyclo[4.4.0.$0^{1,5}$]decan-9-one 4 and an excess of

potassium hydroxide. This solution was stirred for 4 hr at 0^0 and then overnight at room temperature. Following dilution with water and extraction with benzene, the organic phase was washed with water and dried. Evaporation at reduced pressure gave a white crystalline product, which on recrystallization from ether yielded 0.62 g (62%) of hydrindanedione 46. In some preparations yields as high as 75% have been realized by extensive chromatography of the mother liquors on silica gel. It was recently discovered[58] that 48 forms a bisulfite addition, thus making separation of 46 and 48 much easier. An analytical sample had mp $167-168^0$: ir (KBr) 1705, 1735 cm^{-1}; pmr ($CDCl_3$) δ 0.92(s, 3H), 1.17 (s, 3H), 1.32-2.89(m, 10H); mass spectrum (70 eV) m/e (rel intensity) 180(59), 165(55), 152(4), 136(24), 124(45), 109(100), 94(57), 82(51), 67(50), 55(50), 41(65).

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.33; H, 8.88

Found: C, 73.05; H, 8.91.

The mother liquor also contained a trace of 10-methylspiro[4,5]decan-1,7-dione 47 and and ~ 50% of 1-methyl-cis-bicyclo[4.4.0]decan-2,7-dione 48 (19% yield from 4).

(b) Base Catalyzed Reaction of (1R*,5α,6β,10ξ)-5-Hydroxy-6,10-dimethyltricyclo[4.4.0.$0^{1,5}$]decan-9-one (62)

Base treatment of 100 mg (0.52 mmol) of cyclopropanol 62 gave 95 mg of an oil which glpc analysis (4% QF-1, 160^0) showed to consist of spiro diketone 94 (6%) and the epimers 92 and 93 (72% in a 2:1 ratio) as well as other minor products.

(1) 6,10-Dimethylspiro[4,5]dican-2,7-dione 94 had properties consistent with those previously recorded:[37] ir(CCl_4) 1735, 1705 cm^{-1}.

(2) (1α,6α,7β)-1,7-Dimethylbicyclo[4.4.0]decan-2,8-dione 92 had properties identical to those previously reported: ir (CCl_4) 1708 cm^{-1}; pmr($CDCl_3$) δ 0.98(d, J = 6.5 Hz, 3H), 1.33(s, 3H), 1.56-2.95(m, 12H); mass spectrum (70 eV) m/e (rel intensity) 194(51), 127(100), 68(98). Treatment of pure 92 in aqueous methanol at room temperature with either KOH or HCl gave a 2:1 product ratio of 92 to 93.

(3) (1α,6α,7α)-1,7-Dimethylbicyclo[4.4.0]decan-2,8-dione 93 had the following properties: ir(CCl_4) 1708 cm^{-1}; pmr($CDCl_3$) δ 1.01(d, J = 7.0 Hz, 3H), 1.51(s, 3H).

(c) Base treatment of (1R*,5β,6α,7α)-5-Hydroxy-6,7-dimethyltricyclo[4.4.0.$0^{1,5}$]decan-9-one (63)

Base-catalysis of 128 mg (0.66mmol) of cyclopropanol 63 gave 128 mg of crystalline material, shown by glpc analysis to consist of 89% of the trans-hydroindanedione 97. Preparative glcp gave an analytical sample, mp 95-100°: ir(CCl_4) 1710, 1739, 1458, 1378, 1092, 1020 cm^{-1}; nmr($CDCl_3$) δ 0.98 (s, 3H), 1.12(s, 3H), 1.10(d, J = 6.0 Hz, 3H), 2.25-3.05(m, 9H); mass spectrum (70 eV) m/e (rel intensity) 194(27), 179(9), 153(9), 137(13), 124(100), 109(28), 96(51).

(d) Base Treatment of (1R*,5α,6β,7α)-5-Hydroxy-6,7-dimethyltricyclo[4.4.0.0^{1,5}]decan-9-one (50)

Base treatment of 200 mg of a mixture of cyclopropanol 50 and the trans-decalindione 66, prepared from the dissolving metal reduction of enedione 55, gave a quantitative yield of an oil from which three components were separated by preparative glcp (4% QF-1, 195°):

(1) (1R*,3R*,6S*,8R*,10R*)-8-Hydroxy-1,10-dimethyltricyclo[4.4.0.0^{3,8}]decan-2-one 100 (57%) had properties identical to the ketol derived from the base treatment of cis-decalindione 69: ir(CCl_4) 3590, 3400, 1725 cm^{-1};

(2) (1α,6α,10β)-1,10-Dimethylbicyclo[4.4.0]decan-2,8-dione 69 (16%) had properties identical to those of the single product obtained from the catalytic reduction of enedione 55: ir(film) 1720, 1705, 1085 cm^{-1};

(3) (1β,6α,10α)-1,10-Dimethylbicyclo[4.4.0]decan-2,8-dione 66 (26%) had properties identical to the trans-decalindione obtained as in Scheme III: ir(CCl_4) 1710, 1440, 1410 cm^{-1}.

(e) Base Treatment of (1R*,5α,6β,8α)-5-Hydroxy-6,8-dimethyltricyclo[4.4.0.0^{1,5}]decan-9-one (64)

Base treatment of 200 mg (1.04 mmol) of the oily cyclopropanol 64 gave an oil. Preparative glpc (4% QF-1, 185°) separated the two major components:

(1) (1β,6α,8ξ)-1,6,8-Trimethylbicyclo[4.3.0]nona-2,7-dione 102 (80 mg, 40%), mp 90-95° was homogeneous by glpc and tlc: ir(CCl_4) 1739, 1713, 1455, 1375 cm^{-1}; pmr (60 MC, $CDCl_3$) indicated two sets of two singlets each (δ 0.86, 1.16 and 0.96, 1.11) and a doublet (δ 1.24, J = 7.0 Hz) which separated into a pair of doublets (J' = 7.0 Hz, J" = 7.2 Hz) when the spectrum was taken in C_6D_6 at 100 MC and a sweep width of 250 Hz; mass spectrum (70 eV) m/e (rel intensity) 194(59), 179(48), 151(44), 137(38), 125(59), 124(57), 110(98), 95(100).

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34

Found: C, 73.99; H, 9.30.

(2) (1α,6α,9ξ)-1,9-Dimethylbicyclo[4.4.0]decan-2,8-diones 103 and 104 (70 mg, 35%) was homogeneous by glpc and tlc: ir(film) 1708, 1450, 1423, 1375, 1152, and 1095 cm^{-1}; pmr (60 MC, $CDCl_3$) indicated two singlets (δ 1.31 and 1.47) and a pair of doublets (δ 0.95, J = 6.0 Hz and δ 1.01, J = 6.7 Hz) whose coupling constants did not change when the spectrum was taken at 100 MC with a sweep width of 250 Hz; mass spectrum (70 eV) m/e (rel intensity) 194(51), 124(59), 111(100), 95(44), 81(32), 69(56).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34

Found: C, 74.25; H, 9.35.

(1α,3α,6β)-3-Bromo-1,6-dimethylbicyclo[4.3.0]nona-2,7-dione Fig. 1

To a solution of 1.42 g (7.90 mmol) of trans-1,6-dimethylbicyclo[4.3.0]nona-2,7-dione (46) in 50 ml of dry carbon tetrachloride was added 4.40 g (9.59 mmol) of 2-pyrrolidonehydrobribromide, PHT.[38,59] This solution was stirred in the dark at room temperature for 20 hr, during which time a white crystalline solid [bix-(2-pyrolidone) hydrobromide] precipitated. The precipitate and the unreacted PHT were removed by filtration, 100 ml of ether was added to the filtrate and the organic solution was washed with saturated sodium bicarbonate, water and saturated sodium chloride solution. The solvent was evaporated from the dried solution and the residue (2.47 g) was crystallized from ether to give a first crop of 1.10 g and a second crop of 0.60 g for a combined yield of 84%. An analytical sample had mp 144-147°: ir(KBr) 1720, 1740 cm^{-1}; pmr($CDCl_3$) δ 0.95(s, 3H), 1.49(s, 3H), 3.04-1.60(m, 8H), 4.43(dd, 1H, J = 4.0 Hz, J' = 6.8 Hz); mass spectrum (70 eV) m/e (rel intensity) 260(4), 258(4), 245(3), 243(3), 190(3), 188(3), 179(18), 165(23), 151(13), 137(18), 123(25), 110(47), 95(88), 82(75), 67(74), 55(59), 41(100).

Anal. Calcd. for $C_{11}H_{15}O_2Br$: C, 51.01; H, 5.79

Found: C, 51.09; H, 5.90.

(1R*,3R*,6S*,8R*,10R*)-8-Hydroxy-1,10-dimethyltricyclo-[4.4.0.0^{3,8}]decan-2-one (100)

To 2 ml of methanol-water (50:50) which contained one pellet of potassium hydroxide was added 20 mg (0.10 mmol) of (1α,6α,10β)-1,10-dimethylbicyclo[4.4.0]decan-2,8-dione 69. This solution was stirred overnight at room temperature and then diluted with water and extracted with benzene. The organic extract was washed with water and evaporated at reduced pressure. It gave a quantitative recovery of an oil. Glpc analysis (4% QF-1, 195°) of this oil indicated it was a mixture of ketol 100 (71%) and unreacted starting material (29%). Preparative glpc gave an analytical sample (mp 106-107°) which rapidly lost its crystalline properties on exposure to the air and which could not be recrystallized. The spectroscopic properties of 100 were observed to be: ir(CCl_4) 3590, 3400, 1725, 1455, 1378, 1315, and 1070 cm^{-1}; nmr(d_6-DMSO) δ 0.67(d, J = 6.5 Hz, 3H), 0.81(s, 3H), 0.85-2.40(m, 11H), 4.96(s, 1H); mass spectrum (70 eV) m/e (rel intensity) 194(35), 110(91), 95(28), 81(29), 69(75), 55(47), 41(100).

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34

Found: C, 74.14; H, 9.51.

Preparation of trans-1,10-Dimethyl-8(p-bromobenzenesulfonoxy)-tricyclo[4.4.0.$0^{3,8}$]decan-2-one (Fig 2)

A solution of 90 mg (0.22 mmol) of ketol 100 in 2 ml of dry pyridine was treated at 0^0 with a large excess of p-bromobenzenesulfonyl chloride. After complete dissolution the resulting solution was stirred at room temperature for three days, and then poured into water at 0^0, stirred, and extracted with ether. The organic phase was washed sequentially with dilute hydrochloric acid, water, and saturated sdoium bicarbonate solution and dried over anhydrous sodium sulfate. Careful evaporation gave 133 mg (70%) of white crystals. A portion of these were dissolved in ether and placed in a closed vial from which very slow evaporation of the solvent gave excellent single crystals appropriate for collecting three dimensional X-ray data. An analytical sample had mp $124-125^0$: ir(CCl_4) 1734, 1325-1380, 1178, 920, 868 cm^{-1}; nmr ($CDCl_3$) δ 0.88(d, J = 6.5 Hz, 3H), 0.92(s, 3H), 1.20-2.86(m, 11H), 7.78(s, 4H); mass spectrum (70 eV) m/e (rel intensity) 414(3), 412(3), 221(6), 219(6), 193(45), 176(24), 157(14), 155(14), 148(28), 133(12), 120(12), 110(100), 93(17), 81(14), 69(21), 55(21).

Anal. Calcd. for $C_{18}H_{21}BrO_4$: C, 52.31; H, 5.12

Found: C, 52.29; H, 5.21.

Acid Treatment of Substituted Tricyclo[4.4.0.$0^{1,5}$]decan-9-ones

The general method for acid-catalyzed ring opening of tricyclo[4.4.0.$0^{1,5}$]decan-9-ones is illustrated by the

reaction of cyclopropanol 4 with hydrogen chloride in aqueous methanol.

(a) Acid Treatment of (1R*,5α,6β)-5-Hydroxy-6-methyltricyclo[4.4.0.0^{1,5}]decan-9-one (4)

A solution of 200 mg (1.11 mmol) of cyclopropanol 4 in 10 ml of a 50:50 MeOH-H_2O solution was treated with concentrated hydrochloric acid until a pH < 1 was obtained. After the mixture was stirred at room temperature for 2 days, the solution was diluted with water and extracted with benzene. The organic phase was washed with water and saturated sodium chloride solution. Evaporation of the solvent gave an oil which was separated by preparative glpc into five components. Three minor products (46, 13%; 47, 5%; and 48, 15%) were identical to those obtained from the base-catalysis of 4. The two major products were oils, cyclopropyl methyl ethers 91 and 90, which have the following constitution:

(1) (1S*,3α,6α)-3-Methoxy-6-methyltricyclo-[4.4.0.0^{1,3}]decan-9-one 91 (44%): ir(Film) 1705, 1439, 1234, 1045; pmr($CDCl_3$) δ 0.34(d, J = 5.5 Hz, 1H), 0.74(d, J = 5.5 Hz, 1H), 1.32(s, 3H), 1.36-2.80(m, 10H), 3.37(s, 3H); mass spectrum (70 eV) m/e (rel intensity) 194(14), 179(100), 151(26), 138(27), 123(80), 110(35), 91(36);

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34,
Found: C, 73.92; H, 9.45.

(2) (1R*,5α,6β)-5-Methoxy-6-methyltricyclo-[4.4.0.$0^{1,5}$]decan-9-one 90 (20%): ir(film) 1710 cm^{-1}; pmr($CDCl_3$) 1.12(s, 3H), 1.20-2.80(m, 12H), 3.37(s, 3H); mass spectrum (70 eV) m/e (rel intensity) 194(12), 179(100), 151(15), 137(88), 123(31), 105(34), 93(38), 91(50), 79(47).

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34

Found: C, 74.00; H, 9.41.

(b) Acid Treatment of (1R*,5α,6β,10ξ)-5-Hydroxy-6,10-dimethyltricyclo[4.4.0.$0^{1,5}$]decan-9-one 62

Acid-catalyzed ring opening of 250 mg (1.29 mmol) of cyclopropanol 62 yielded 248 mg of an oil. Preparative glpc (4% QF-1, 170°) gave three products [92 (21%); 93 (11%); and 94 (3%)], identical to those obtained from the base-catalysis of 62, and two methoxy ethers which had the following properties:

(1) (1R*,2S*,6R*,7R*)-2-Methoxy-1,7-dimethyl-tricyclo[4.4.0.$0^{2,7}$]decan-8-one (95, 31% yield): ir(film) 1708, 1318, 1231, 1065, 1042 cm^{-1}; pmr($CDCl_3$) δ 0.94 (s, 3H), 1.30(s, 3H), 1.32-2.85(m, 11H), 3.28(s, 3H); mass spectrum (79 eV) m/e (rel intensity) 208(22), 193(100), 175(18), 165(20), 161(16), 151(23), 137(52), 124(38), 105(53), 91(44), 79(44).

Anal. Calcd. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68

Found: C, 74.94; H, 9.62.

(2) (1R*,2S*,4S*,6S,7R*)-2-Methoxy-1,7-dimethyltricyclo[4.4.0.0^{2,9}]decan-8-one (96, 6% yield): ir(film) 1710, 1450, 1150, 1014 cm^{-1}; pmr($CDCl_3$) δ 1.04(s, 3H), 1.05 (d, 7.0 Hz, 3H), 1.20-2.70(m, 11H), 3.26(s, 3H); mass spectrum (70 eV) m/e (rel intensity) 208(18), 151(100), 137(32), 121(26), 105(26), 91(33), 79(31).

Anal. Calcd. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68

Found: C, 74.69; H, 9.62.

(c) Acid Treatment of (1R*,5β,6α,7α)-5-Hydroxy-6,7-dimethyltricyclo[4.4.0.0^{1,5}]decan-9-one (63)

Acid treatment of 130 mg (0.67 mmol) of cyclopropanol 63 yielded 124 mg of an oily residue. The trans-hydrindandione 97 (11%), identical to the major product obtained from the base catalysis of 63, and two methoxy ethers were separated by preparative glpc (4% QF-1, 180°):

(1) (1S*,3α,5α,6α)-3-Methoxy-5,6-dimethyltricyclo-[4.4.0.0^{1,3}]decan-9-one 99 (57%): ir(film) 1708, 1325, 1234, 1050 cm^{-1}; pmr($CDCl_3$) δ 0.32(d, J = 5.5 Hz, 1H), 0.80-0.99 [m, 4H, simplifying to a doublet (J = 6.0 Hz, 3H) upon spin decoupling at 0.32], 1.23(s, 3H), 1.32-2.79(m, 11H), 3.30(s, 3H); mass spectrum (70 eV) m/e (rel intensity) 208(16), 193(54), 165(80), 137(70), 123(100), 105(36), 91(40), 79(38).

(2) (1R*,5β,6α,7α)-5-Methoxytricyclo[4.4.0.0^{1,5}]dec-9-one 98 (27%): ir(film) 1708 cm^{-1}; pmr($CDCl_3$)

δ 0.92(s, 3H), 1.06(d, J = 6.5 Hz, 3H), 1.20-2.81(m, 13H), 3.32(s, 3H); mass spectrum (70 eV) m/e (rel intensity) 208(19), 193(26), 177(17), 165(35), 151(41), 138(100), 123(39), 105(28), 93(44), 91(37).

(d) Acid Treatment of (1R*,5α,6β,7α)-5-Hydroxy-6,7-dimethyltricyclo[4.4.0.0^{1,5}]decan-9-one (50)

Acid treatment of 230 mg (1.18 mmol) of a mixture of cyclopropanol 50 and the trans-decalindione 66, prepared by the dissolving metal reduction of enedione 55, gave a quantitative yield of an oil from which four components were separated by preparative glpc. In addition to 66 (23%), two of these products [100 (26%), 69 (36%)] were identical to those obtained from base-catalyzed reaction of 50. A minor product, 101 (5%), which had properties identical to the methyl ether obtained from the treatment of cis-decalindione 69 in methanol with HCl, was also isolated.

(e) Acid Treatment of (1R*,5α,6β,8α)-5-Hydroxy-6,8-dimethyltricyclo[4.4.0.0^{1,5}]decan-9-one (64)

Acid treatment of 300 mg (1.54 mmol) of 64 yielded 237 mg of crude product, from which three compounds were separated by preparative glpc (4% QF-1, 185°). Two of these products [the empimeric cis-decalindiones 103 and 104 (combined yield 19%) and the epimeric trans-hydrindanes 102 (5%)] were identical to those obtained from the base-catalyzed ring opening of 64. A rearranged cyclopropyl

methyl ether, (1S*,3α,4β,6α)-3-methoxy-4,6-dimethyltricyclo-[4.4.0.0^{1,3}]decan-7-one 105 (oil, 32%) was also isolated: ir(film) 1708, 1445, 1232, 1050, 1018 cm^{-1}; pmr($CDCl_3$) δ 0.24(d, J = 5.5 Hz, 1H), 0.73(d, J = 5.5 Hz, 1H), 0.98(d, J = 6.5 Hz, 3H), 1.32(s, 3H), 1.41-2.78(m, 9H), 3.33(s, 3H); mass spectrum (70 eV) m/e (rel intensity) 208(10), 193(100), 176(8), 165(30), 152(18), 137(57), 123(54), 105(33), 91(33), 72(42).

Synthesis of Substituted 8-Methoxy Twistane Derivatives

The general procedure for the preparation of 8-methoxy-twistane derivatives from their corresponding cis-decalin-diones is illustrated by the reaction of 69 in anhydrous MeOH with dry HCl.

(a) (1R*,3R*,6S*,8R*,10R*)-8-Methoxy-1,10-dimethyl-tricyclo[4.4.0.0^{3,8}]decan-2-one (101)

A solution of 22.5 mg (0.108 mmol) of (1α,6α,10β)-1,10-dimethylbicyclo[4.4.0]decan-2,8-dione 64 in 4 ml of absolute methanol was maintained at 0° while anhydrous hydrogen chloride was added over a 2 minute period. The reaction was then allowed to warm to room temperature and stirred for 1 hour, following which the solvent was removed at reduced pressure. The residue was dissolved in ether, washed sequentially with saturated sodium chloride solution and saturated sodium bicarbonate solution and dried. Removal of the solvent gave an oil which was purified by

passing through a short silica gel column. Removal of the solvent gave 23.8 mg (98%) of 101 as an oil with the following physical properties: ir(neat) 1726, 1451, 1135, 1110, 1090, and 1074 cm^{-1}; pmr($CDCl_3$) δ 0.80(d, H, J = 6.0 Hz), 0.91(s, 3H), 1.00-2.42(m, 11H), 3.23(s, 3H); mass spectrum (70 eV) m/e (rel intensity) 208(13), 193(4), 176(8), 110(100), 99(63).

Anal. Calcd. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68

Found: C, 74.96; H, 9.72.

The oil thus obtained could be crystallized from wet ether (mp 45-46°); however, ir absorption at 3410 cm^{-1} suggested water was incorporated in the crystal lattice. The carbonyl absorption appeared unchanged.

(b) (1R*,3R*,6S*,8R*,9S*)-8-Methoxy-1,9-dimethyltricyclo[4.4.0.$0^{3,8}$]decan-2-one (106)

Acid treatment of 41 mg (0.21 mmol) of 106 yielded a single product (106, 44%), separated as an oil from unreacted starting material by preparative glpc (4% QF-1, 180°): ir(film) 1728, 1450, 1182, 1167, 1082, 1047, 995 cm^{-1}; pmr (CCl_4) δ 0.90(s, 3H), 0.91(d, J = 7.0 Hz, 3H), 1.09-3.68 (m, 11H), 3.15(s, 3H); mass spectrum (70 eV) m/e (rel intensity) 208(16), 110(100).

Acid Treatment of Cyclopropanol 117

To 50 mg (0.28 mmol) of cyclopropanol 4 in 9 ml of absolute MeOH was added 32.6 mg (16 meq) of solid $NaBH_4$.

The resulting solution was stirred for 3 1/2 hr at -44°, and then quenched with HOAc. After it was warmed to room temperature, 4 ml of water and 1/2 ml of concentrated hydrochloric acid was added and the resulting solution was stirred overnight. Following the addition of more water and extraction with benzene, the organic phase was washed sequentially with water and saturated $NaHCO_3$ solution. Glpc analysis (4% QF-1, 185°) indicated the formation of the isomeric spiro ketols 118 and 119 in a 93:6 product ratio. Jones oxidation gave the spiro diketone 47 in 94% yield: ir(CCl_4) 1710, 1739 cm^{-1}. The amount of trans-hydrinandione 46 or cis-decalindione 48 produced was less than 1%.

Base Treatment of Cyclopropanol 117

Cyclopropanol 117, prepared as previously described by the reduction of 300 mg (1.66 mmol) of cyclopropanol 4 with 160 mg (4.21 mmol) of $NaBH_4$ in 15 ml of absolute MeOH, was treated in situ with KOH until a pH > 13 was achieved. The resulting solution was stirred overnight and then diluted with water and thoroughly extracted with benzene. The benzene extracts were washed with water, dried, and evaporated to give an oil. Glpc analysis (4% QF-1, 185°) indicated two components, spiro diketone 47 and cis-decalindione 48, in a 58:42 product ratio. Each product displayed spectral properties identical to those of the compound and melting points (47, 59-61°; 48, 64-66°) which remained unchanged when each was mixed with an authentic sample.

Reduction and Cleavage of (1S*,3α,6α)-3-Methoxy-6-methyltricyclo[4.4.0.0^{1,3}]decan-7-one (91)

(a) Cleavage with Boron Tribromide

To 130 mg (0.67 mmol) of cyclopropyl methyl ether 91 in 5 ml of absolute EtOH at 0^0 was added 25 mg (0.66 mmol) of $NaBH_4$. The reaction was stirred for 1 hr, quenched with HOAc, the solvent was evaporated at reduced pressure, and the residue was dissolved in water and thoroughly extracted with ether. The organic phase was washed with water and dried. Evaporation of the solvent gave an oil, which was dissolved in 5 ml of dry CH_2Cl_2 and cooled to a -78^0. This solution was treated with 0.20 ml (2.11 mmol) of BBr_3, and stirred for 1 hr.[60] The reaction mixture was then poured into cold water, extracted with benzene, and the organic phase washed with water and dried. Evaporation of the solvent followed by Jones oxidation[61] of the residue gave a single product, the trans-hydrindandione 46, and some starting material (cyclopropyl methyl ether 91) in a 72:28 ratio respectively. Spectra of the trans-hydrindandione were identical to those obtained for the major product (46) obtained from the base treatment of cyclopropanol 4 and the melting point (167-168^0) was undepressed when mixed with an authentic sample.

(b) Cyclopropyl methyl ether 91 (98 mg, 0.50 mmol) was reduced with 50 mg (1.31 mmol) of $NaBH_4$ in absolute EtOH

as previously described. The product obtained was dissolved in absolute MeOH, cooled to 0^0, and saturated with dry HCl. After it was stirred overnight, the solution was diluted with water, thoroughly extracted with benzene, and the organic phase was washed with water and saturated $NaHCO_3$ solution. Evaporation of the solvent followed by Jones oxidation of the residue yielded the trans-hydrindandione 46 (72%). None of the spiro diketone 47 or the cis-decalindione 48 were detected.

Preparation of Cyclopropyl Acetates 76 and 77

A solution of 0.18 ml (1.22 mmol) of diisopropyl amine in 0.6 ml HMPA at 0^0 was treated with 0.70 ml (1.33 mmol) of 1.9M n-BuLi, and stirred for 15 min. To the resulting lithium amide was added 200 mg (1.11 mmol) of cyclopropanol 4 in 1.2 ml DME followed by the addition of 0.7 ml of TMEDA. After it was stirred for 1 1/2 hr, during which period the solution gradually warmed to room temperature, the reaction was quenched with 6 ml of Ac_2O and stirred for an additional 15 min. This mixture was poured into ice water saturated with $NaHCO_3$, stirred for 1 hr, and then thoroughly extracted with ether. The organic extracts were washed with water and dried over Na_2SO_4. Evaporation of the solvent gave an oil, best analyzed by a combination of 4% QF-1 and 4% SE-30 columns, and thereby shown to consist of four components:

(1) (1S*,3α,6α)-3-Acetoxy-6-methyltricyclo[4.4.0.0^{1,3}]-decan-7-one (77, 30%): ir(film) 1750, 1708, 1213 cm^{-1}; pmr($CDCl_3$) δ 0.37(d, J = 5.5 Hz, 1H), 0.95(d, J = 5.5 Hz, 1H); 1.03-2.90[m, 16H including one singlet at δ 1.45(3H) and another singlet at δ 2.07(3H)]; mass spectrum (70 eV) m/e (rel intensity) 222(1), 180(22), 147(62), 43(100).

Anal. Calcd. for CHO_2: C, 70.24; H, 8.16

Found: C, 70.22; H, 8.21.

(2) trans-1,6-Dimethylbicyclo[4.3.0]nona-2,7-dione (46, 16%): The pmr spectrum was identical to that of an authentic sample.

(3) (1R*,5α,6β)-5-Acetoxy-6-methyltricyclo[4.4.0.0^{1,5}]-decan-7-one (77, 40% yield): ir(film) 1745, 1715, 1265, 1215 cm^{-1}; pmr($CDCl_3$) δ 1.17(s, 3H), 1.21-2.70(n, 15H, including a singlet at δ 2.05); mass spectrum (70 eV) m/e (rel intensity) 222(2), 180(31), 162(48), 137(49), 43(100).

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 70.24; H, 8.16

Found: C, 70.17; H, 8.03.

(4) An enol acetate, isolated in 11% yield, was identified as 6-acetoxy-trans-dimethylbicyclo[4.4.0]non-6-ene-2-one on the strength of its pmr and mass spectra: pmr($CDCl_3$) 3 singlets at δ 1.11, 1.38, and 2.15 are superimposed on a multiplet, 5.29(m, 1H); mass spectrum (70 eV) m/e (rel intensity) 222(1), 180(86), 165(54), 162(41), 40(100).

Base Treatment of (1S*,3α,6α)-3-Acetoxy-6-methyltricyclo-[4.4.0.$0^{1,3}$]decan-7-one (77)

To 1 mg of cyclopropyl acetate 77 in 8 drops of MeOH was added 2 drops of 0.43M methanolic KOH, and the reaction was monitored by glcp with a 4% SE-30 analytical column. After several minutes, the reaction was complete. Glcp analysis (4% SE-30 and 4% QF-1) indicated the formation of a single major product, the trans-hydrindandione 46. No spiro diketone 47 or cis-decalindione 48 were observed from this reaction.

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APPENDIX A

SPECTRA

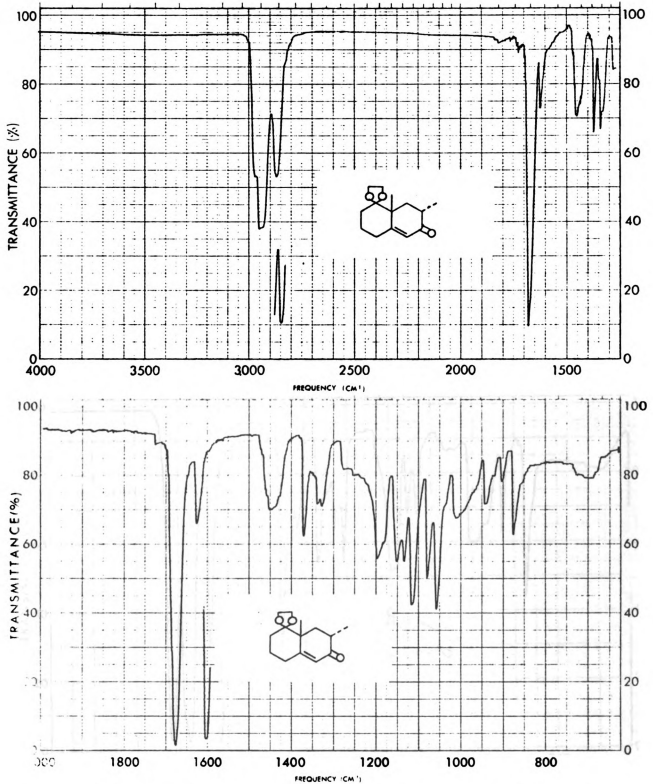


Figure 3. Infrared spectrum of trans-1,9-dimethylbicyclo-[4.4.0]dec-6-ene-2,8-dione 2-ethylene ketal (60).

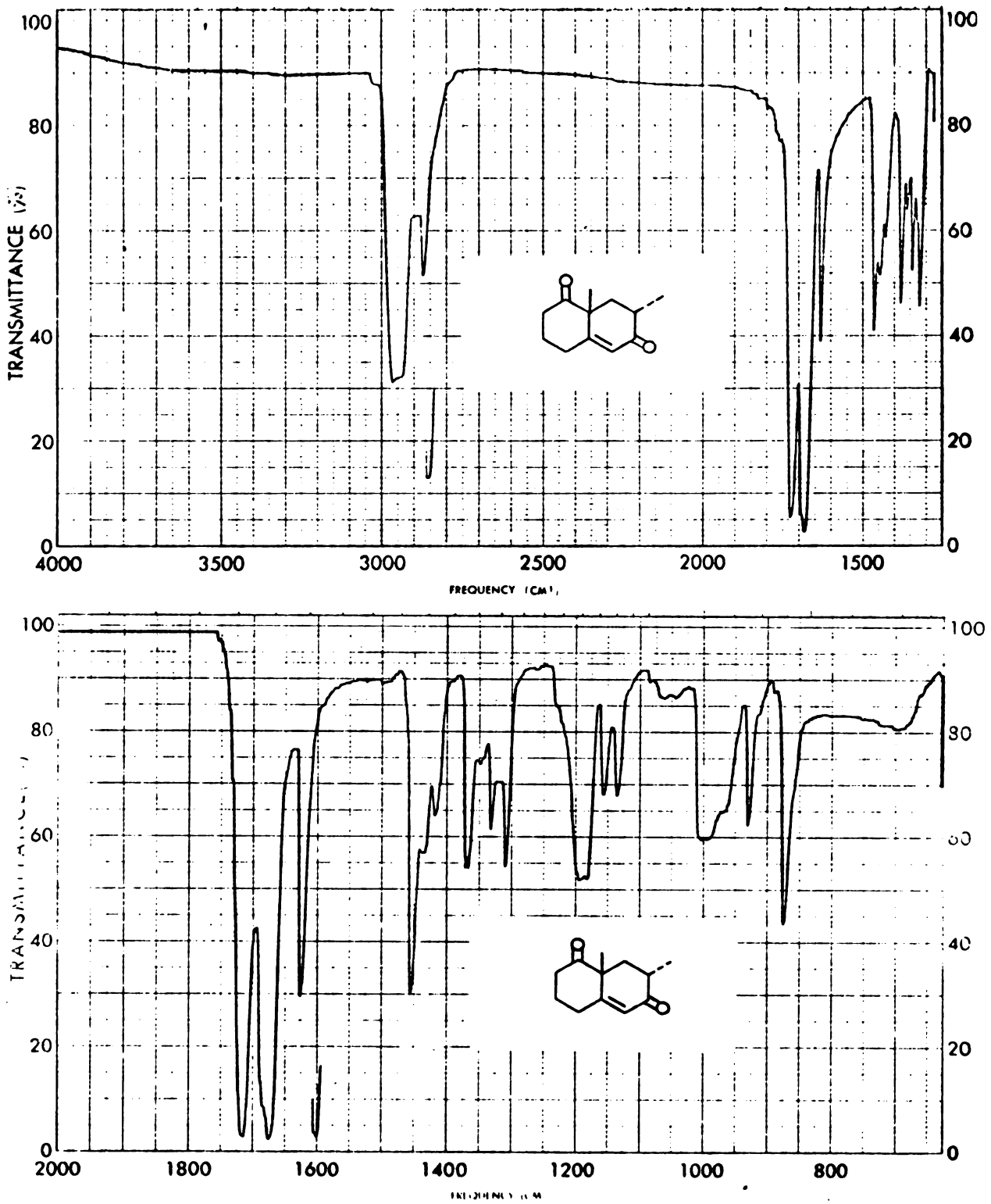


Figure 4. Infrared spectrum of trans-1,9-dimethylbicyclo-[4.4.0]dec-6-ene-2,8-dione (56).

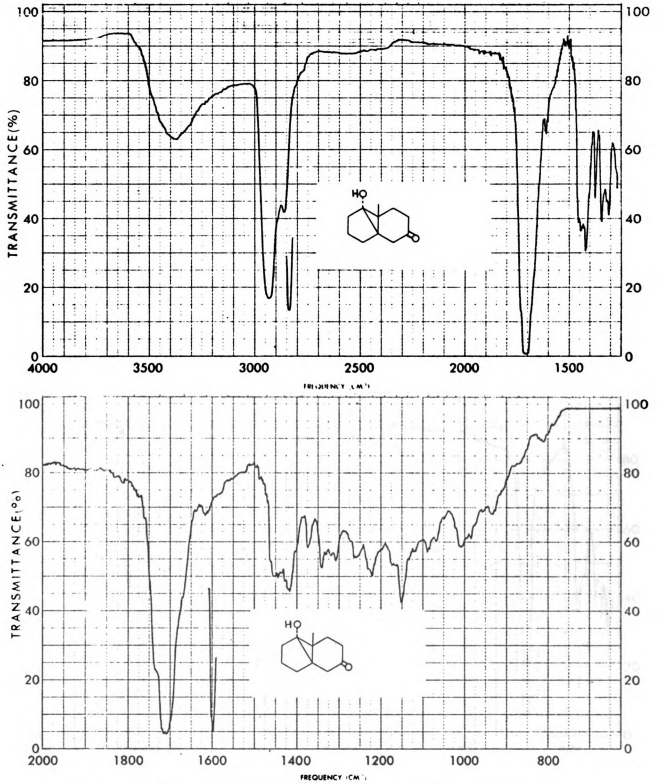


Figure 5. Infrared spectrum of (1R*,5α,6β)-5-hydroxy-6-methyltricyclo[4.4.0.0^{1,5}]decan-9-one (4).

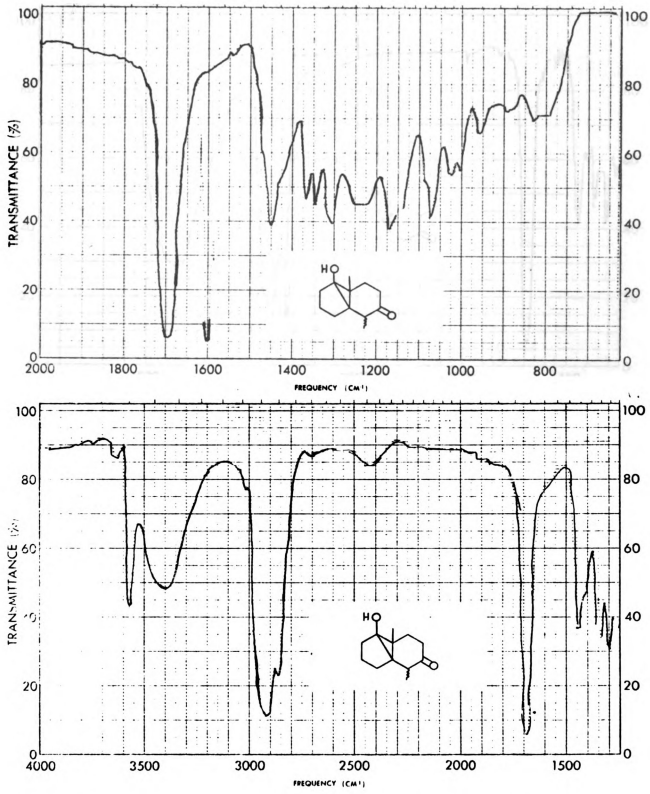


Figure 6. Infrared spectrum of (1R*,5α,6β,10β)-5-hydroxy-6,10-dimethyltricyclo[4.4.0.0^{1,5}]decan-9-one (62).

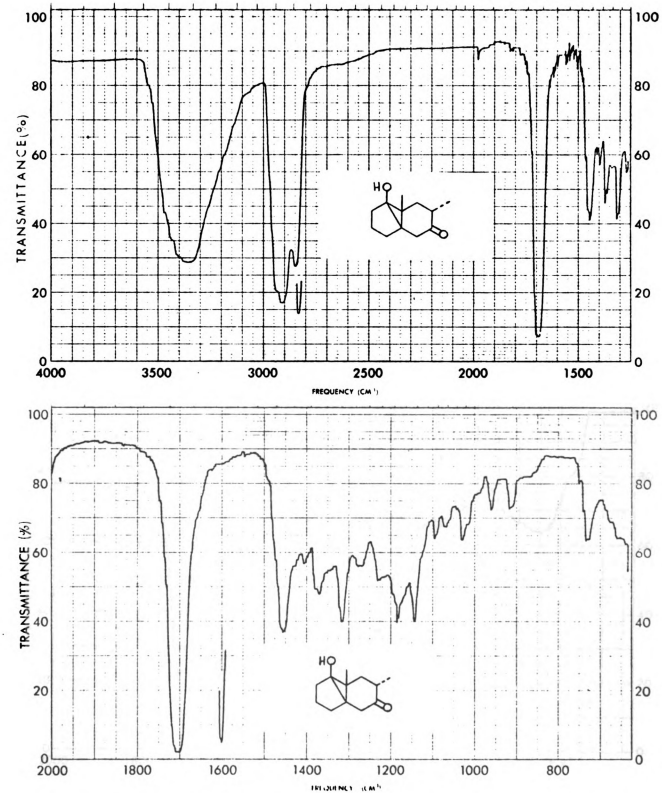


Figure 7. Infrared spectrum of (1R*,5α,6β,8α)-5-hydroxy-6,8-dimethyltricyclo[4.4.0.0^{1,5}]decan-9-one (64).

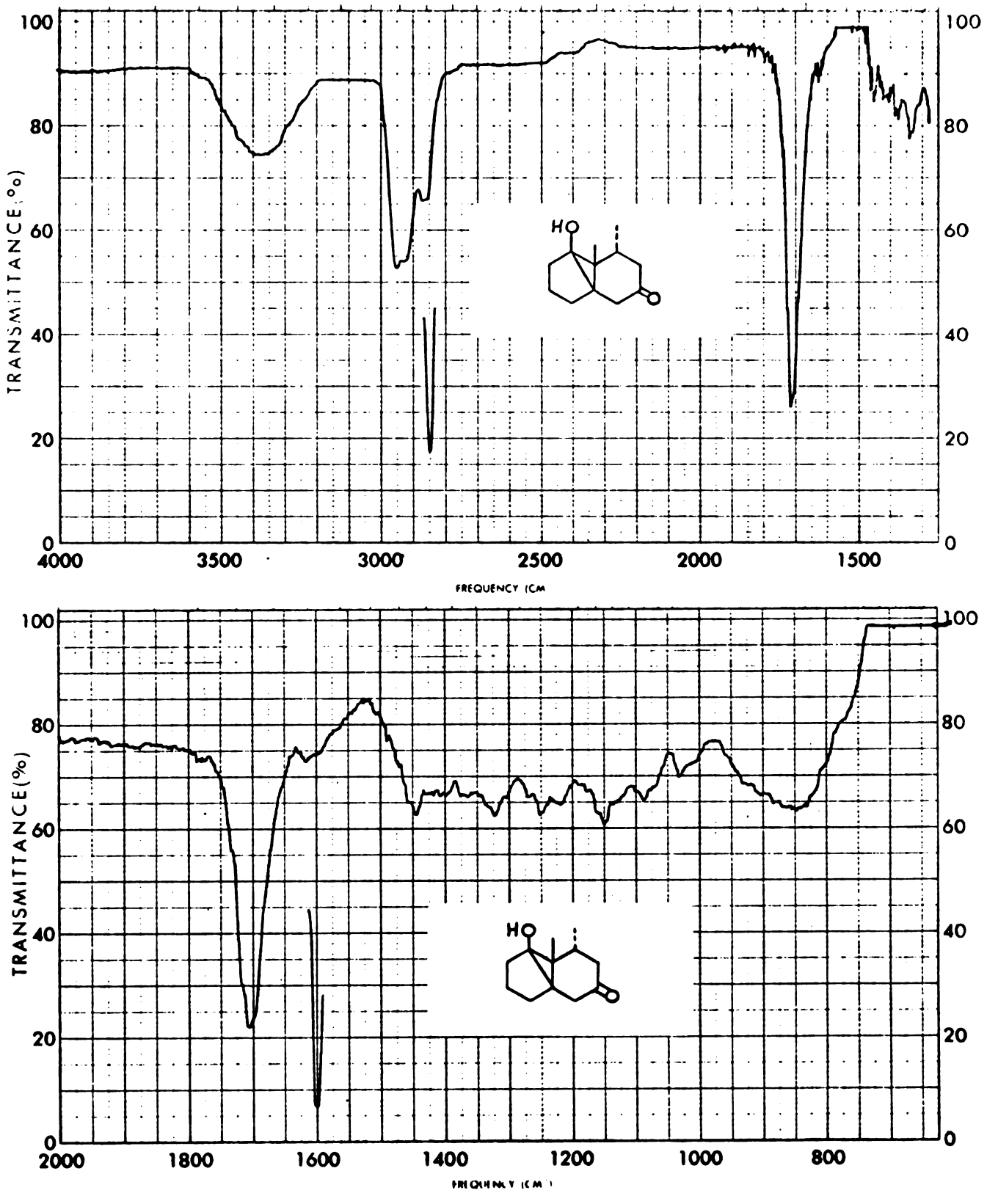


Figure 8. Infrared spectrum of (1R*,5α,6β,7α)-5-hydroxy-6,7-dimethyltricyclo[4.4.0.$\bar{0}^{1,5}$]decan-9-one (50).

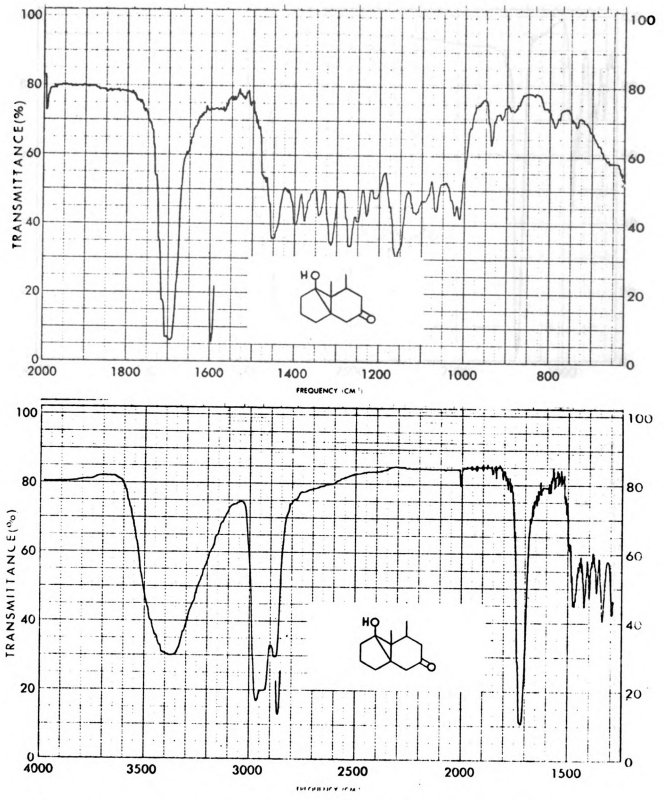


Figure 9. Infrared spectrum of (1R*,5β,6α,7α)-5-hydroxy-6,7-dimethyltricyclo[4.4.0.$0^{1,5}$]decan-9-one (63).

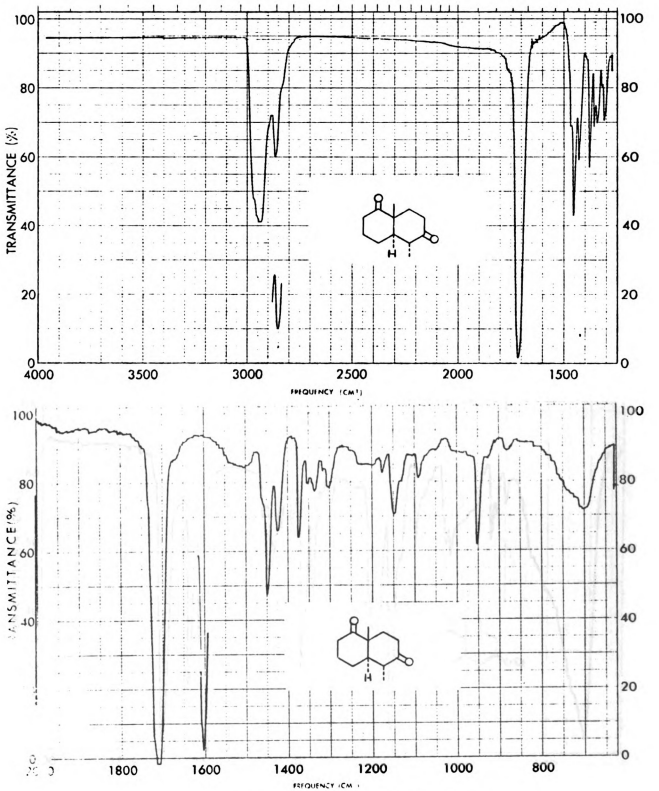


Figure 10. Infrared spectrum of (1β,6α,7 α)-1,7-dimethyl-bicyclo[4.4.0]decan-2,8-dione (65).

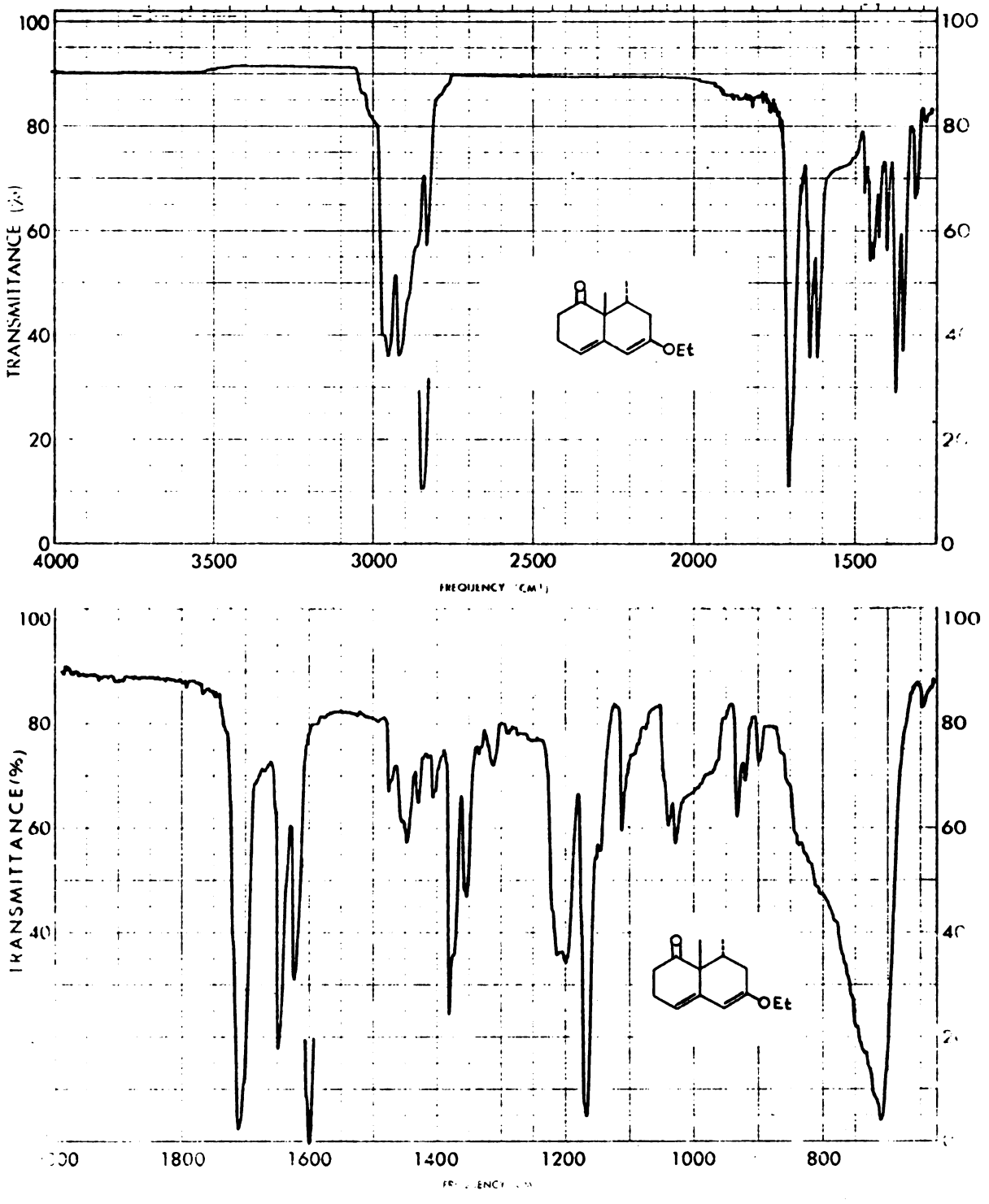


Figure 11. Infrared spectrum of 8-ethoxy-trans-1,10-dimethyl-bicyclo[4.4.0]dec-5,7-diene-2-one (58).

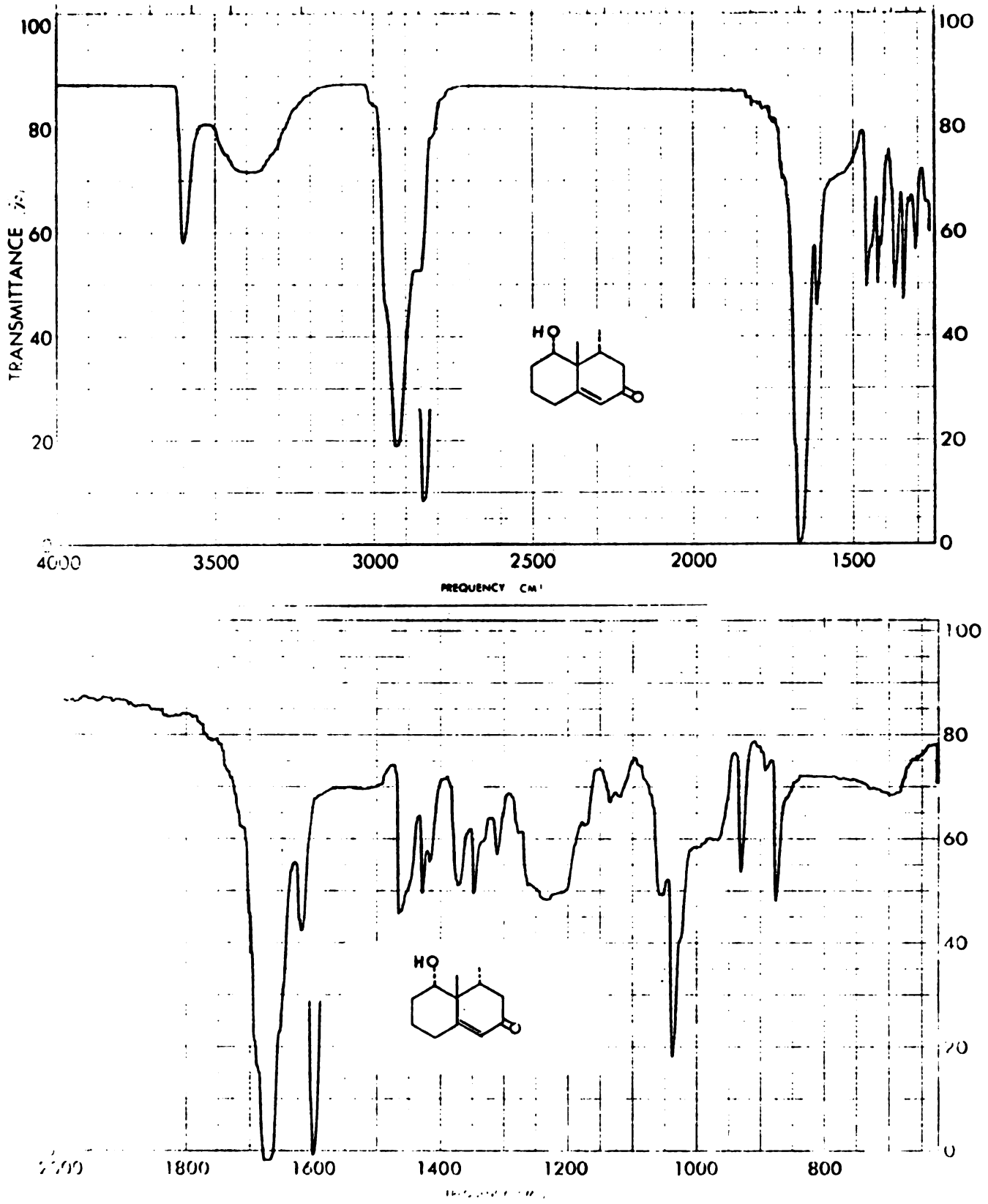


Figure 12. Infrared spectrum of (5α,6β,7α)-7-hydroxy-5,6-dimethylbicyclo[4.4.0]dec-1-ene-3-one (67).

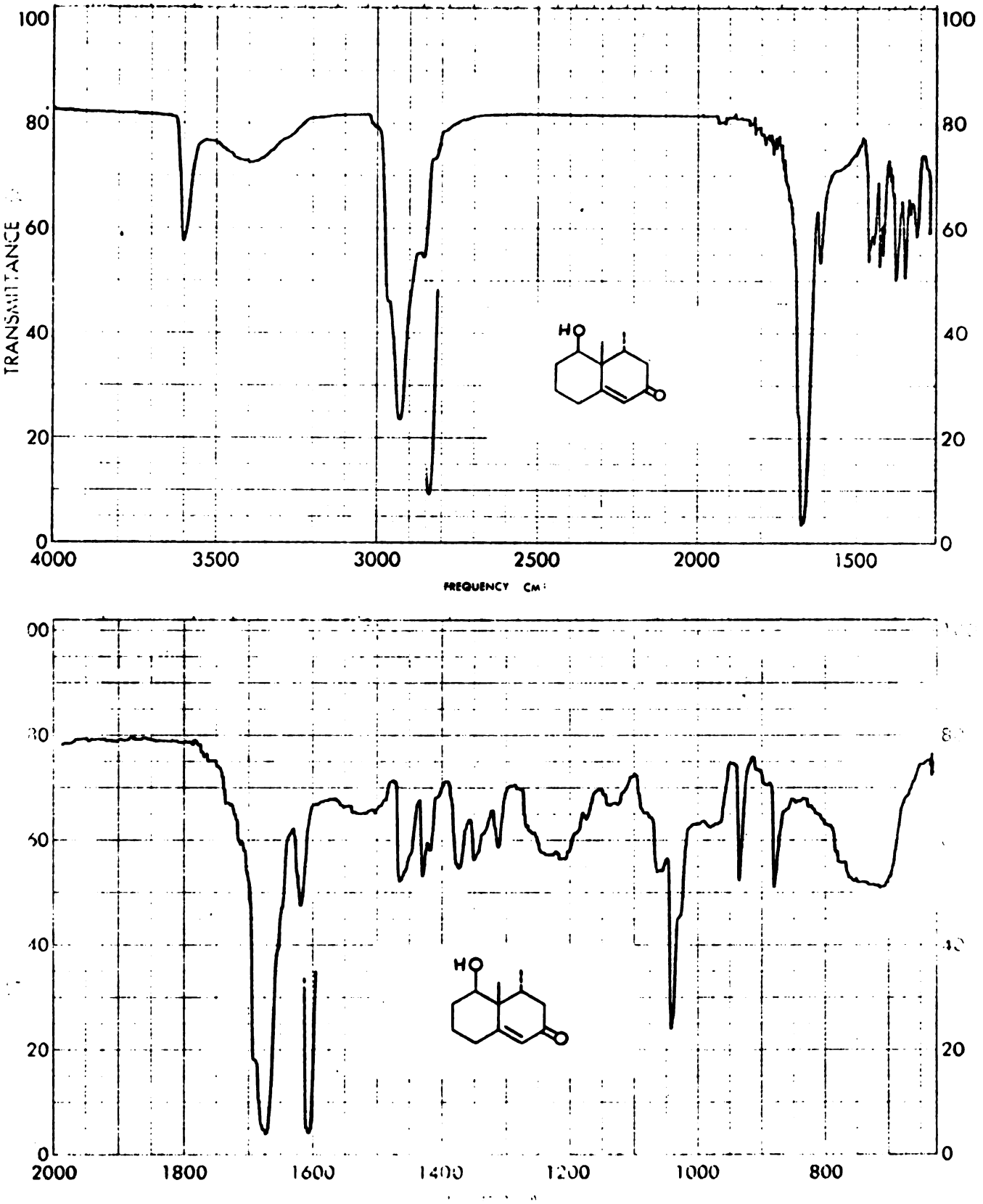


Figure 13. Infrared spectrum of (5β,6α,7α)-7-hydroxy-5,6-dimethylbicyclo[4.4.0]dec-1-ene-3-one (68).

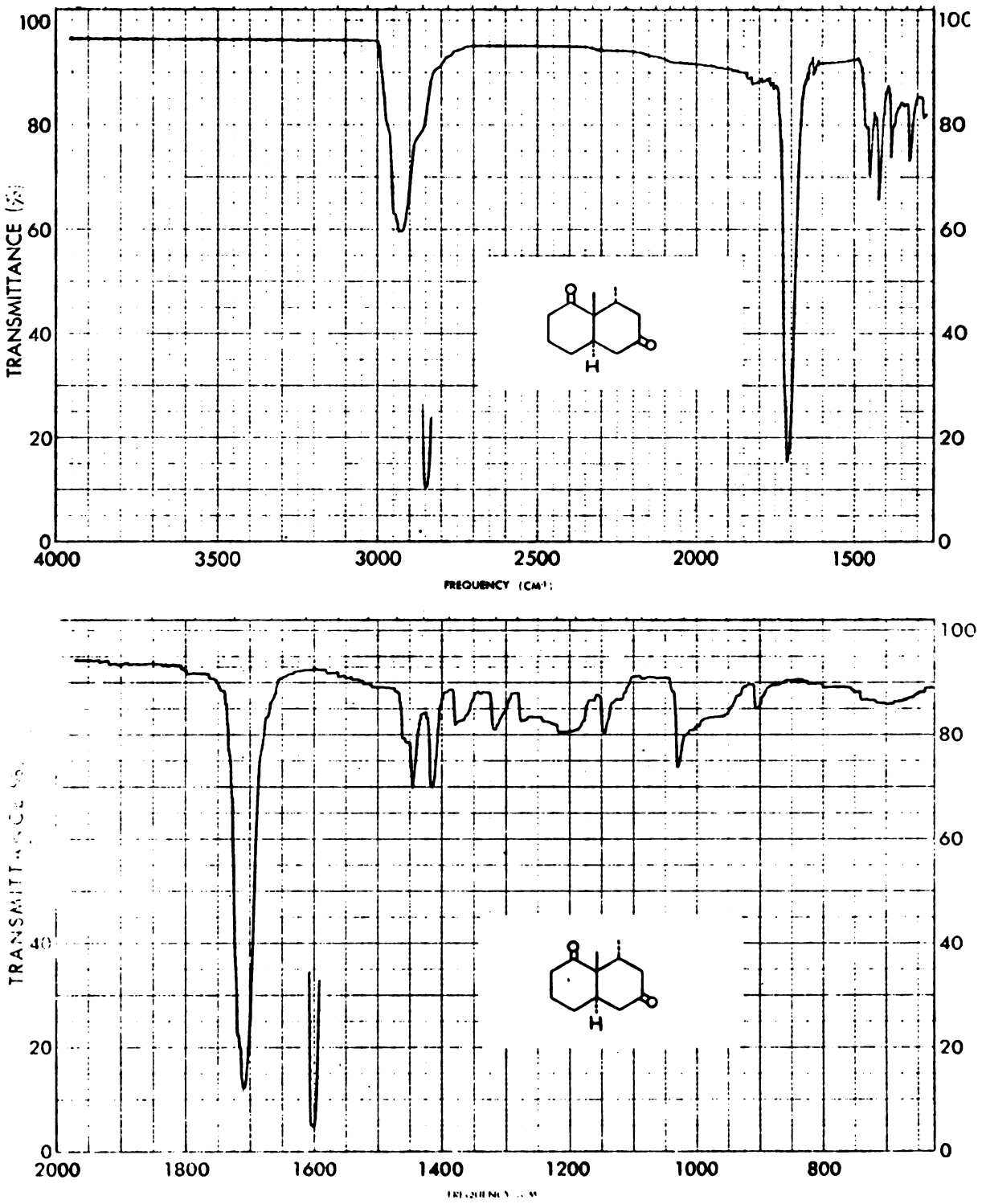


Figure 14. Infrared spectrum of (1β,6α,10α)-1,10-dimethyl-bicyclo[4.4.0]decan-2,8-dione (66).

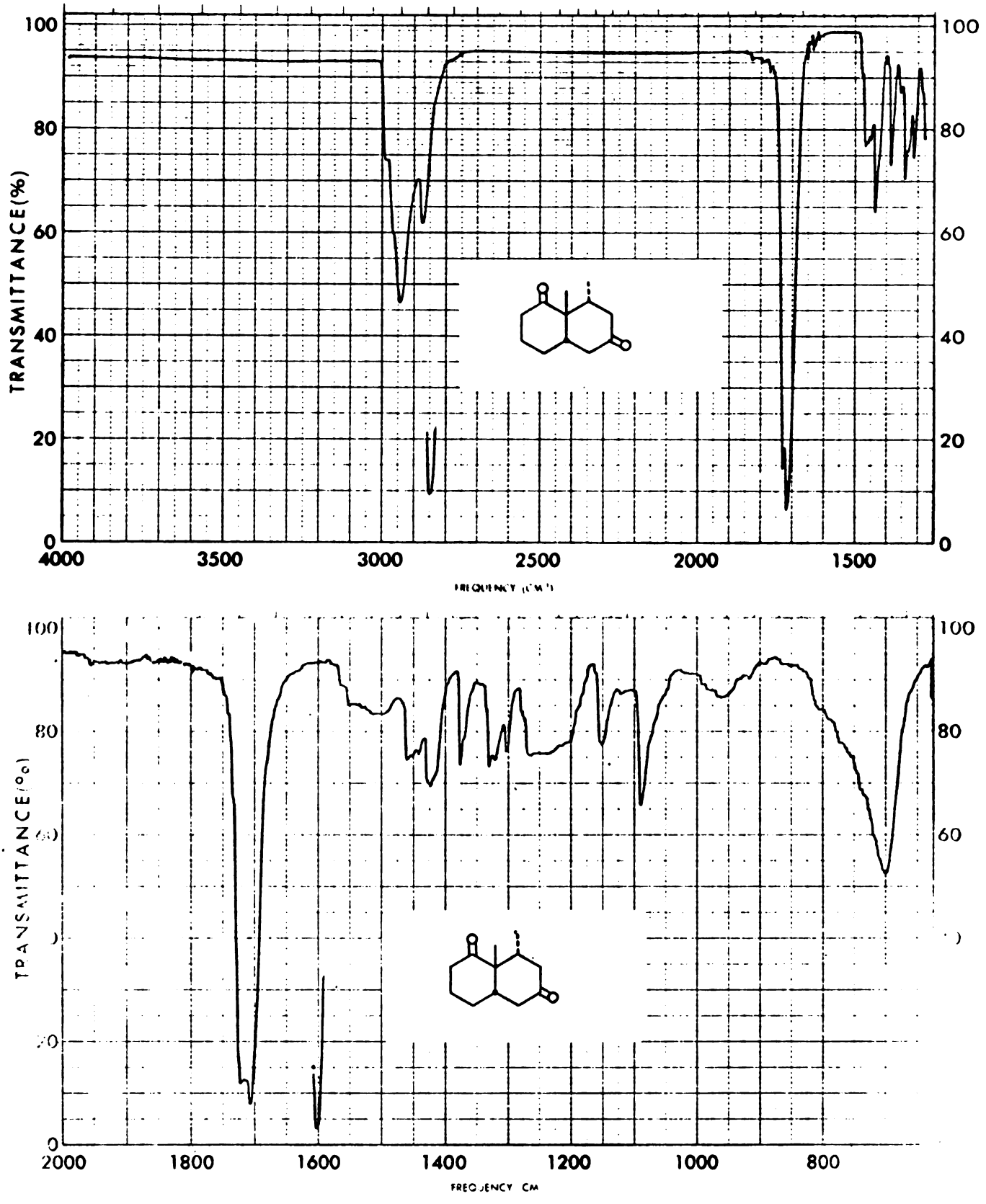


Figure 15. Infrared spectrum of (1α,6α,10β)-1,10-dimethyl-bicyclo[4.4.0]decan-2,8-dione (69).

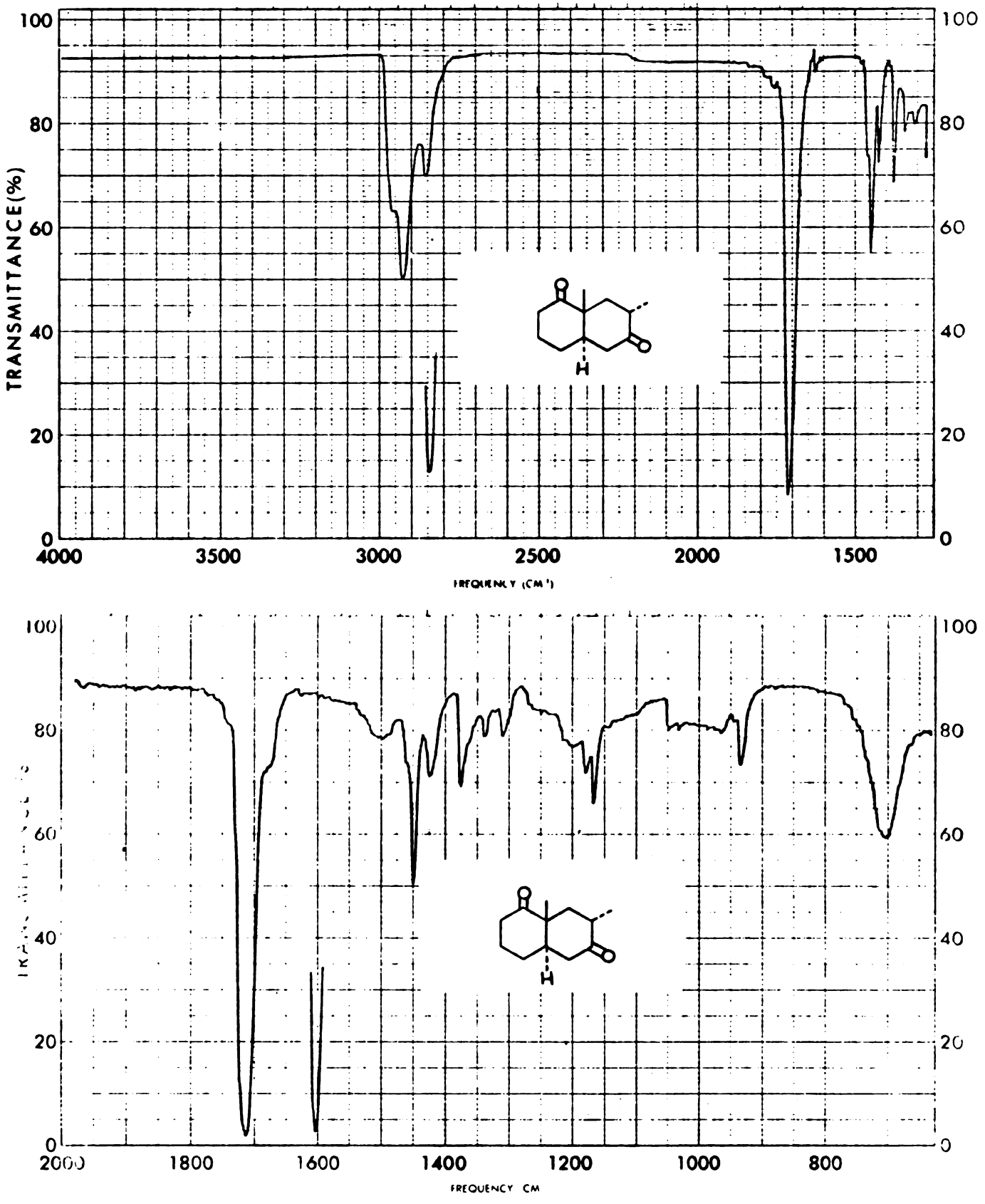


Figure 16. Infrared spectrum of (1β,6α,9α)-1,9-dimethyl-bicyclo[4.4.0]decan-2,8-dione (110).

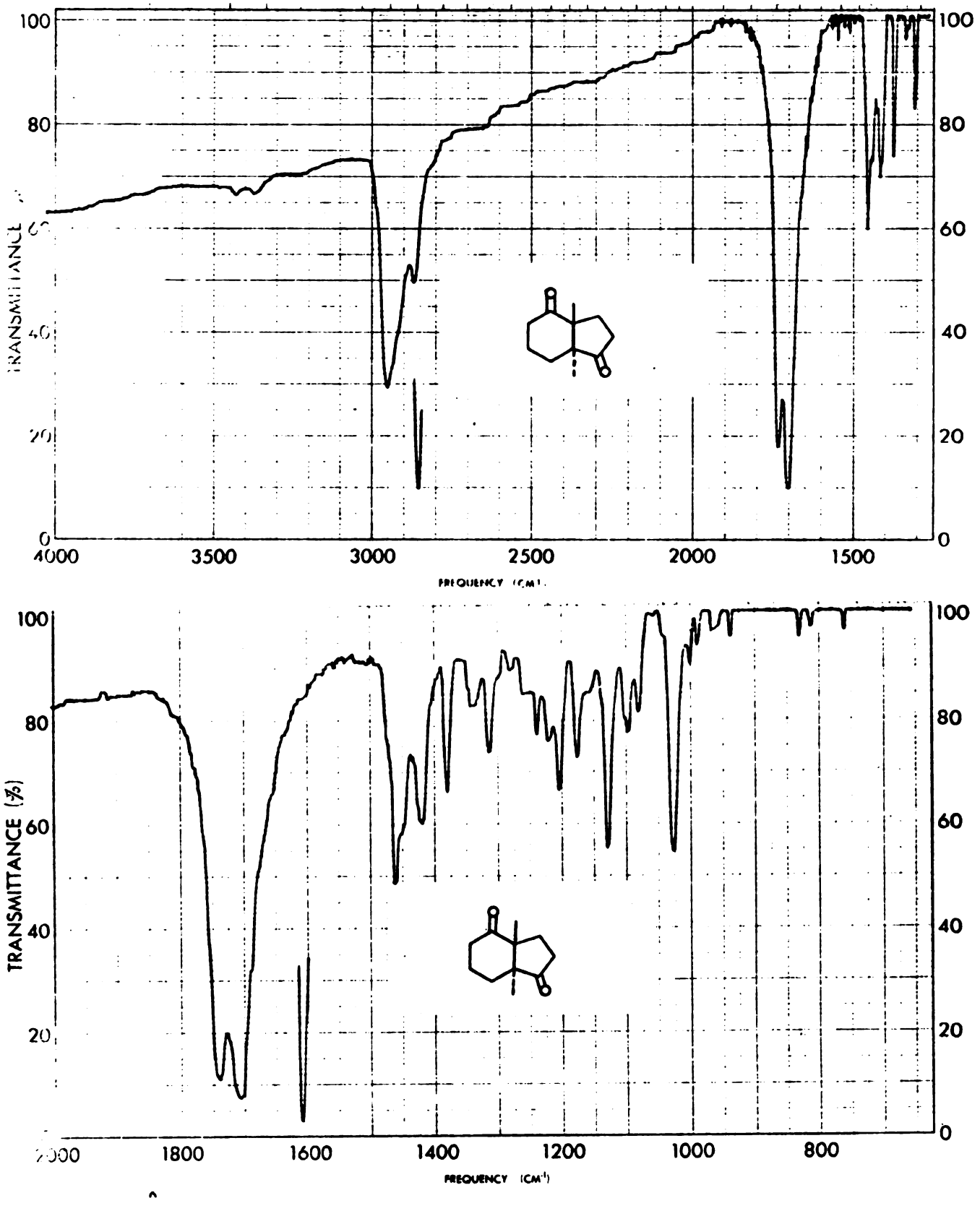


Figure 17. Infrared spectrum of trans-1,6-dimethylbicyclo-[4.3.0]nona-2,7-dione (46).

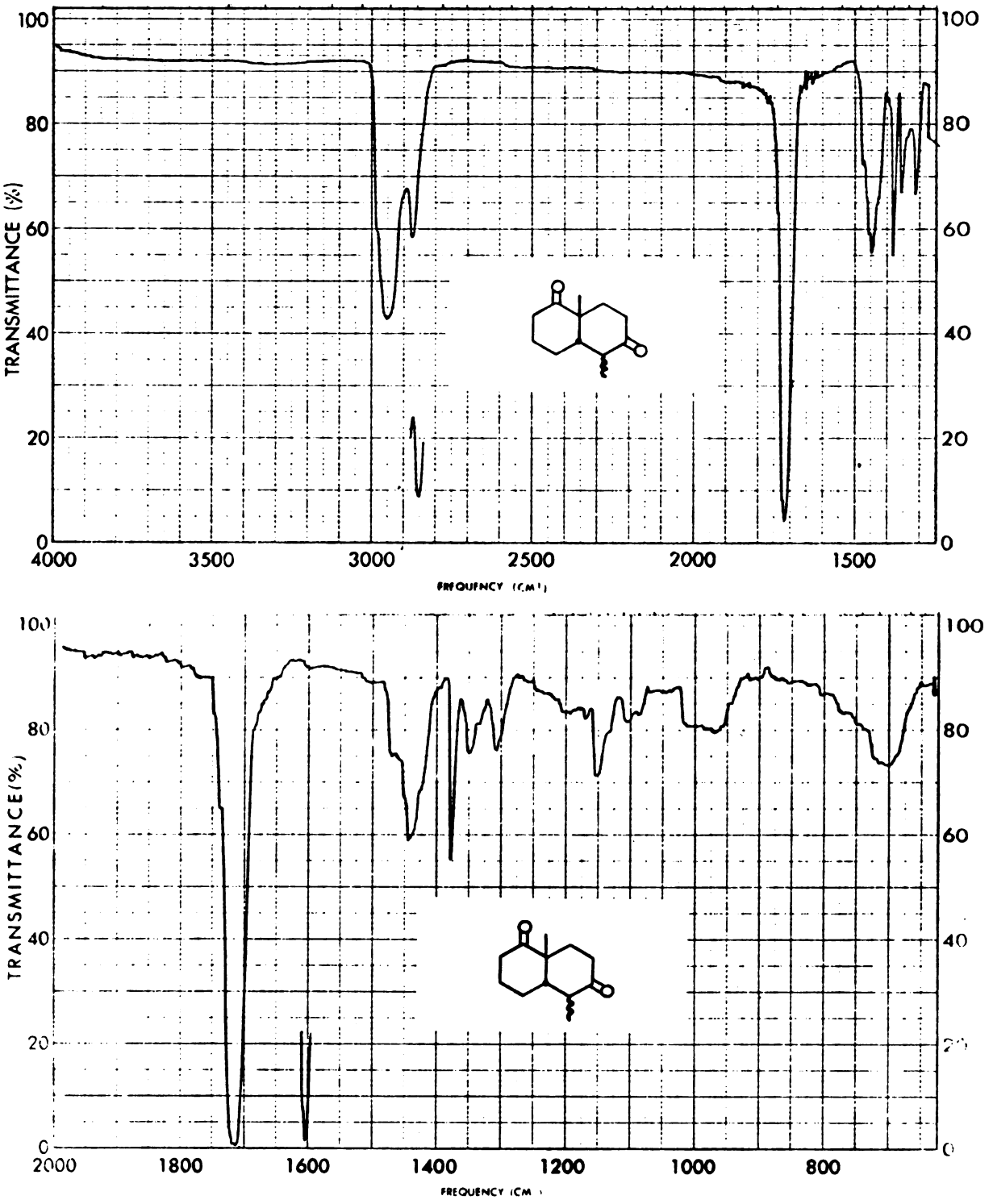


Figure 18. Infrared spectrum of (1α,6α,7ξ)-1,7-dimethylbicyclo[4.4.0]decan-2,8-dione (92 and 93).

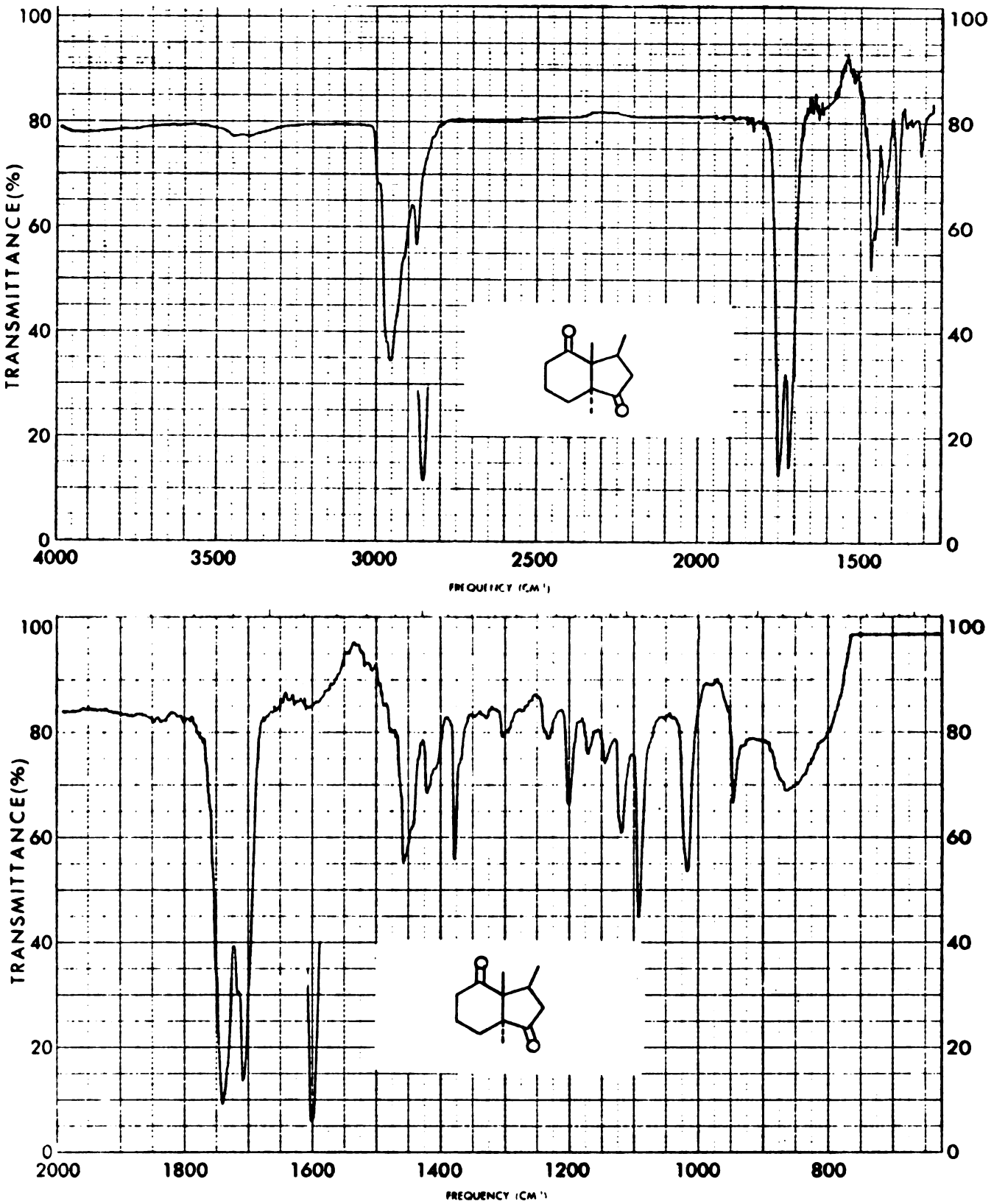


Figure 19. Infrared spectrum of (1α,6β,9α)-trimethylbicyclo-[4.3.0]nona-2,7-dione (97).

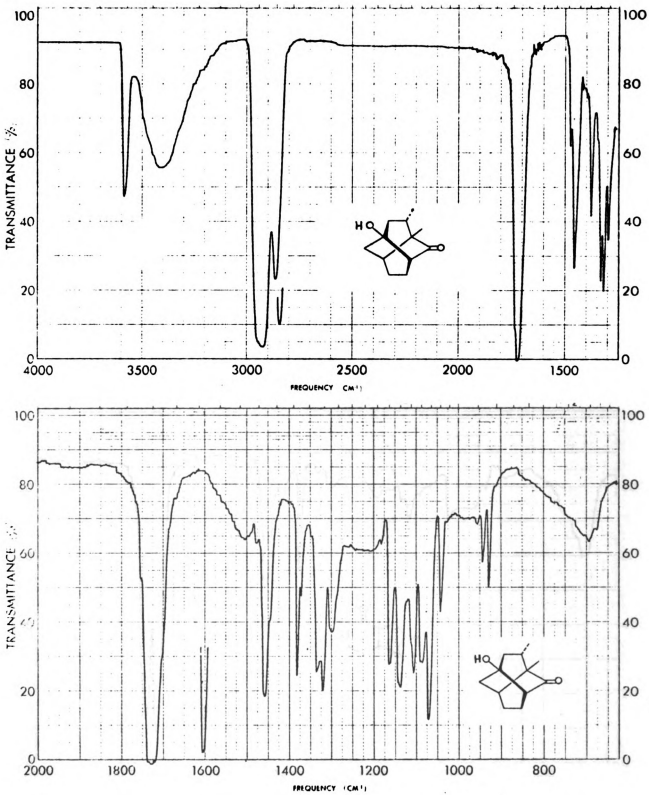


Figure 20. Infrared spectrum of (1R*,3R*,6S*,8R*,10R*)-8-hydroxy-1,10-dimethyltricyclo[4.4.0.0^{3,8}]decan-2-one (100).

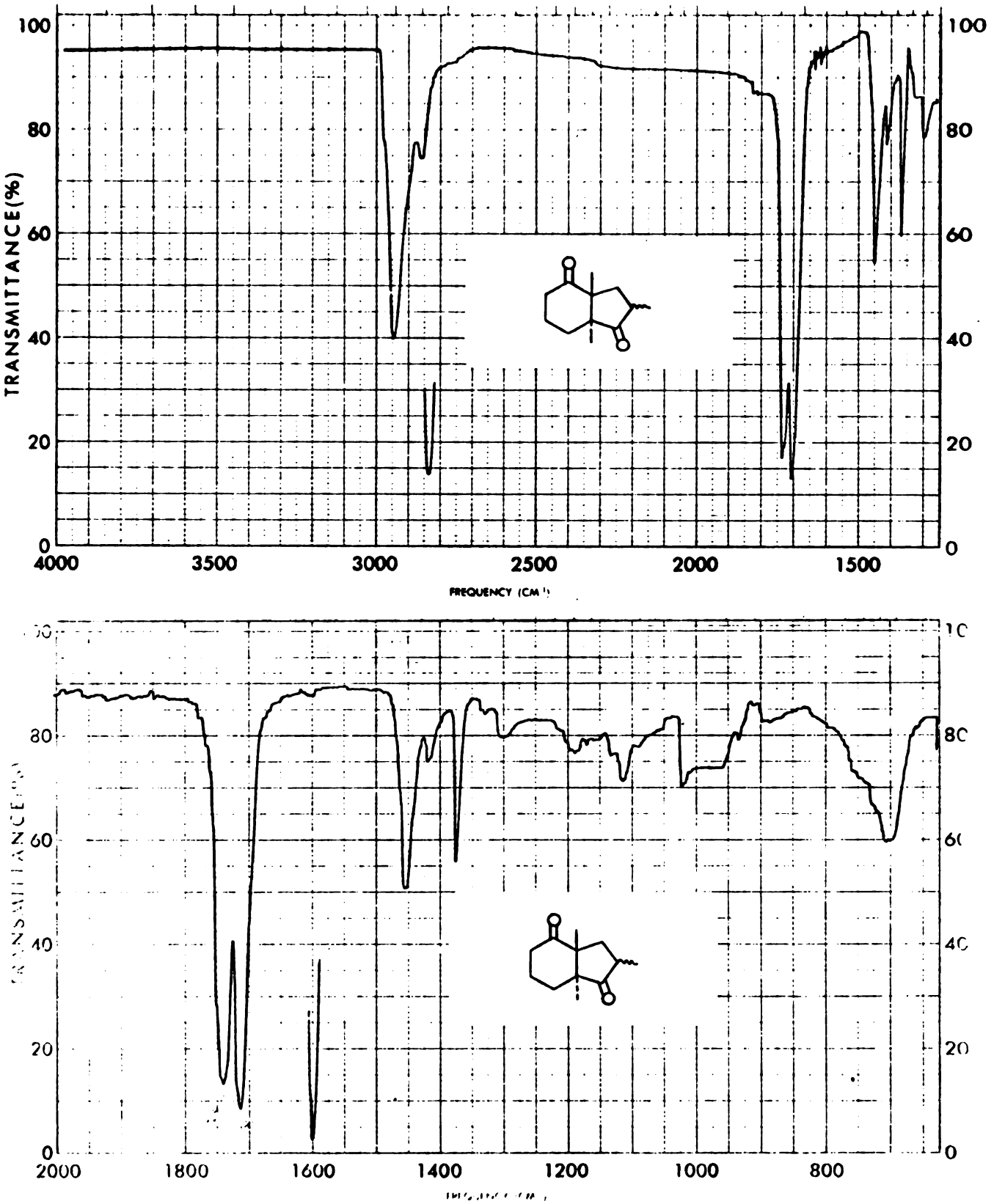


Figure 21. Infrared spectrum of (1α,6β,8ξ)-1,6,8-trimethyl-bicyclo[4.3.0]decan-2,8-dione (102).

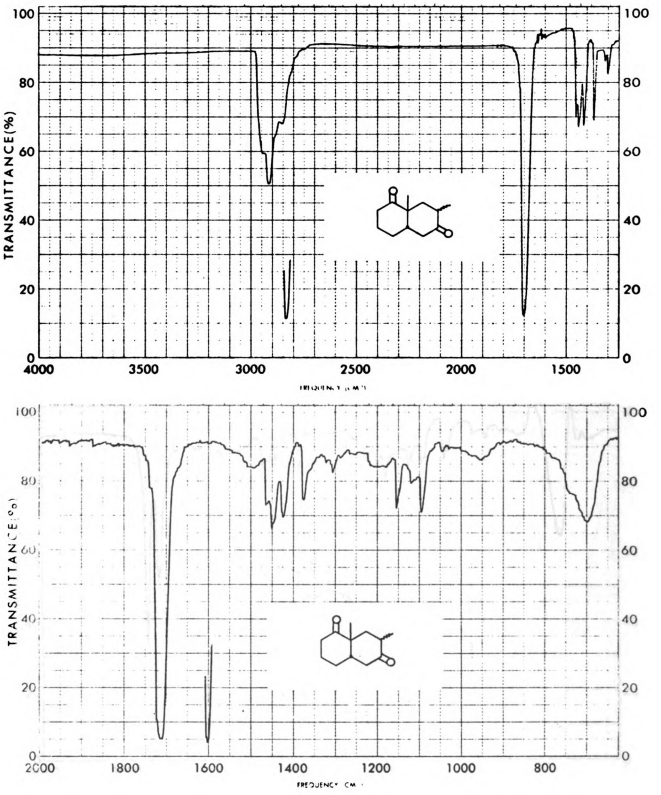


Figure 22. Infrared spectrum of (1α,6α,9ξ)-1,9-dimethylbicyclo[4.4.0]decan-2,8-dione (103 and 104).

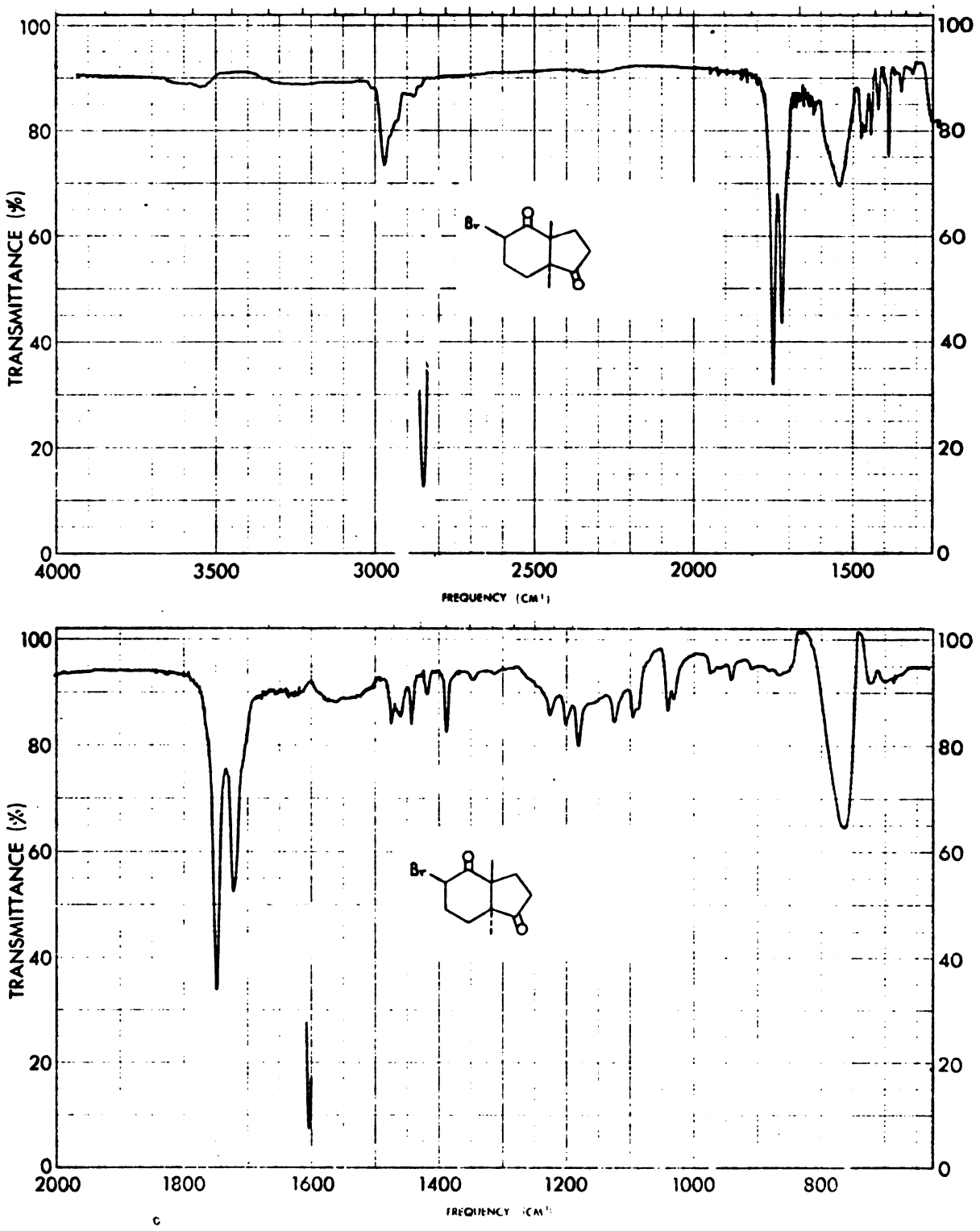
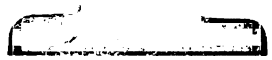


Figure 23. Infrared spectrum of (1α,3α,6β)-3-bromo-1,6-dimethylbicyclo[4.3.0]nona-2,7-dione (Figure 1).



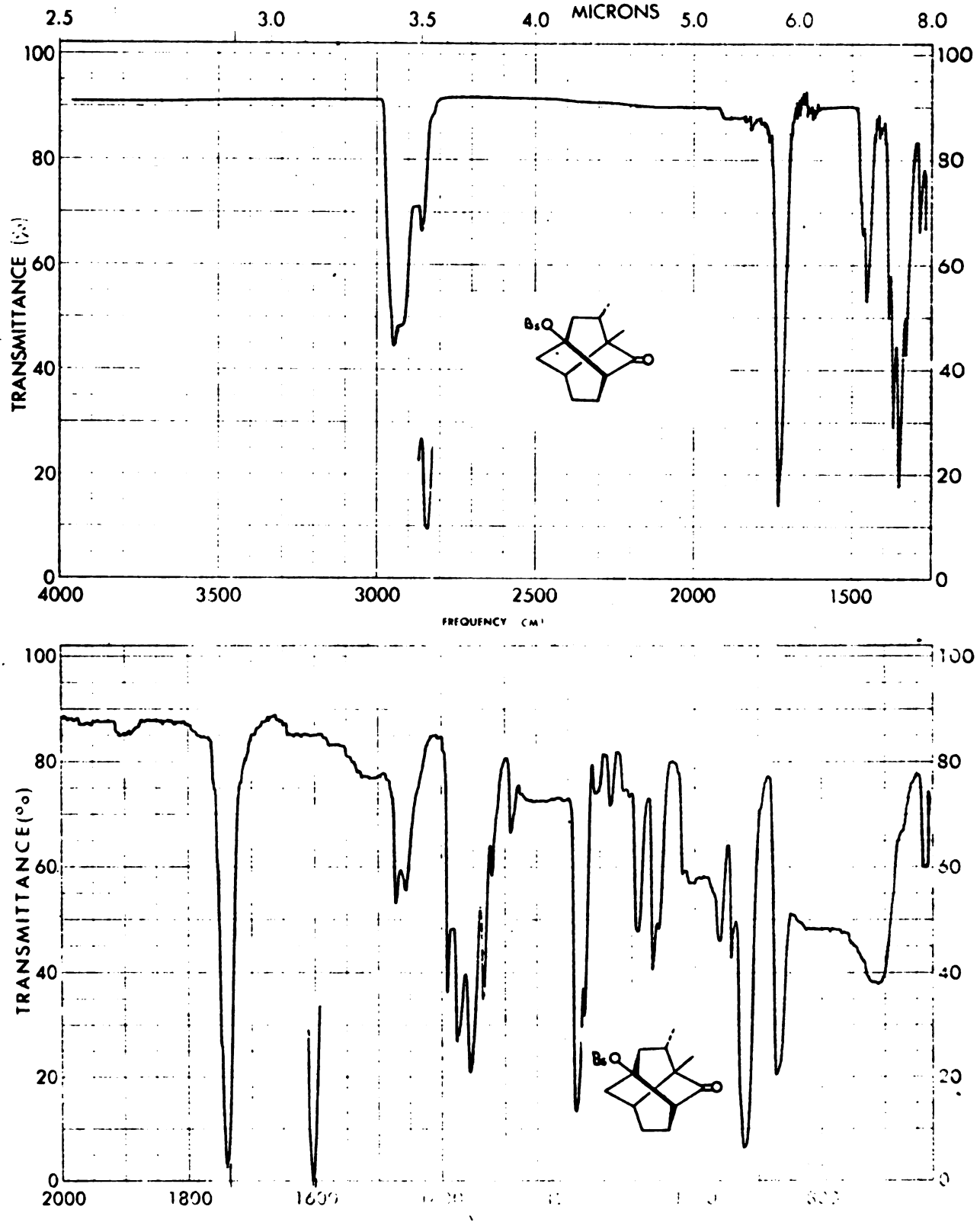


Figure 24. Infrared spectrum of (1R*,3R*,6S*,8R*,10R*)-8-(p-bromobenzenesulfonoxy)-1,10-dimethyltricyclo-[4.4.0^{3,8}]decan-2-one (Figure 2).

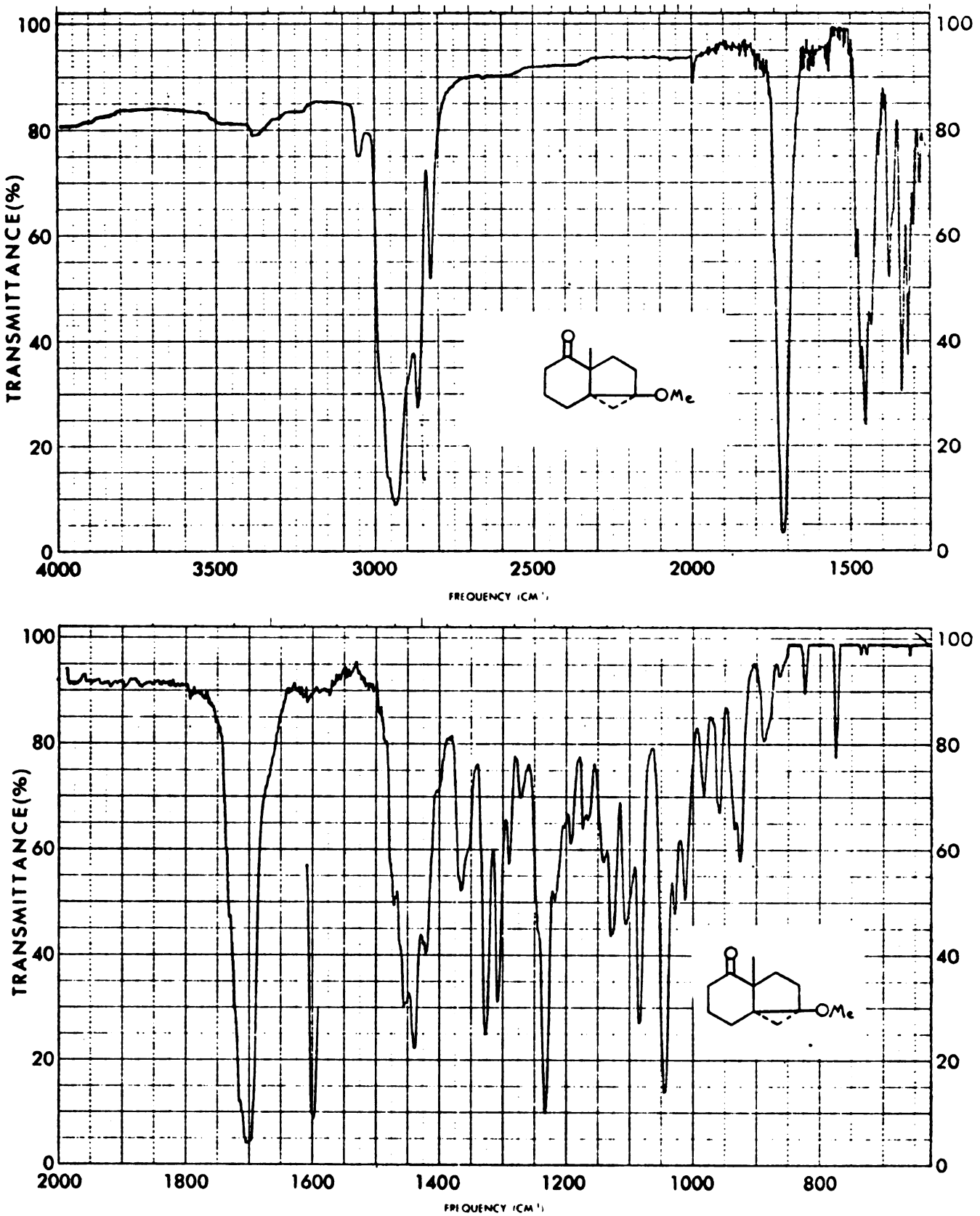


Figure 25. Infrared spectrum of (1S*,3α,6α)-3-methoxy-6-methyltricyclo[4.4.0.0^{1,3}]decan-7-one (91).

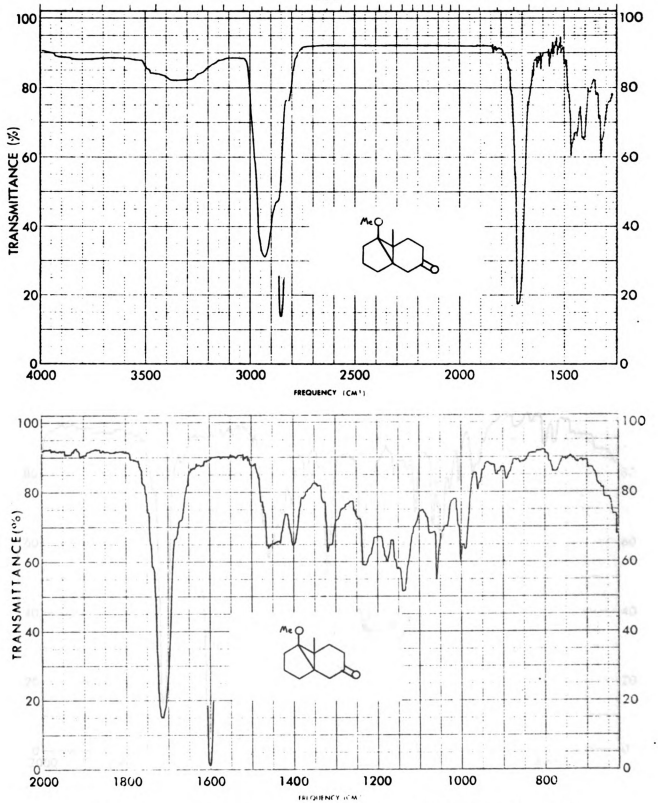


Figure 26. Infrared spectrum of (1R*,5α,6β)-5-methoxy-6-methyltricyclo[4.4.0.0^{1,5}]decan-9-one (90).

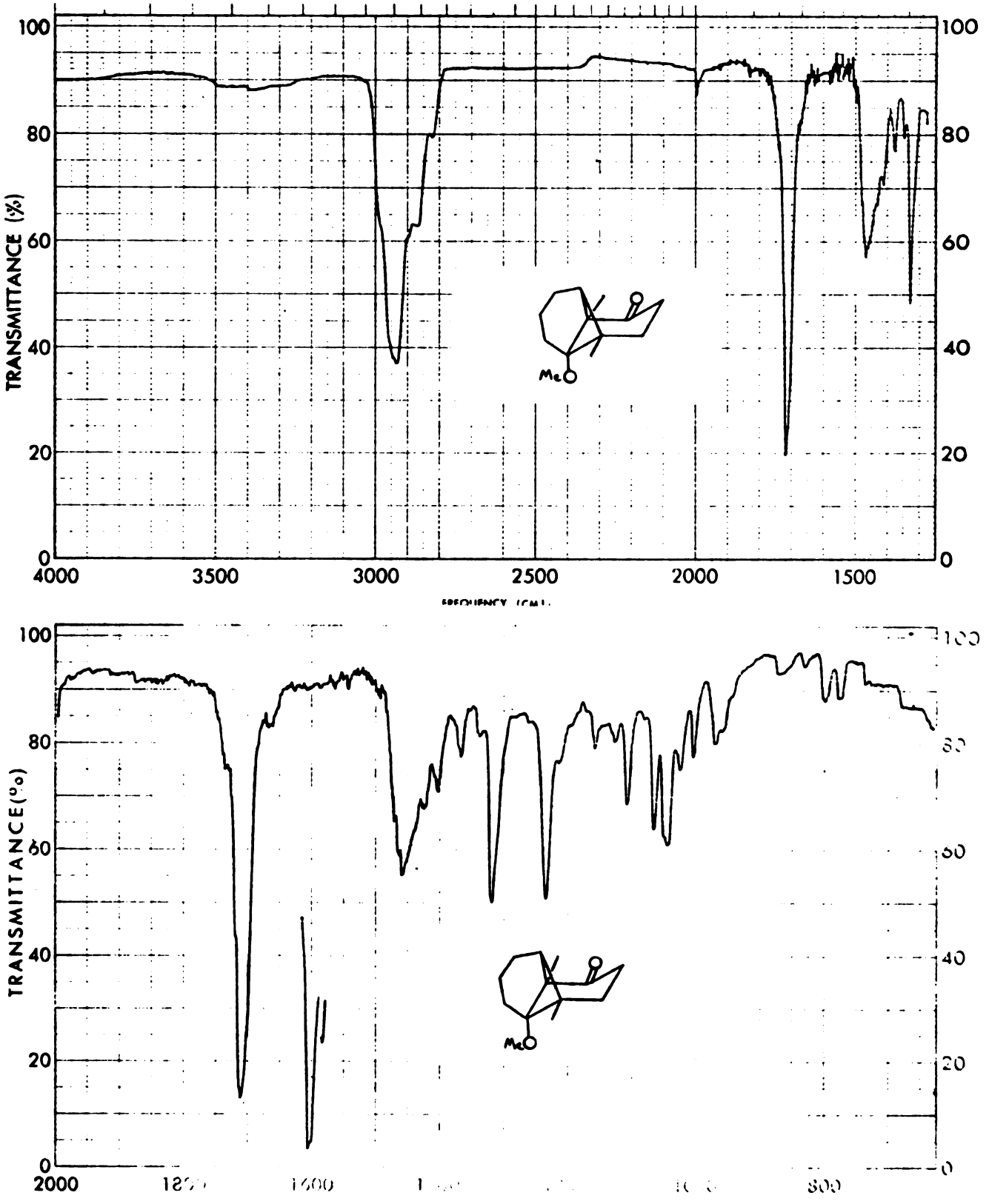


Figure 27. Infrared spectrum of (1R*,2S*,6R*,7R*)-2-methoxy-1,7-dimethyltricyclo[4.4.0.0^{2,7}]decan-8-one (95).

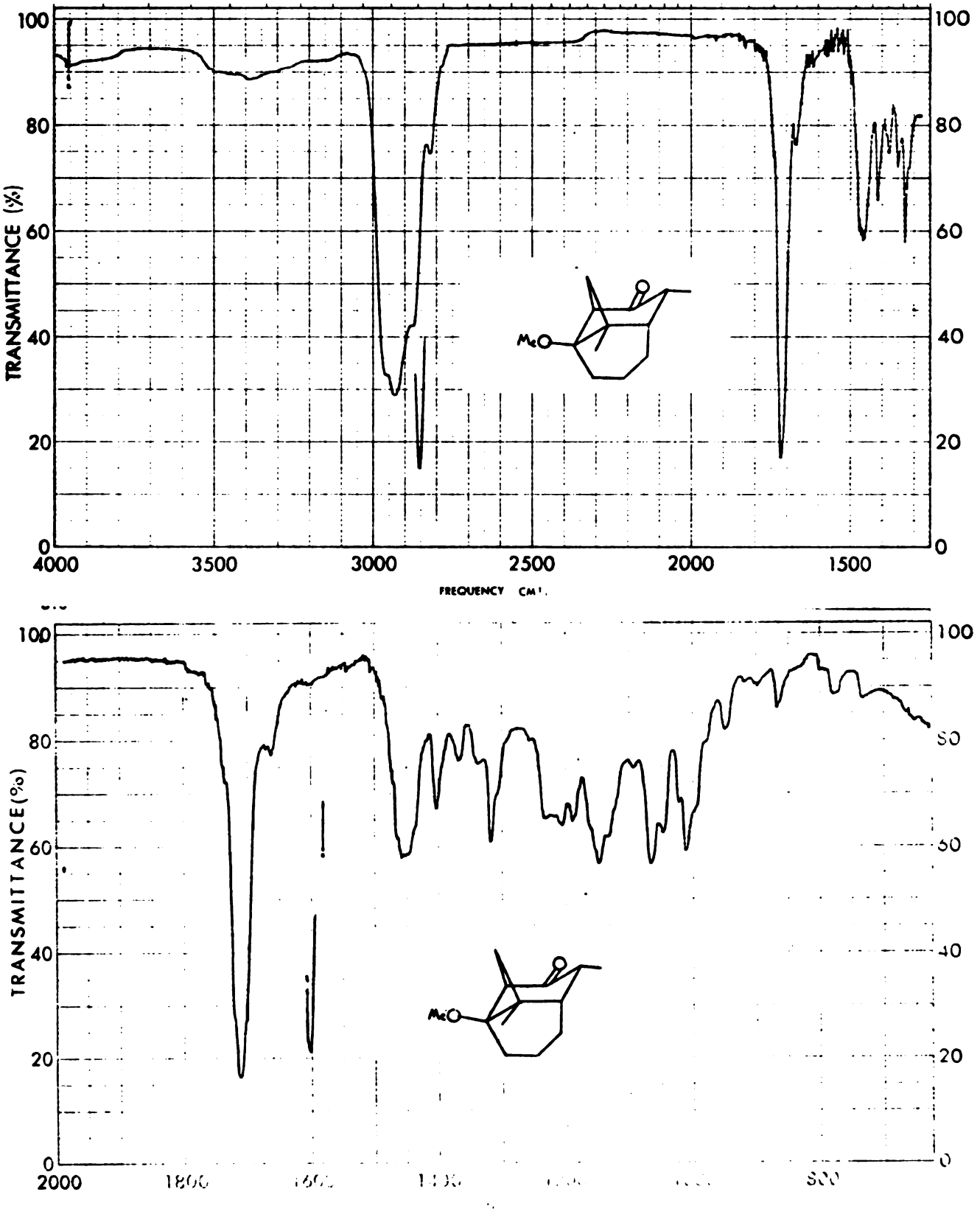


Figure 28. Infrared spectrum (1R*,2S*,4S*,6S*,7R*)-2-methoxy-1,7-dimethyltricyclo[4.4.0.0^{2,9}]decan-8-one (96).

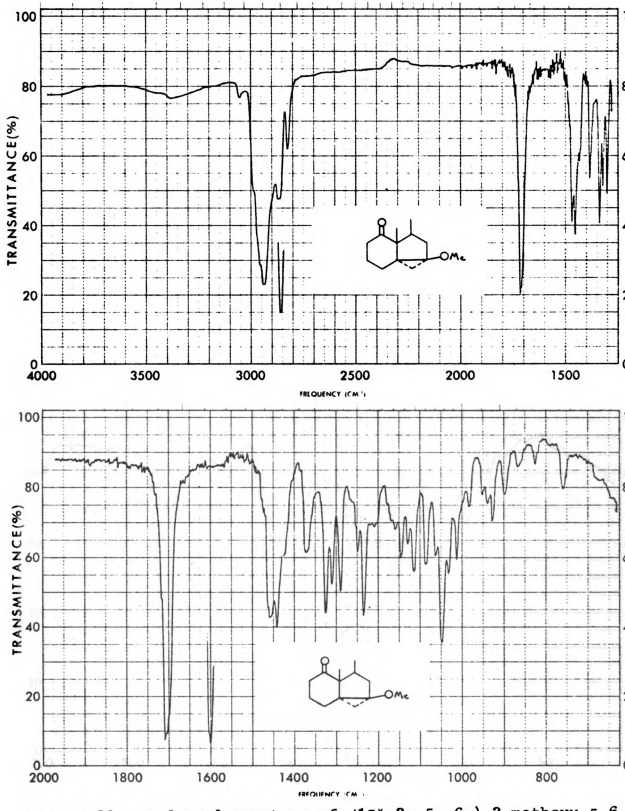


Figure 29. Infrared spectrum of (1S*,3α,5α,6α)-3-methoxy-5,6-dimethyltricyclo[4.4.0.0^{1,3}]decan-7-one (99).

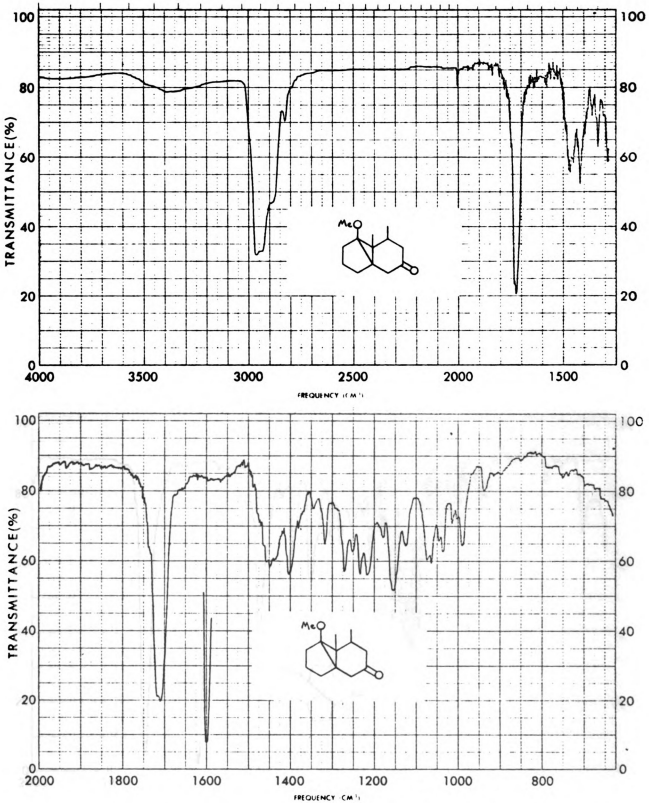


Figure 30. Infrared spectrum of (1R*,5β,6α,7α)-5-methoxy-6,7-dimethyltricyclo[4.4.0.0^{1,5}[decan-9-one (98).

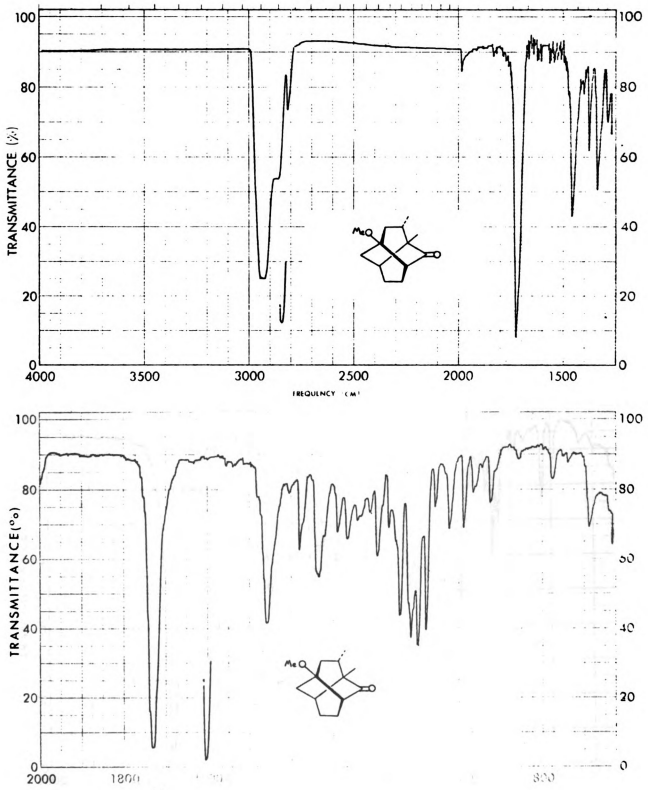


Figure 31. Infrared spectrum of (1R*,3R*,6S*,8R*,10R*)-8-methoxy-1,10-dimethyltricyclo[4.4.0.0^{3,8}]decan-2-one (101).

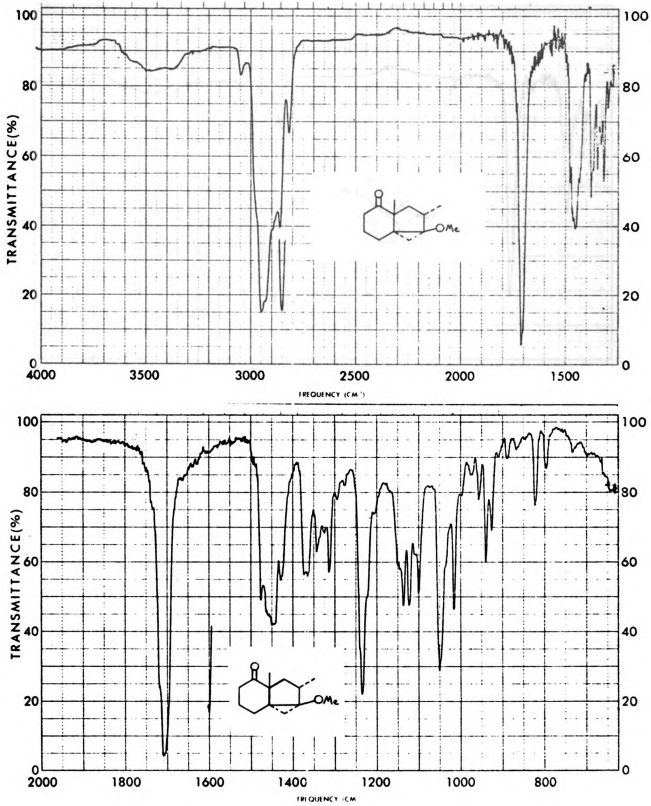


Figure 32. Infrared spectrum of (1S*,3α,4β,6α)-3-methoxy-4,6-dimethyltricyclo[4.4.0.0^{1,3}]decan-7-one (105).

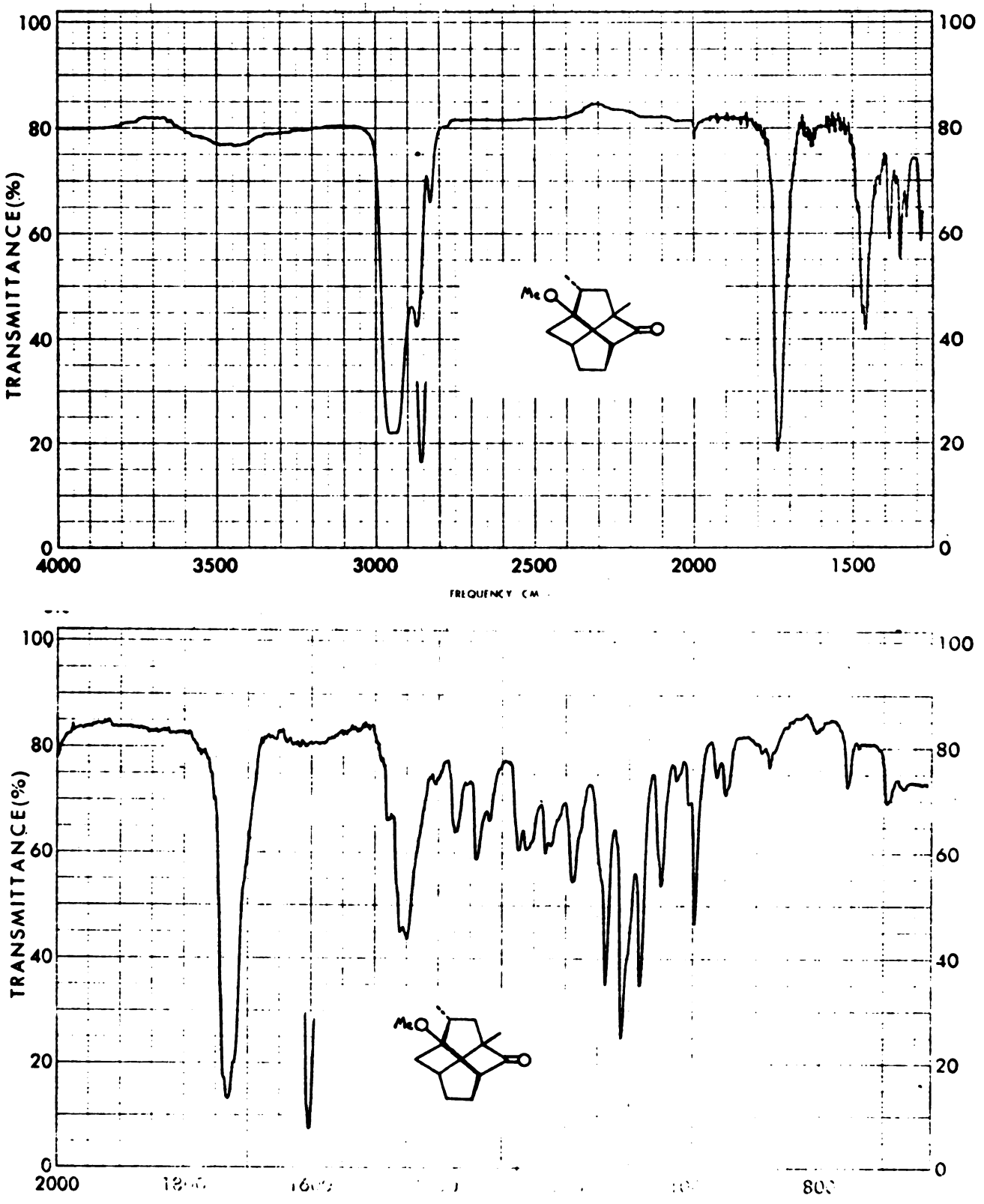


Figure 33. Infrared spectrum of (1R*,3R*,6S*,8R*,9S*)-8-methoxy-1,9-dimethyltricyclo[4.4.0.0^{3,8}]decan-2-one (106).

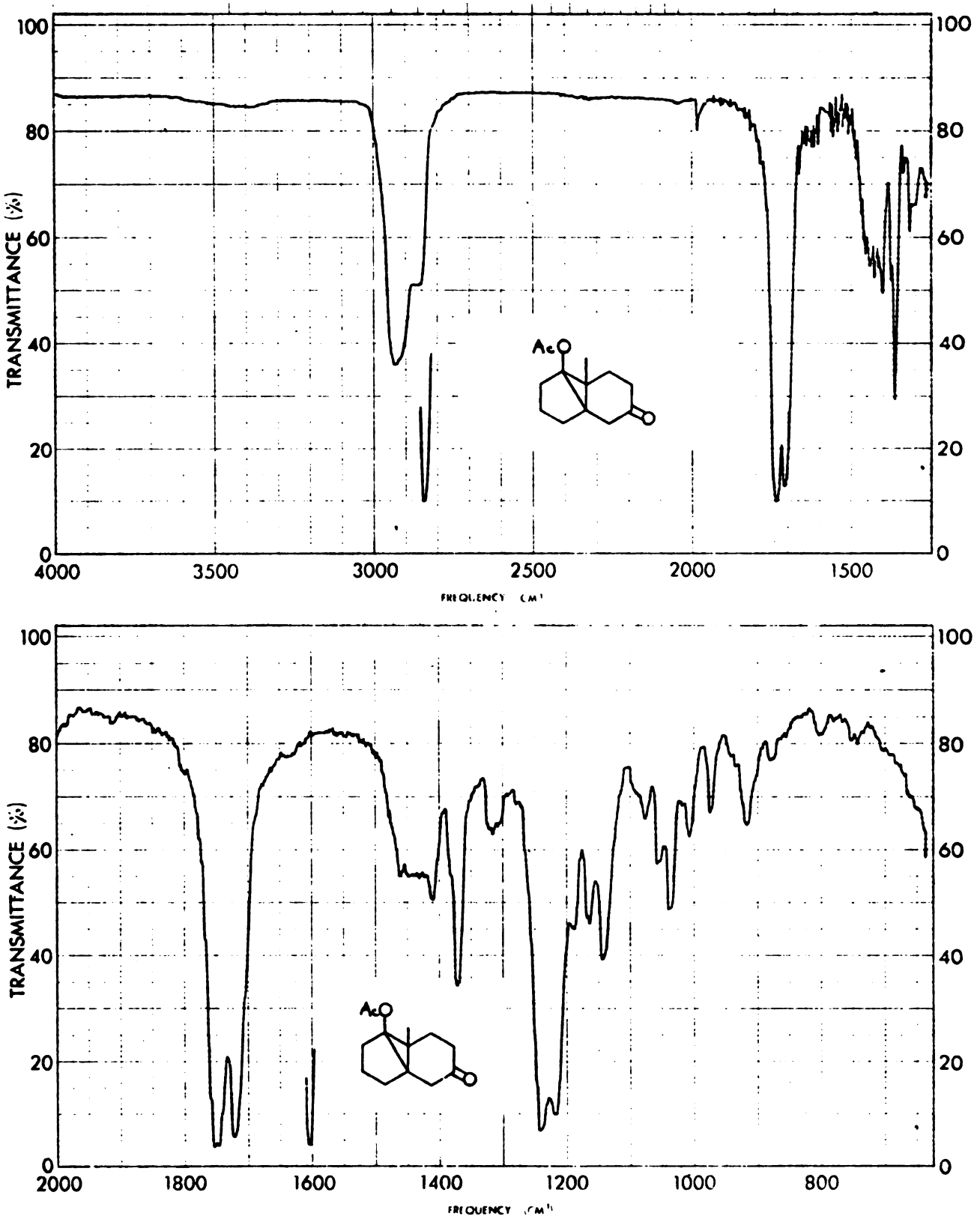


Figure 34. Infrared spectrum of (1R*,5α,6β)-5-acetoxy-6-methyltricyclo[4.4.0.0^{1,5}]decan-9-one (76).

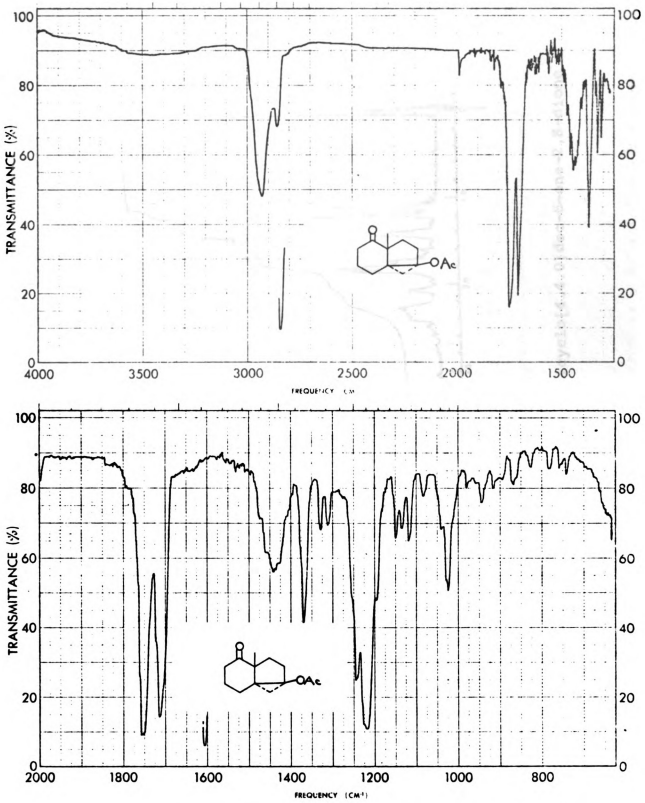


Figure 35. Infrared spectrum of (1S*,3α,6α)-3-acetoxy-6-methyltricyclo[4.4.0.0^{1,3}]decan-7-one (77).

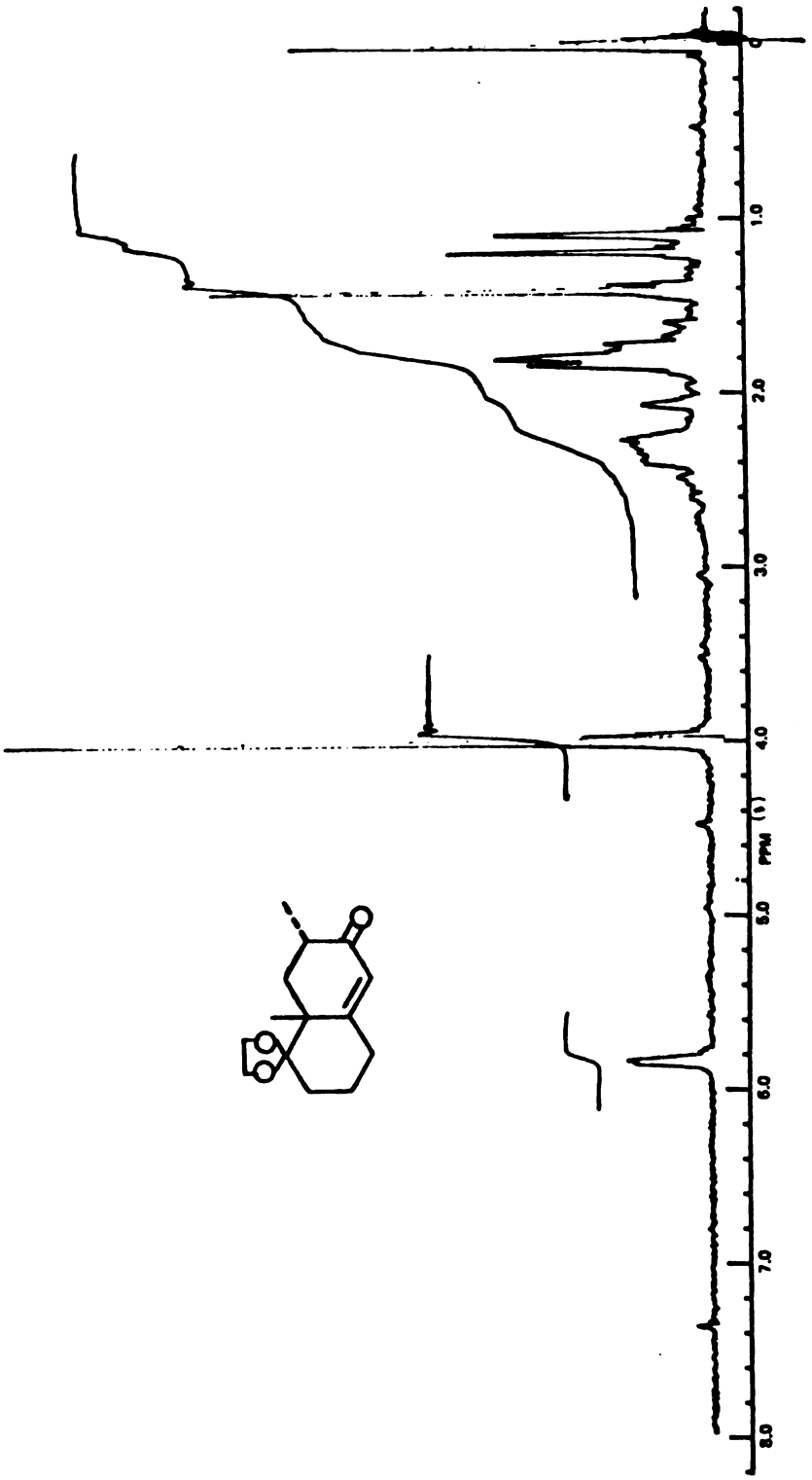


Figure 36. Pmr spectrum of trans-1,9-dimethylbicyclo[4.4.0]dec-6-ene-2,8-dione 2-ethylene ketal (60) ($CDCl_3$).

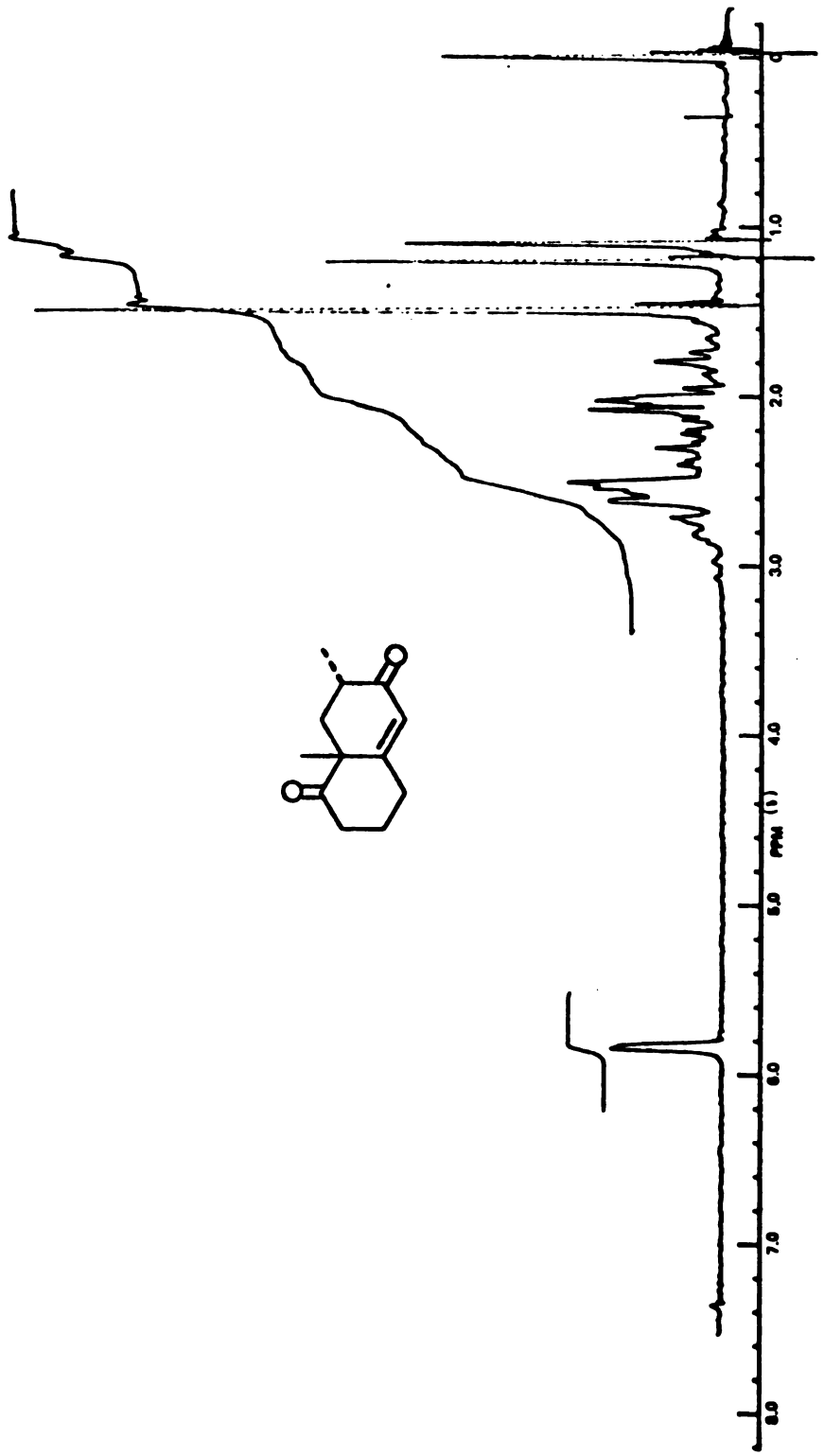


Figure 37. Pmr spectrum of trans-1,9-dimethylbicyclo[4.4.0]-dec-6-ene-2,8-dione (56) ($CDCl_3$).

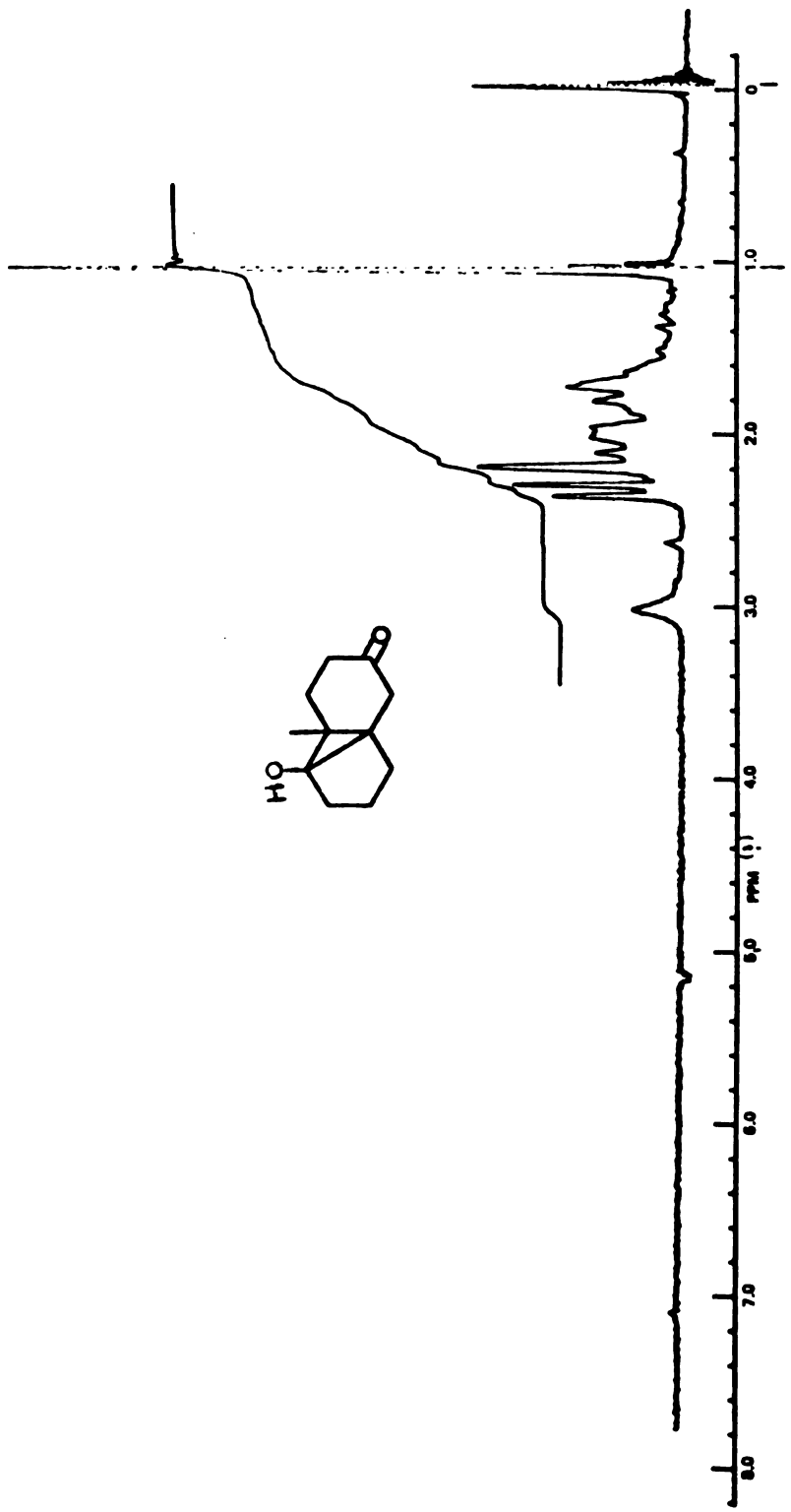


Figure 38. Pmr spectrum of (1R*,5α,6β)-5-hydroxy-6-methyltricyclo[4.4.0.0^{1,5}]decan-9-one (4) ($CDCl_3$).

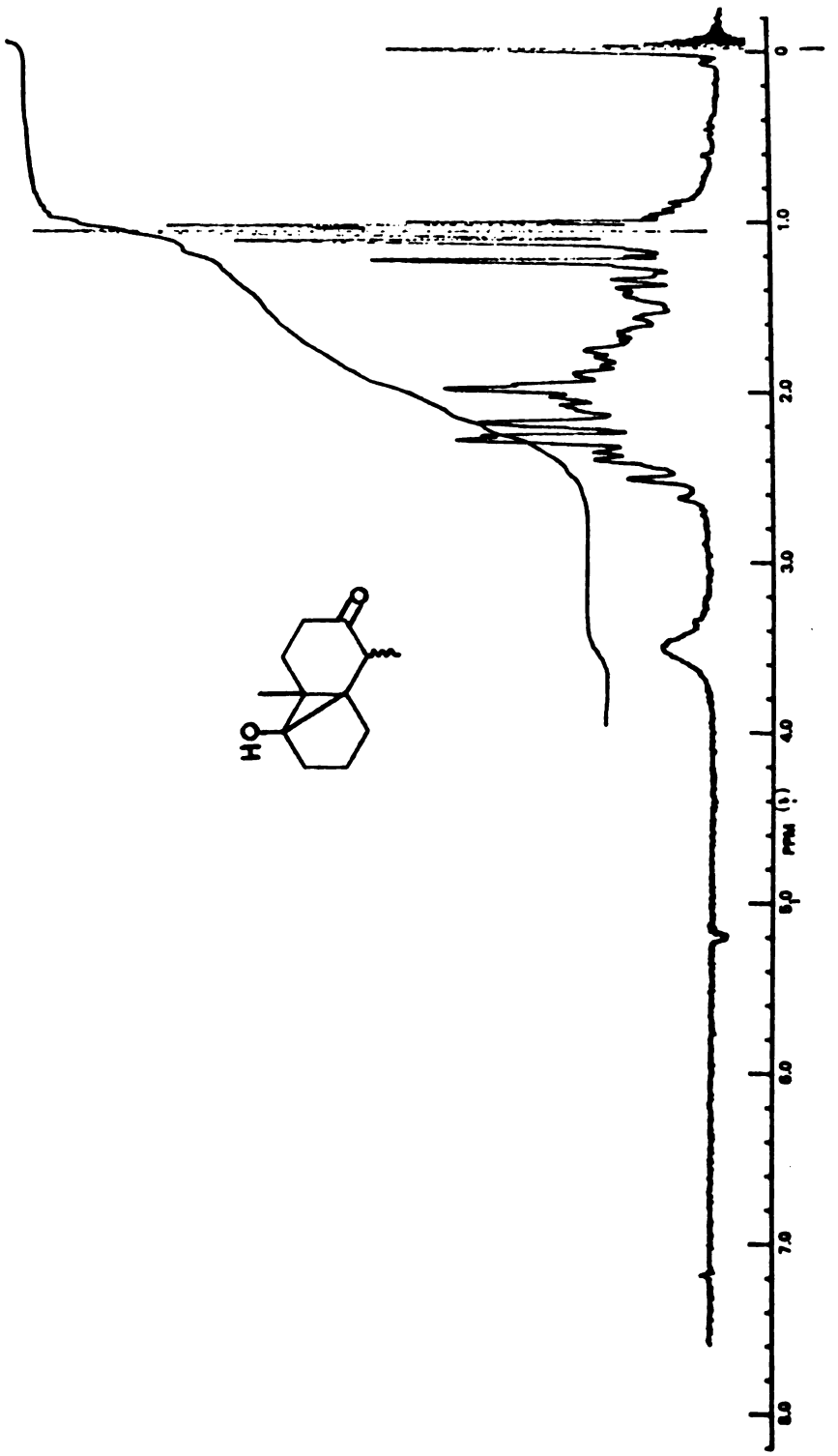


Figure 39. Pmr spectrum of (1R*,5α,6β,10ξ)-5-hydroxy-6,10-dimethyltricyclo-[4.4.0.0^{1,5}]decan-9-one (64) ($CDCl_3$).

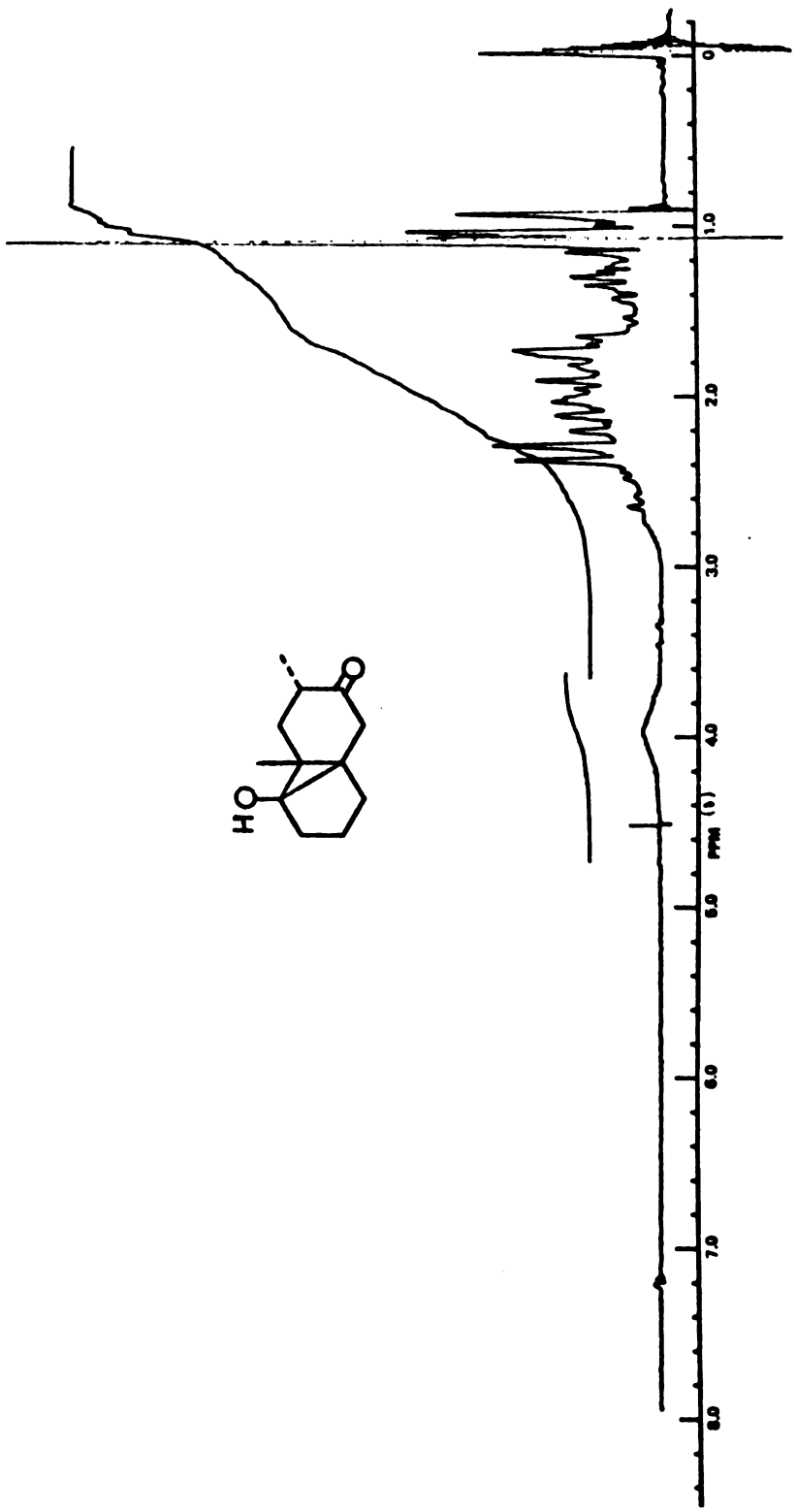


Figure 40. Pmr spectrum of (1R*,5α,6β,8α)-5-hydroxy-6,8-dimethyltricyclo[4.4.0.0^{1,5}]-decan-9-one (64) ($CDCl_3$).

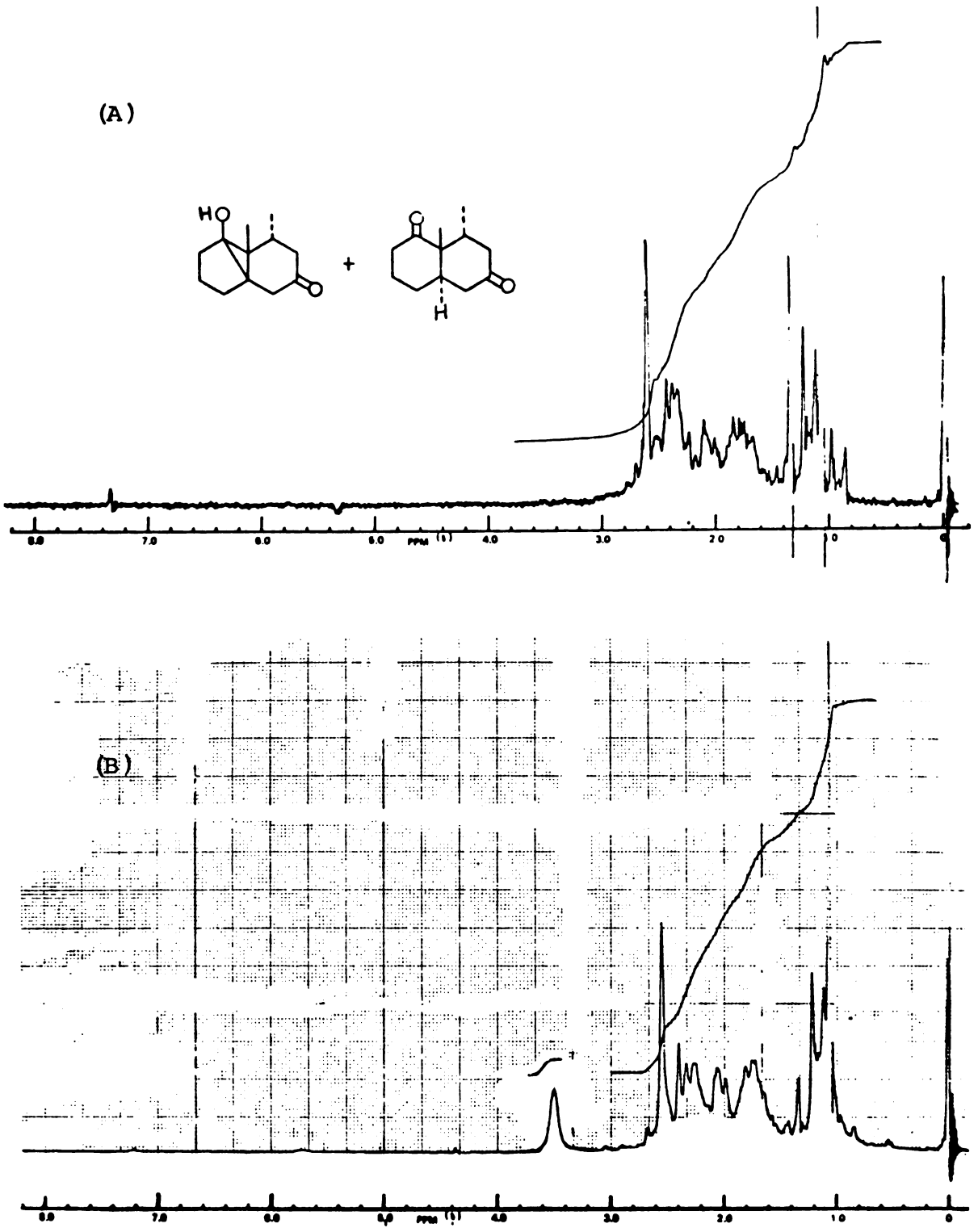


Figure 41. (A) Pmr spectrum of a mixture of (1R*,5α,6β,7α)-5-hydroxy-6,7-dimethyltricyclo[4.4.0.0^{1,5}]decan-9-one (50) and (1β,6α,10α)-1,10-dimethylbicyclo[4.4.0]decan-2,8-dione (66) ($CDCl_3$). (B) Pmr spectrum of (50) after Kugelwöhr distillation of a mixture of (50) and (66) ($CDCl_3$).

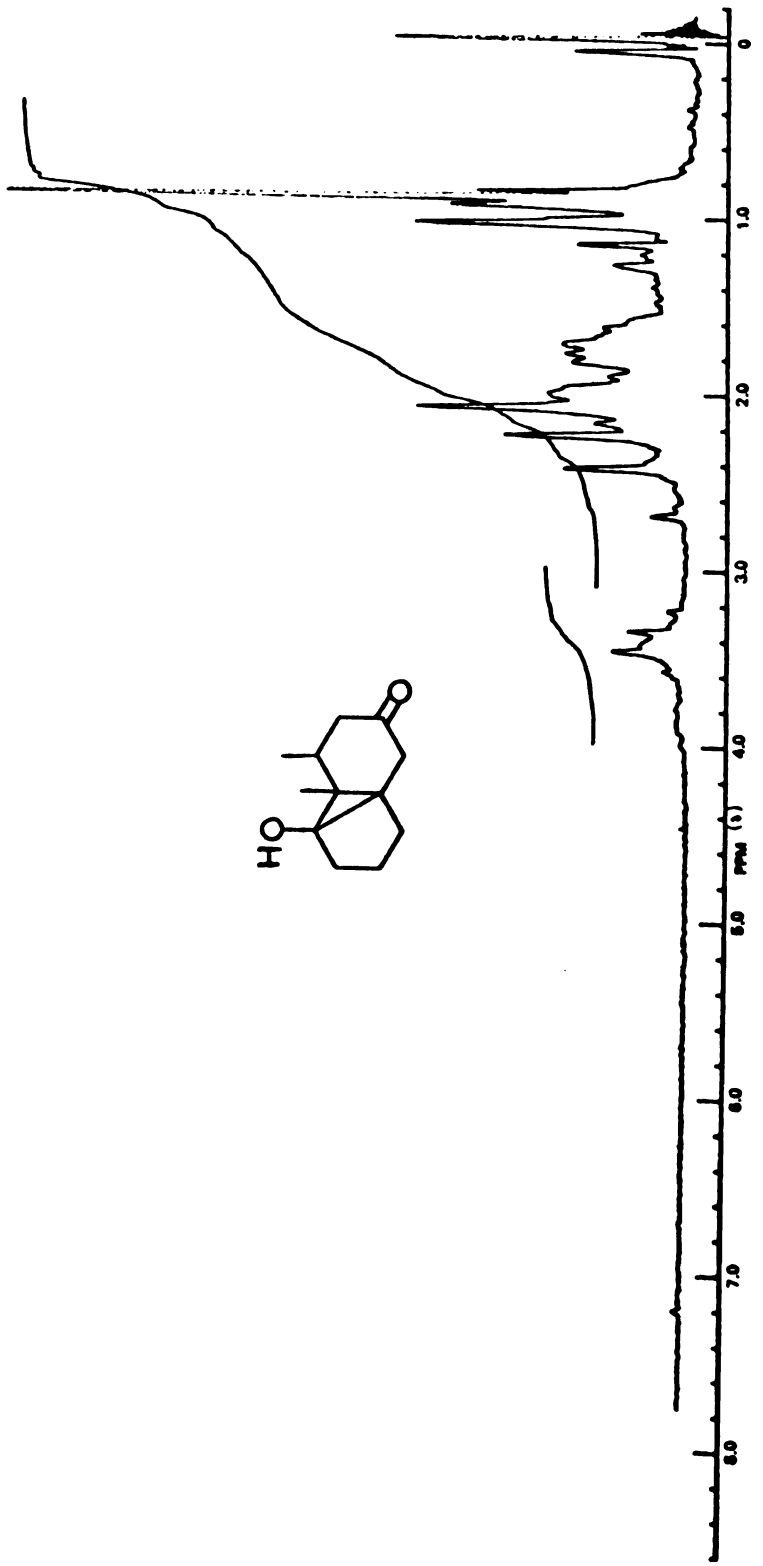


Figure 42. Pmr spectrum of (1R*,5β,6α,7α)-5-hydroxy-6,7-dimethyl[4.4.0.0^{1,5}]decan-9-one in ($CDCl_3$).

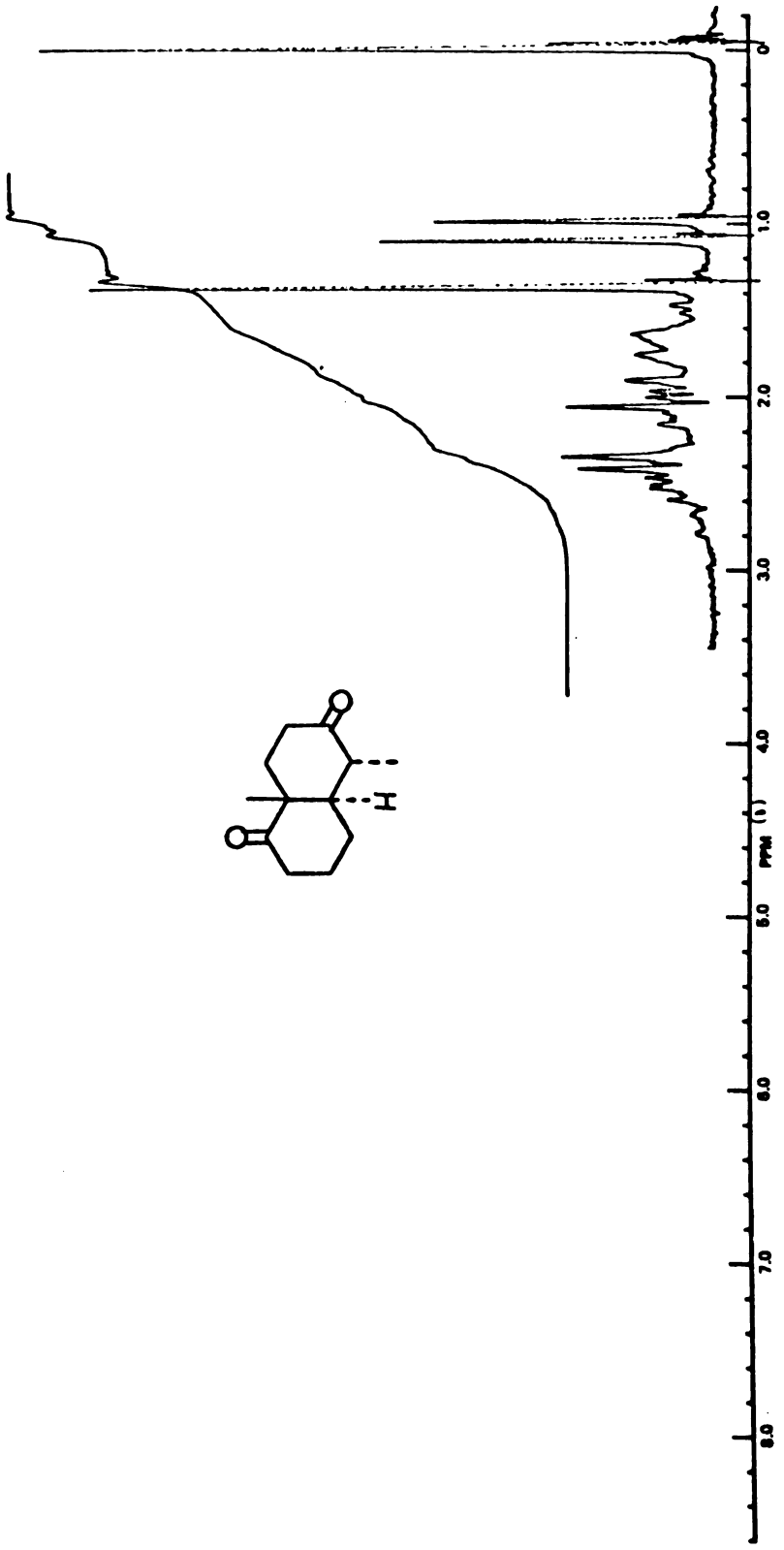


Figure 43. Pmr spectrum of (1β,6α, 7 α)-1, 7 -dimethylbicyclo[4.4.0]decan-2,8-dione (66) ($CDCl_3$).

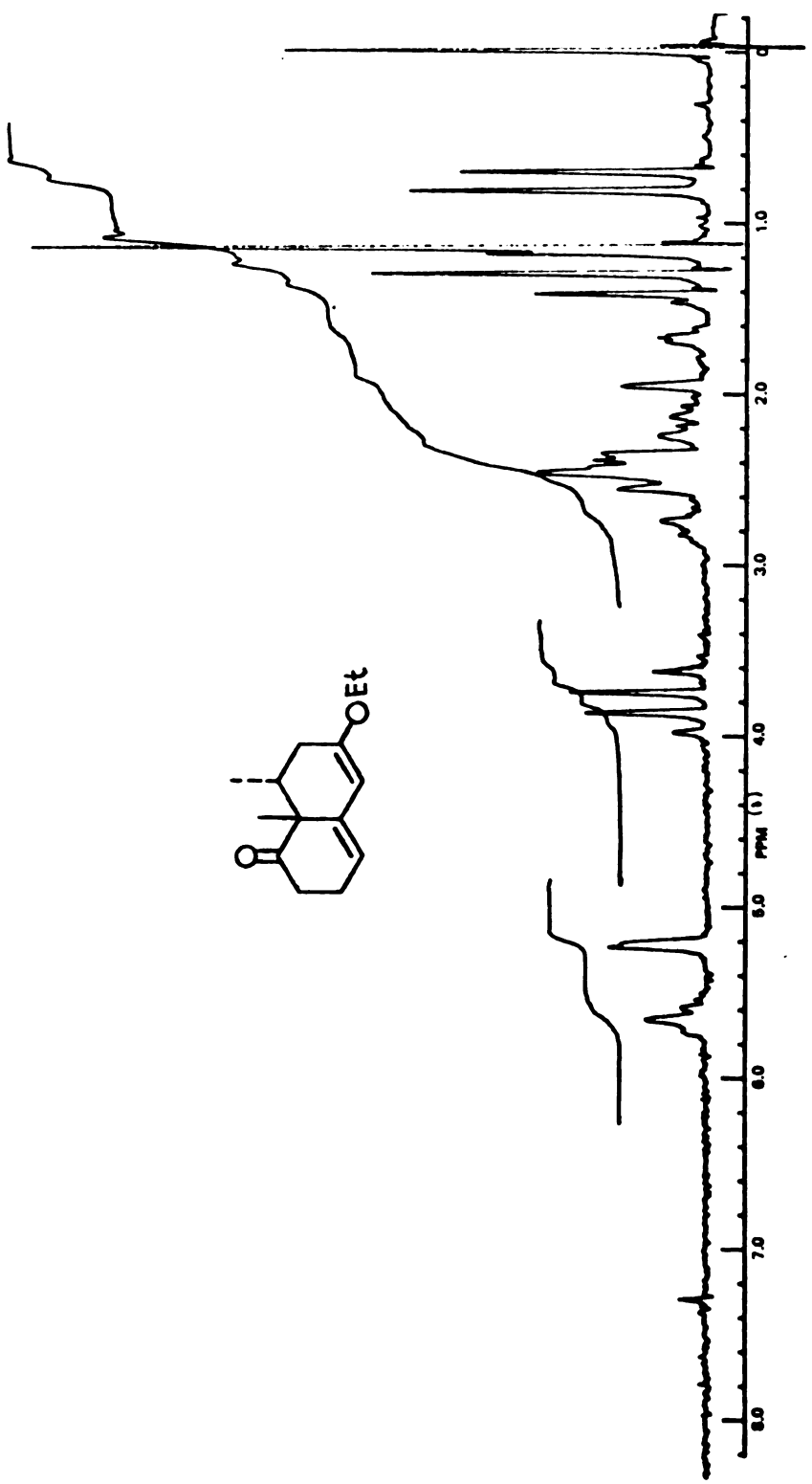


Figure 44. Pmr spectrum of 8-ethoxy-trans-1,10-dimethylbicyclo[4.4.0]dec-5,7-diene-2-one (58) ($CDCl_3$).

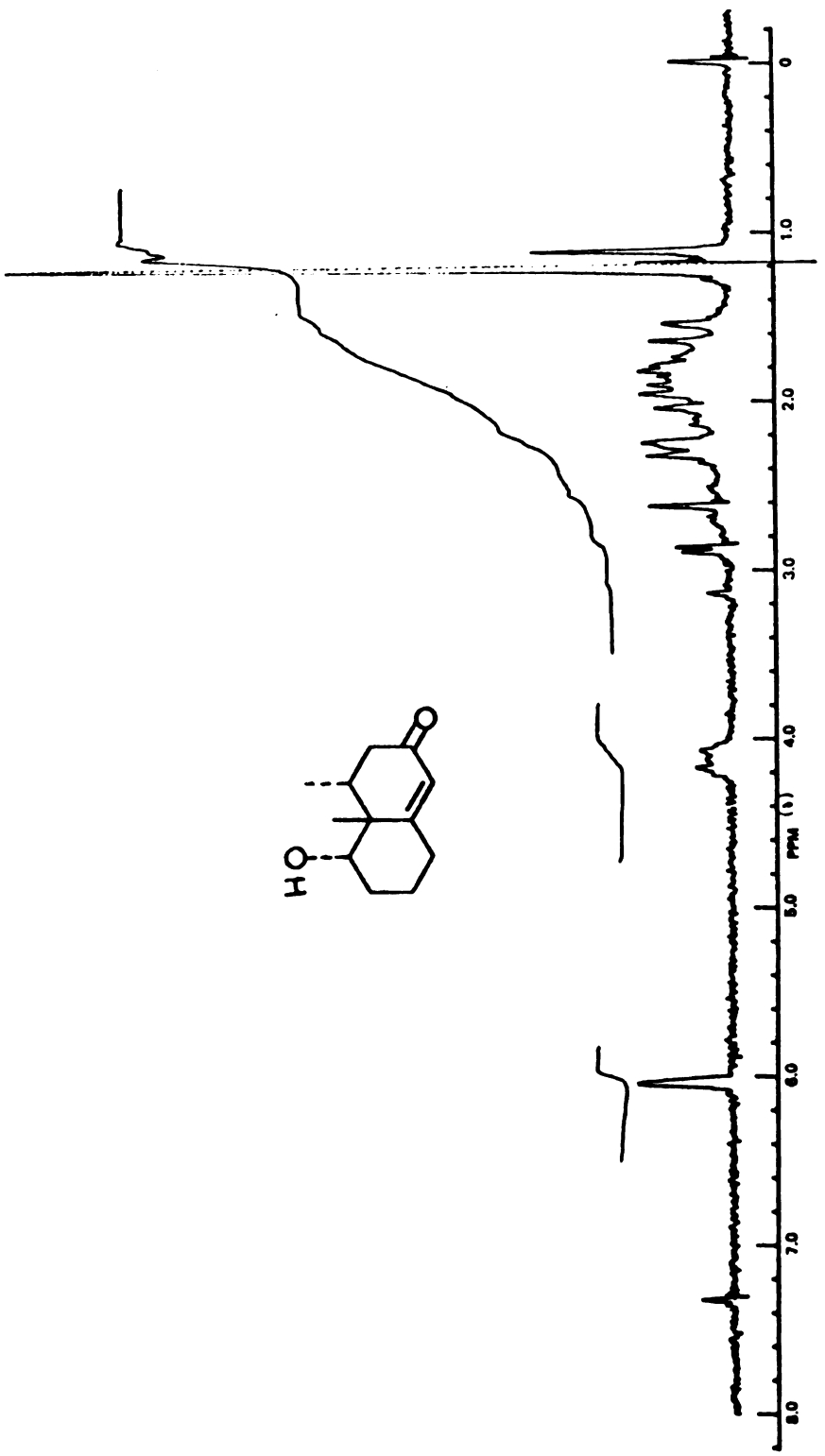


Figure 45. Pmr spectrum of (5α,6β,7α)-7-hydroxy-5,6-dimethylbicyclo[4.4.0]dec-1-ene-3-one (67) ($CDCl_3$).

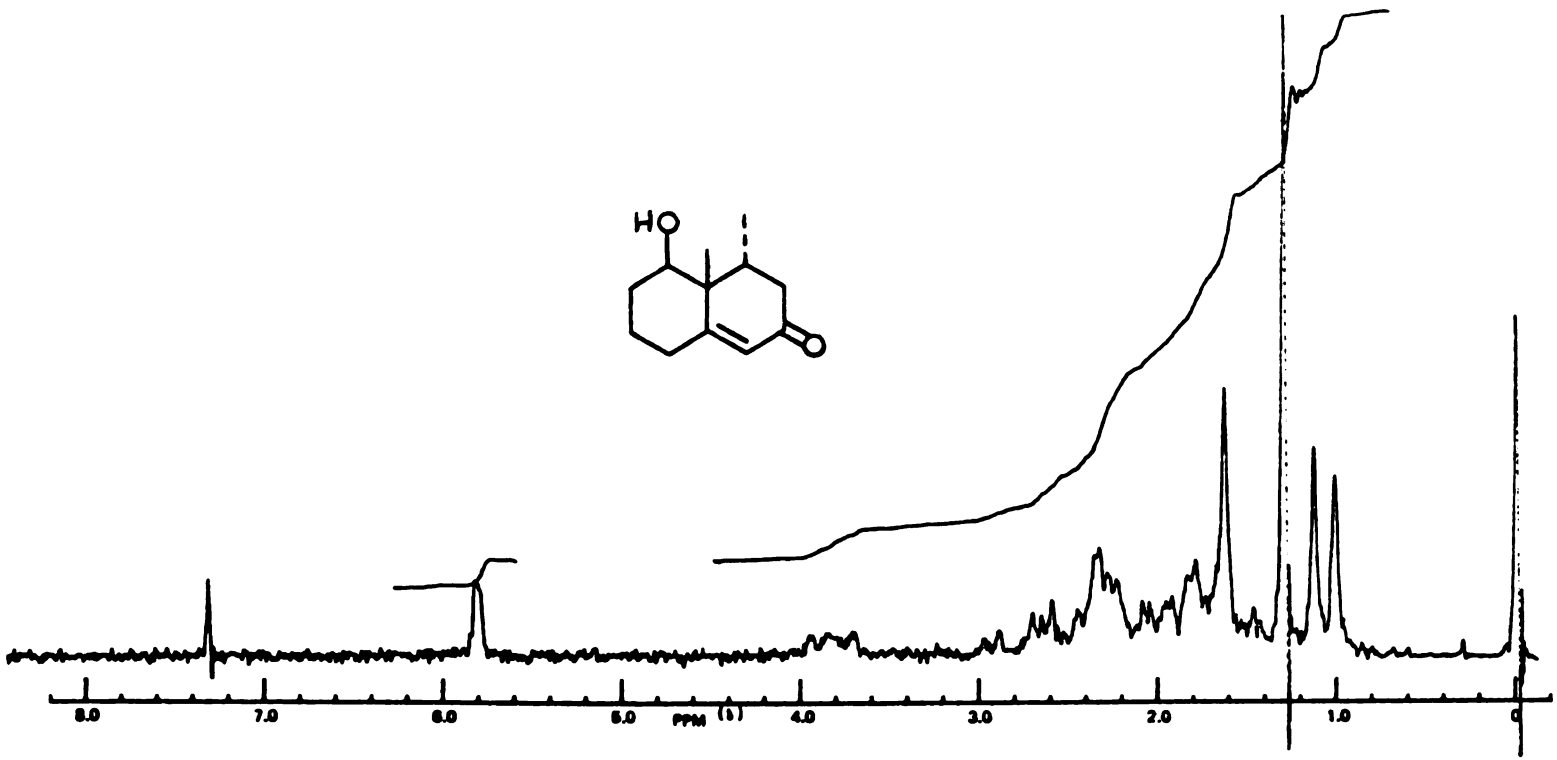


Figure 46. Pmr spectrum of (5β,6α,7α)-7-hydroxy-5,6-dimethylbicyclo[4.4.0]dec-1-ene-3-one (68) ($CDCl_3$).

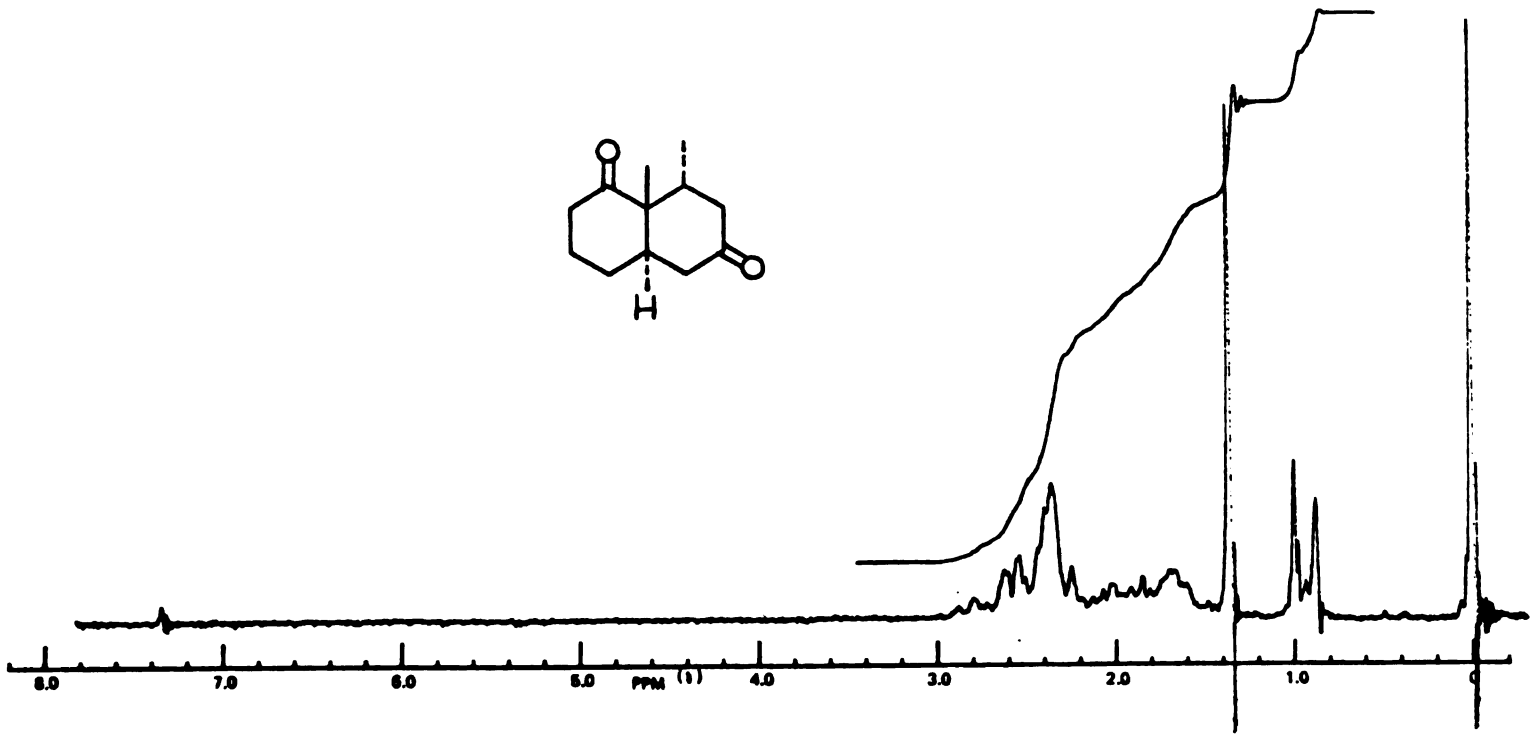


Figure 47. Pmr spectrum of (1β,6α,10α)-1,10-dimethylbicyclo[4.4.0]decan-2,8-dione (69).

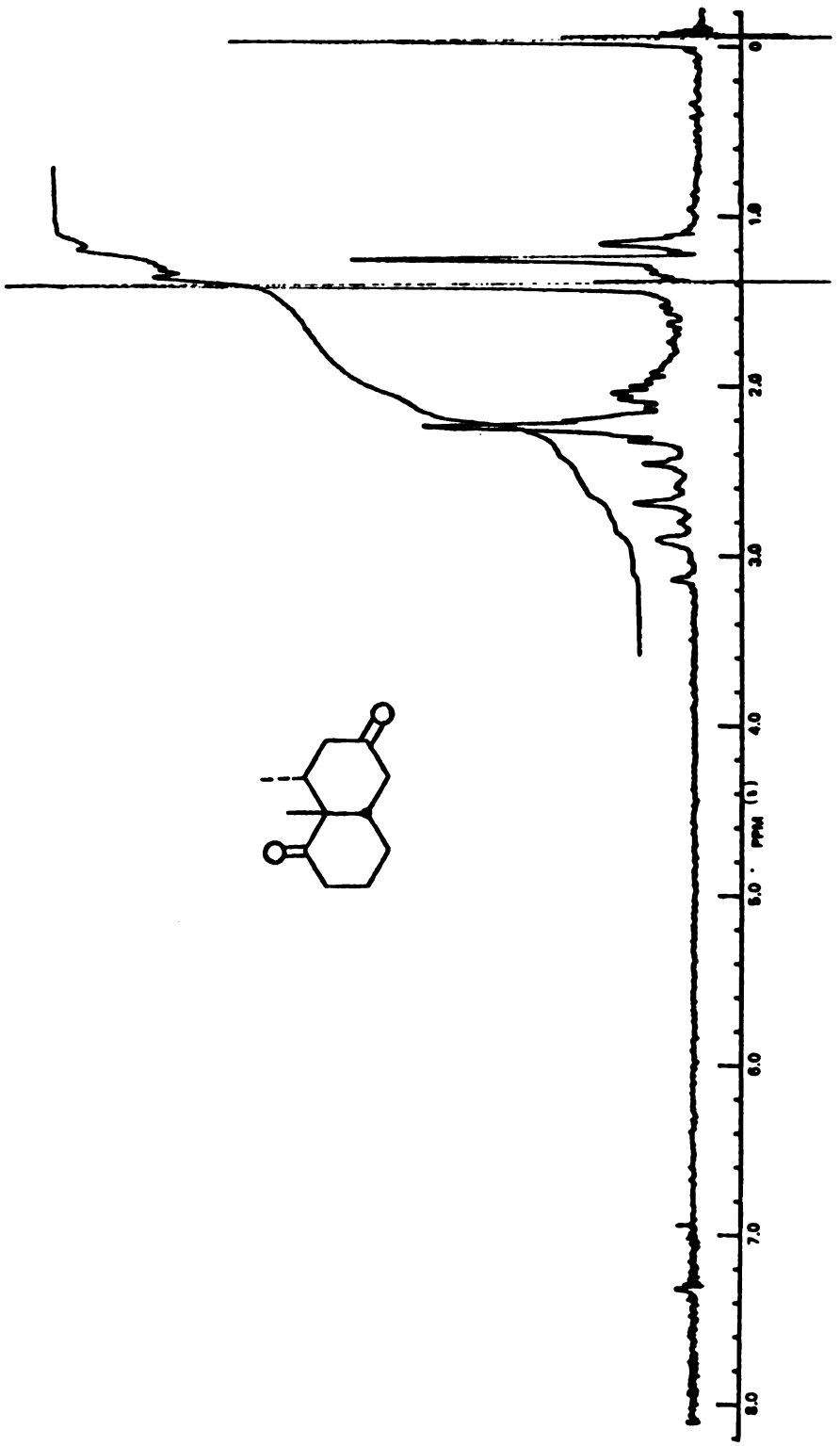


Figure 48. Pmr spectrum of (1α,6α,10β)-1,10-dimethylbicyclo[4.4.0]decan-2,8-dione (69).

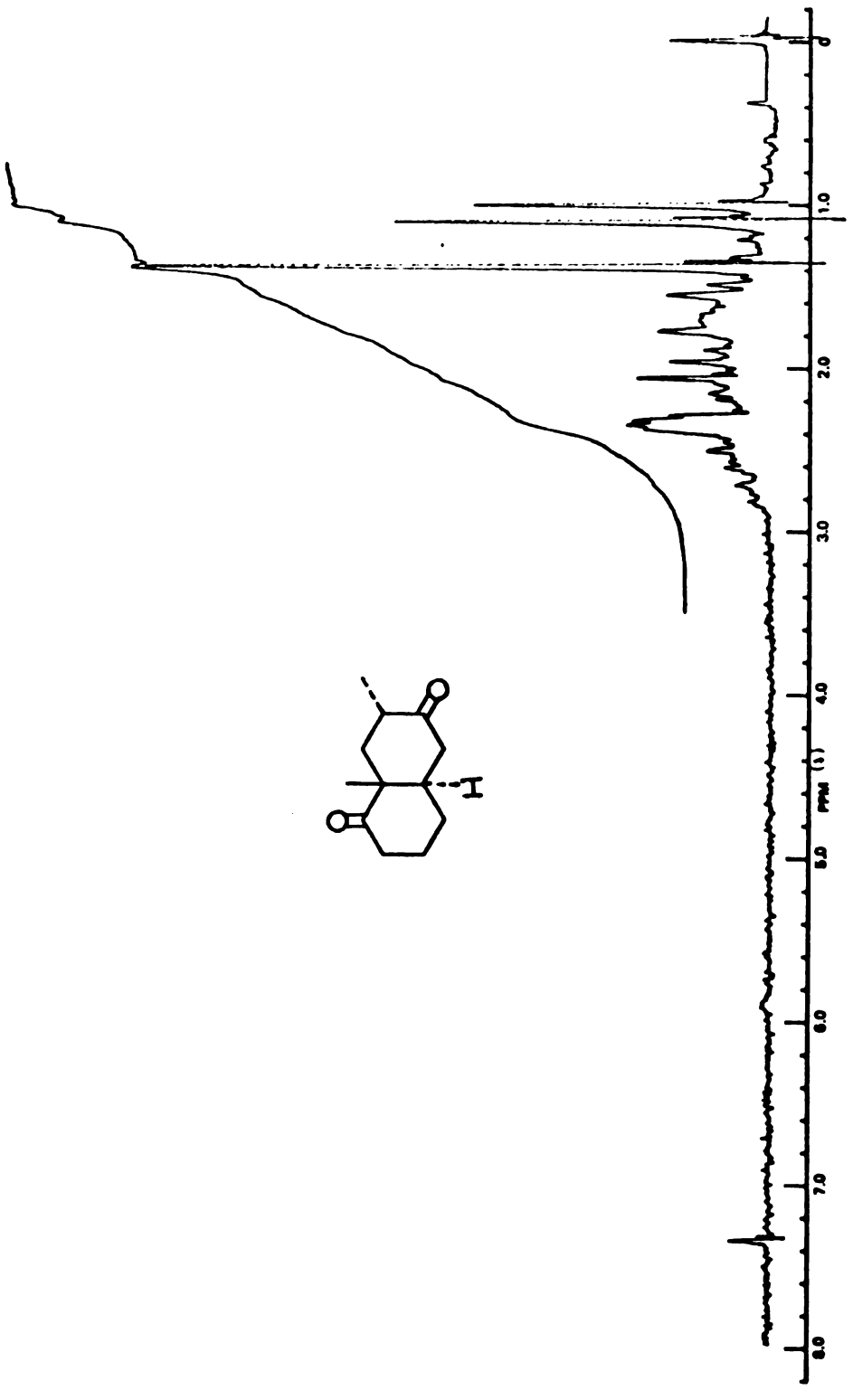


Figure 49. Pmr spectrum of (1β,6α,9α)-1,9-dimethylbicyclo[4.4.0]decan-2,8-dione (110) ($CDCl_3$).

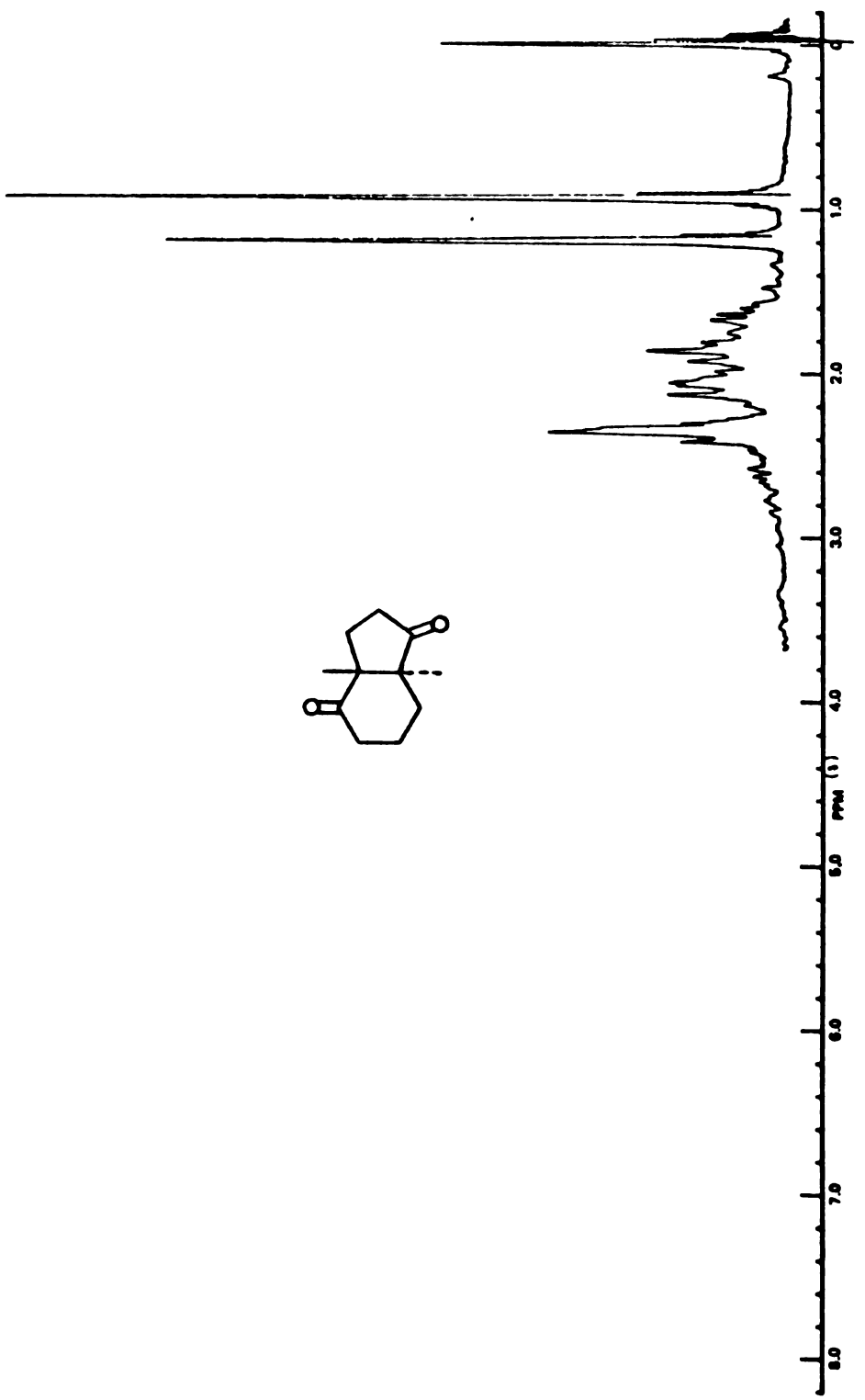


Figure 50. Pmr spectrum of trans-1,6-dimethylbicyclo[4.3.0]nona-2,7-dione (46) ($CDCl_3$).

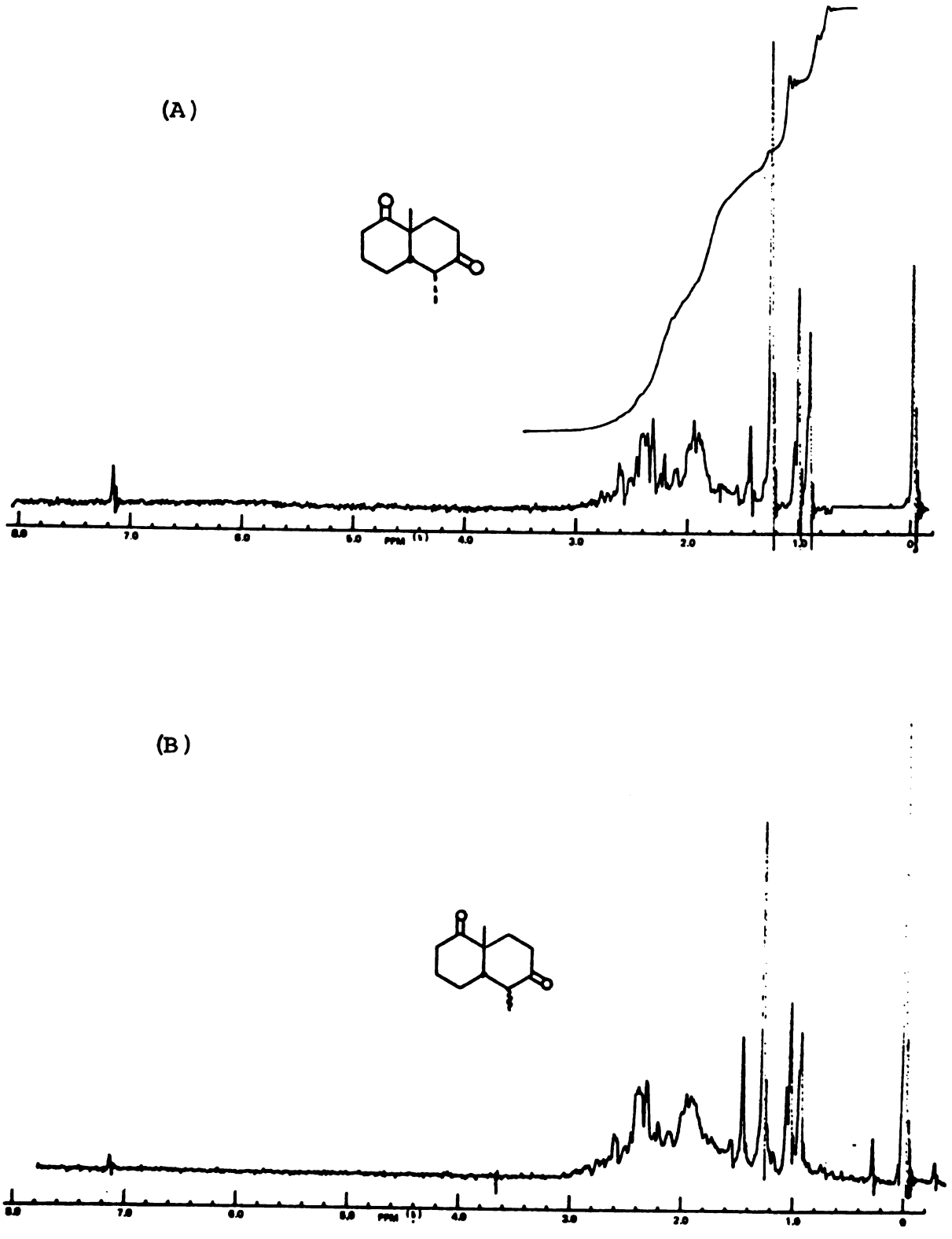


Figure 51. (A) Pmr spectrum of (1α,6α,7β)-1,7-dimethylbicyclo[4.4.0]decan-2,8-dione (92) ($CDCl_3$). (B) Pmr spectrum of a mixture of 92 and 93 ($CDCl_3$).

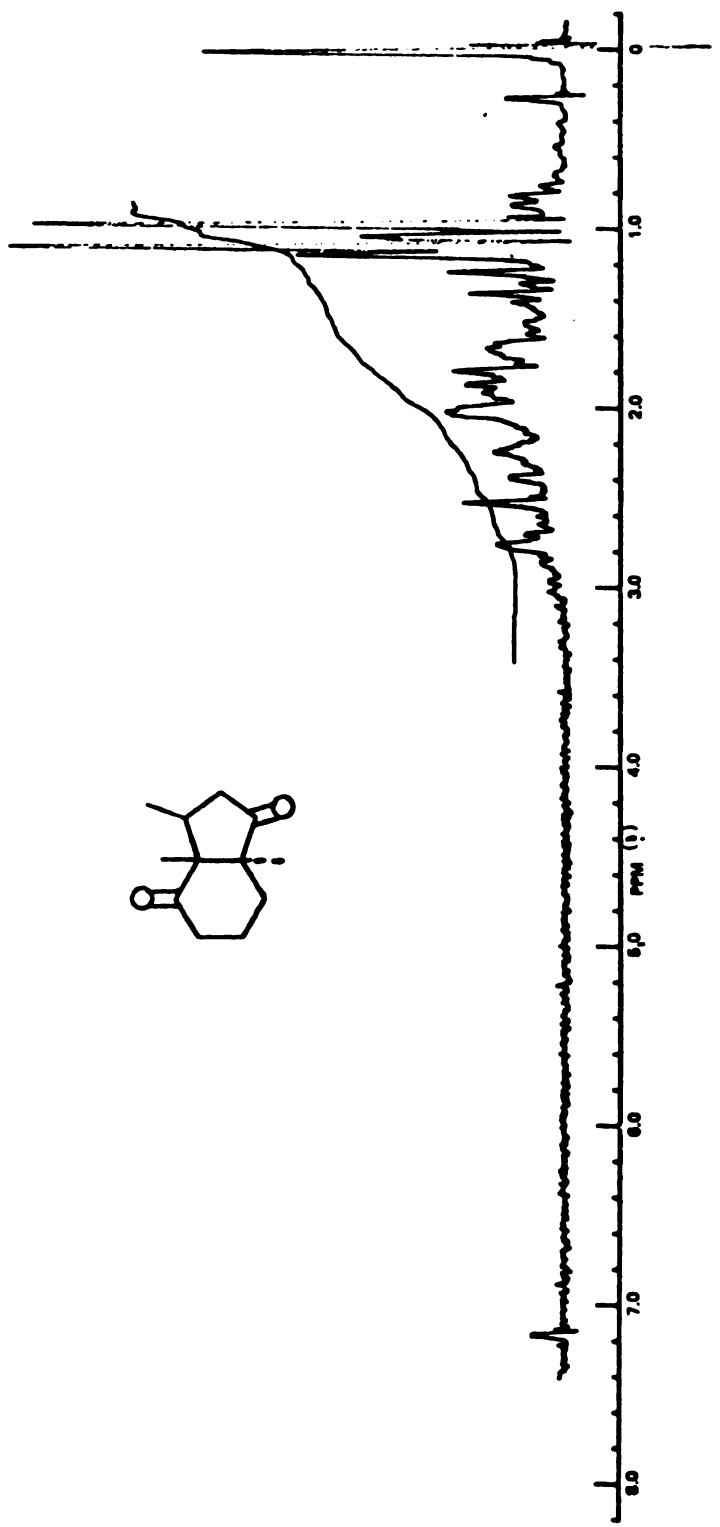


Figure 52. Pmr spectrum of (1α,6ℰ,9α)-trimethylbicyclo[4.3.0]nona-2,7-dione (97) ($CDCl_3$).

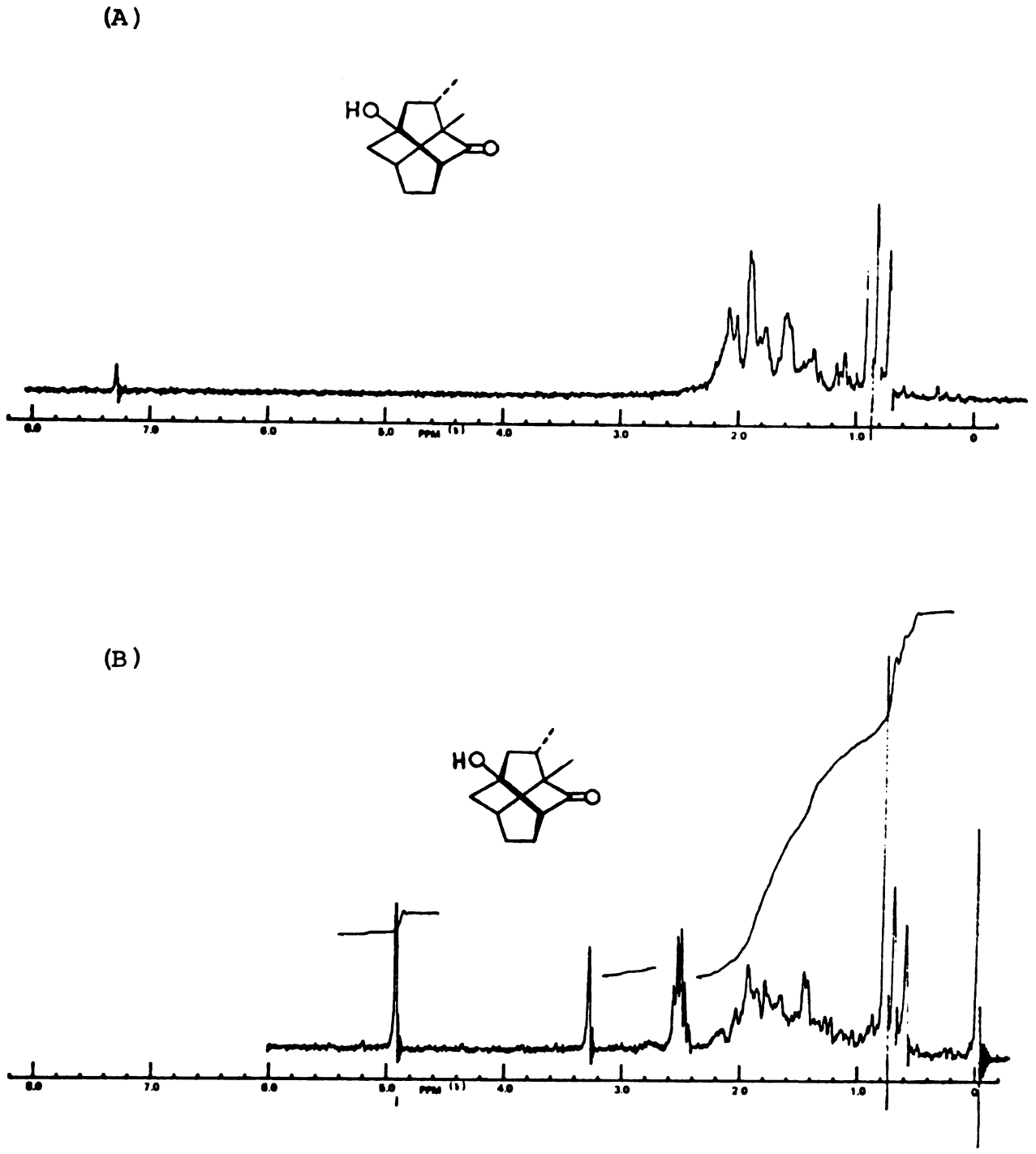


Figure 53. (A) Pmr spectrum of (1R*,3R*,6S*,8R*,10R*)-8-hydroxy-1,10-dimethyltricyclo[4.4.0.0^{3,8}]decan-2-one (100) ($CDCl_3$). (B) Same spectrum taken with d_6-DMSO as the solvent.

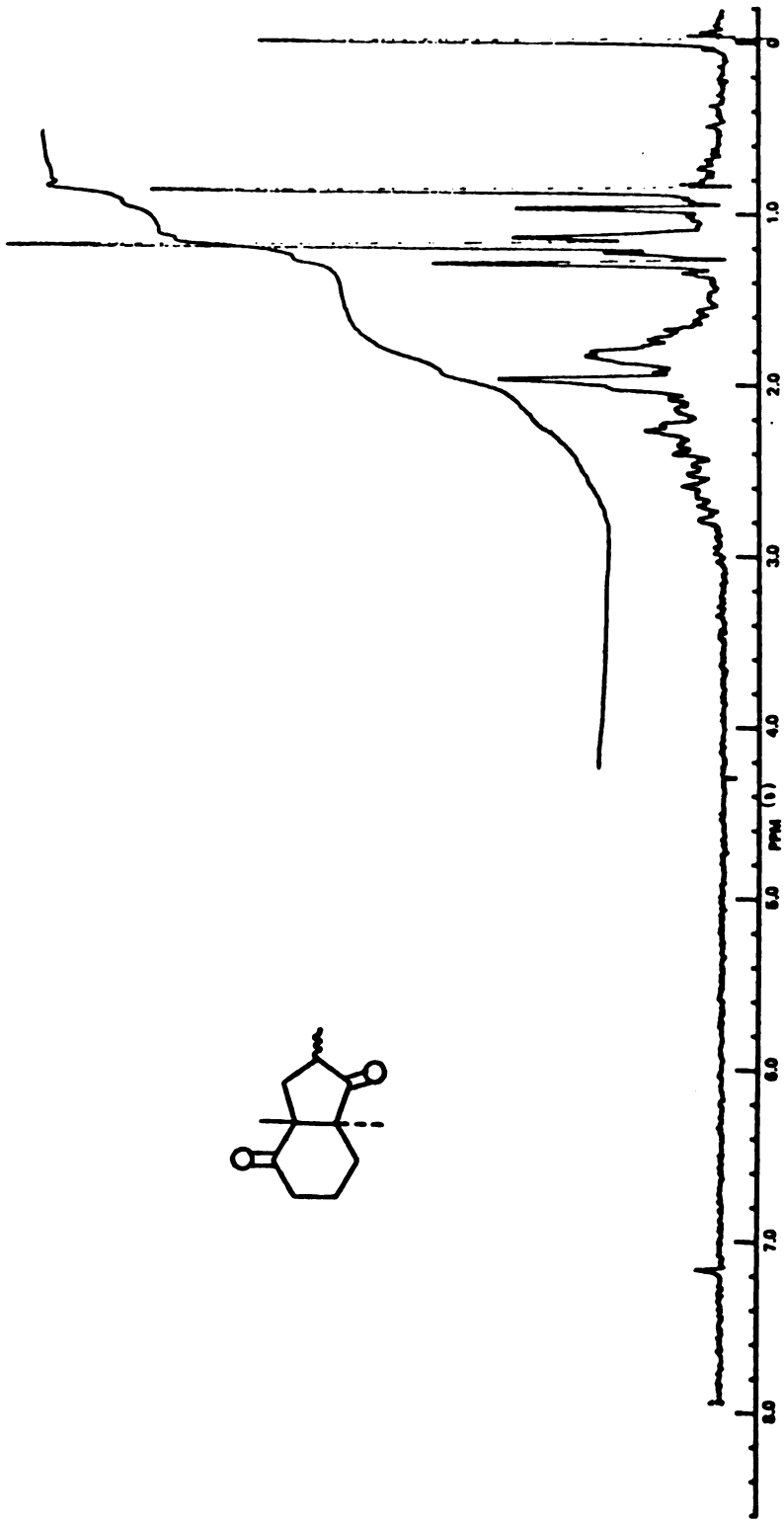


Figure 54. Pmr spectrum of (1α,6β,8ξ)-1,6,8-trimethyltricyclo[4.3.0]nona-2,7-dione (102) ($CDCl_3$).

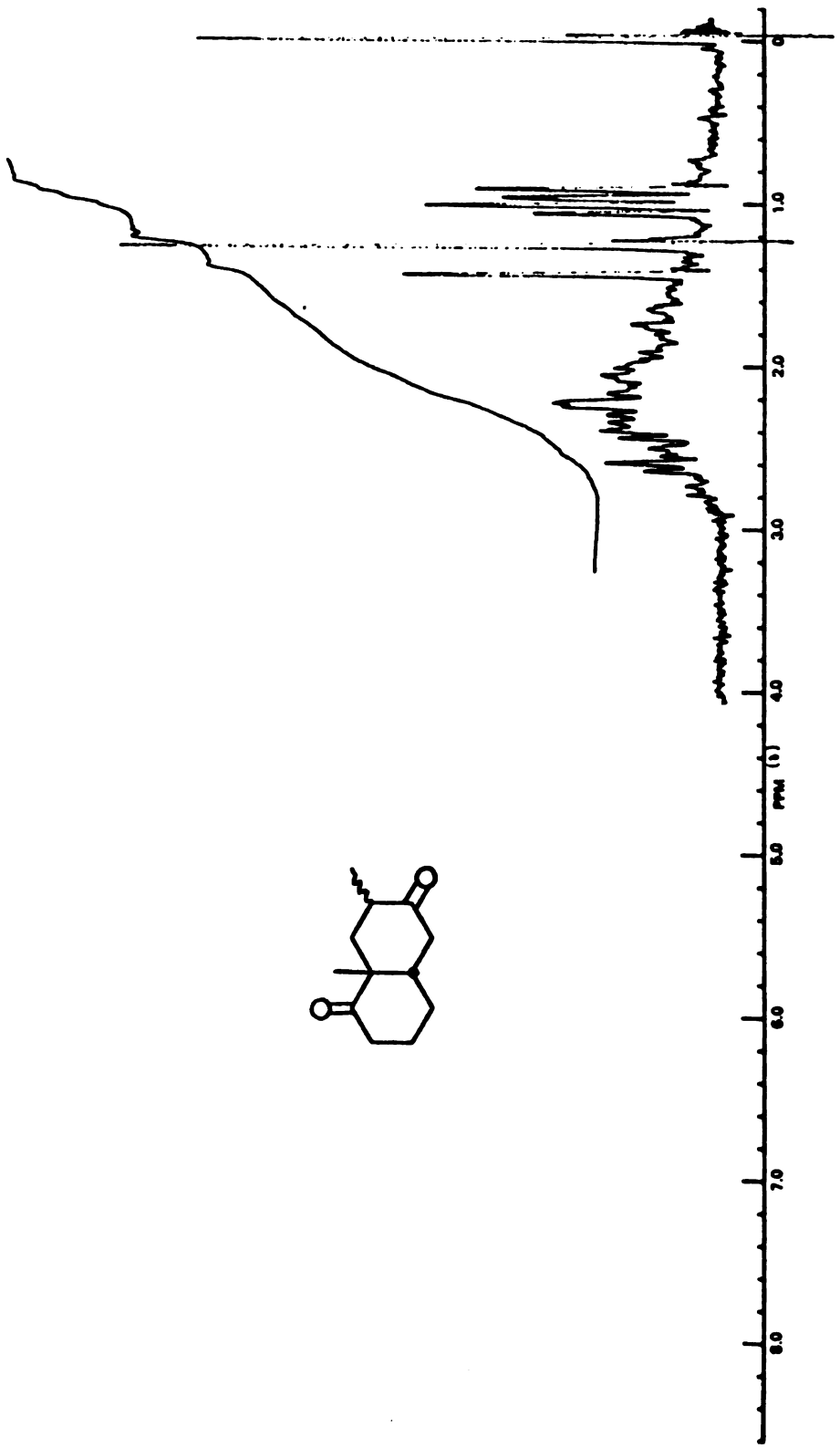


Figure 55. Pmr spectrum of (1α,6α,9β)-1,9-dimethylbicyclo[4.4.0]decan-2,8-dione (103 and 104) ($CDCl_3$).

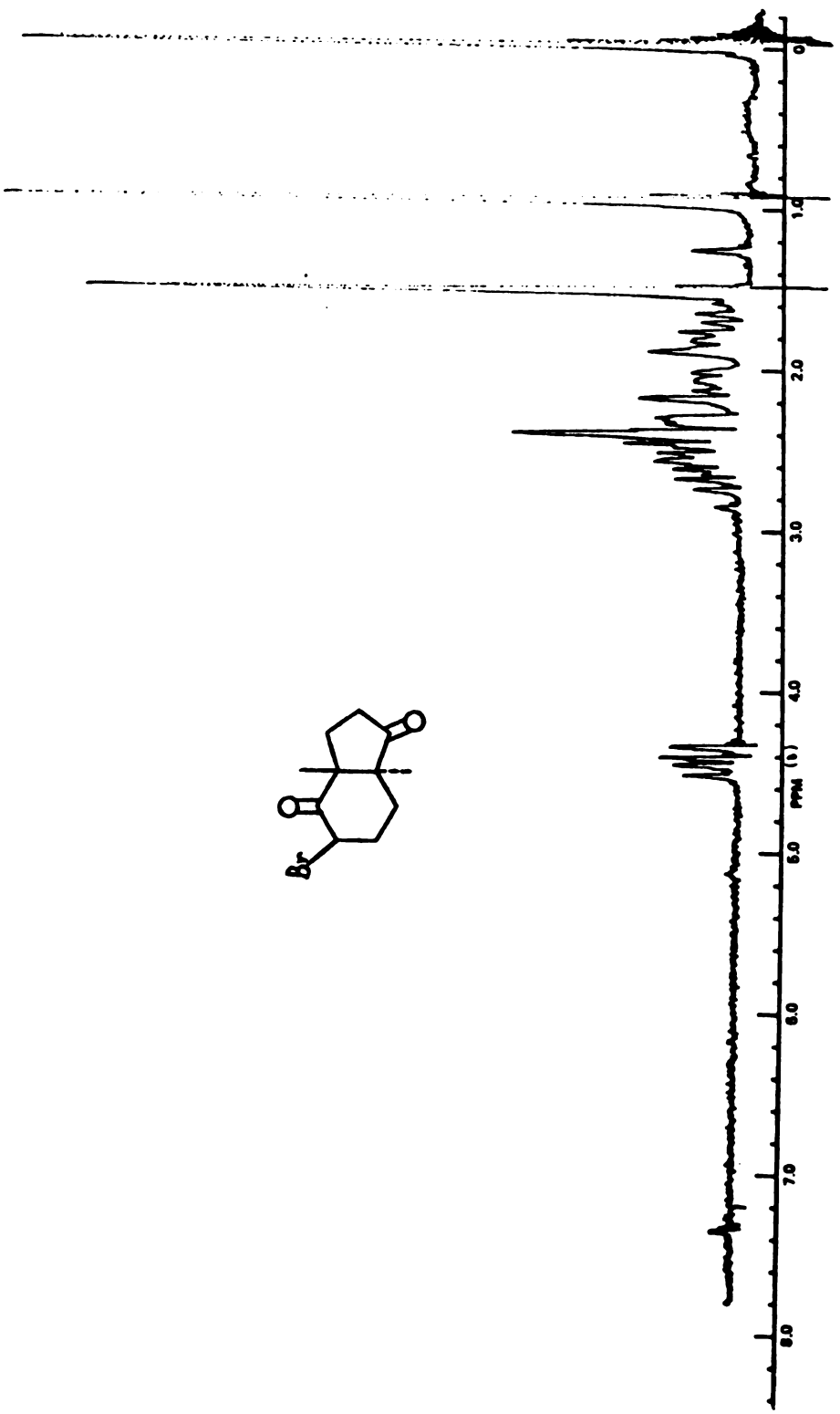


Figure 56. Pmr spectrum of (1α,3α,6ξ)-3-bromo-1,6-dimethylbicyclo[4.3.0]nona-2,7-dione (Figure 1) ($CDCl_3$).

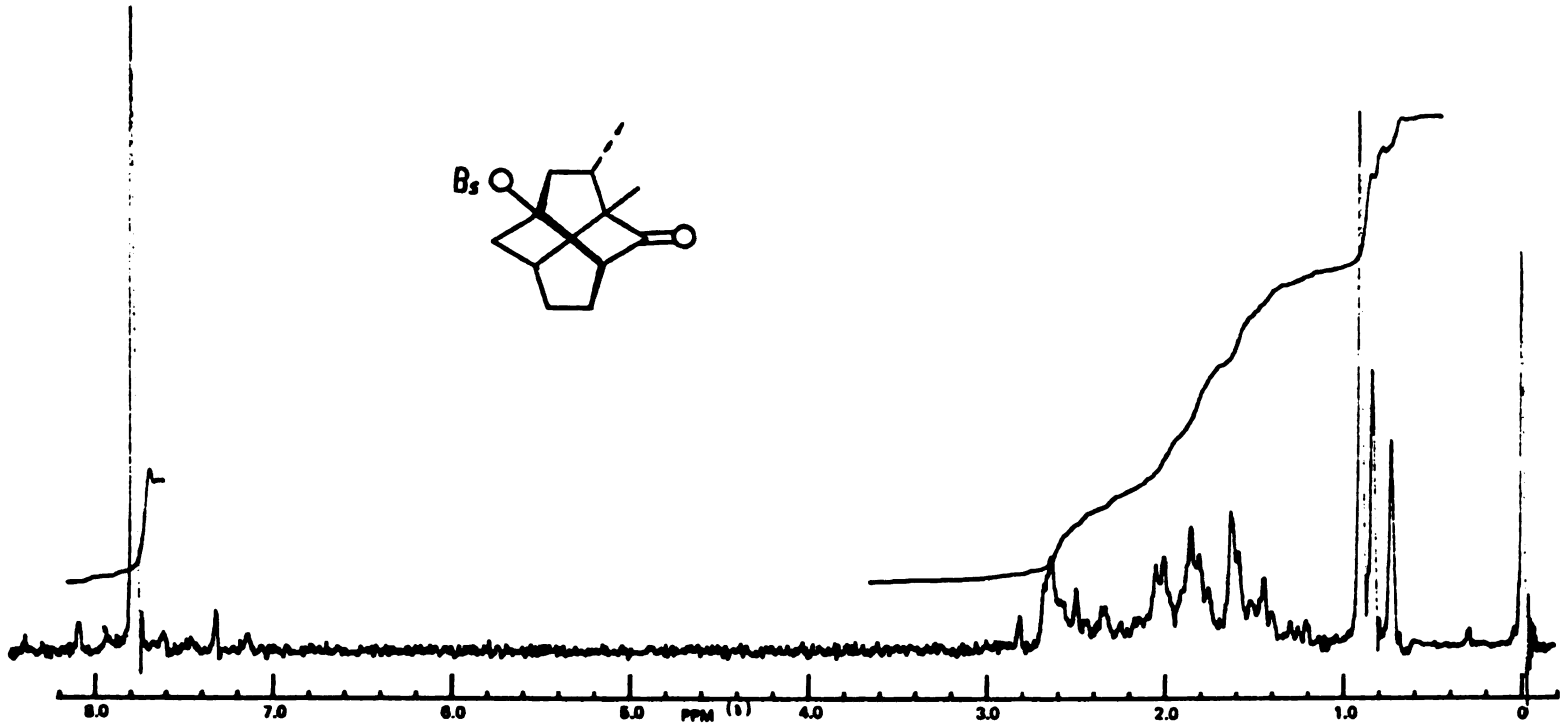


Figure 57. Pmr spectrum of (1R*,3R*,6S*,8R*,10R*)-8-(p-bromobenzenesulfonoxy)-1,10-dimethyltricyclo[4.4.0.0.^{3,8}]decan-2-one (Figure 2) ($CDCl_3$).

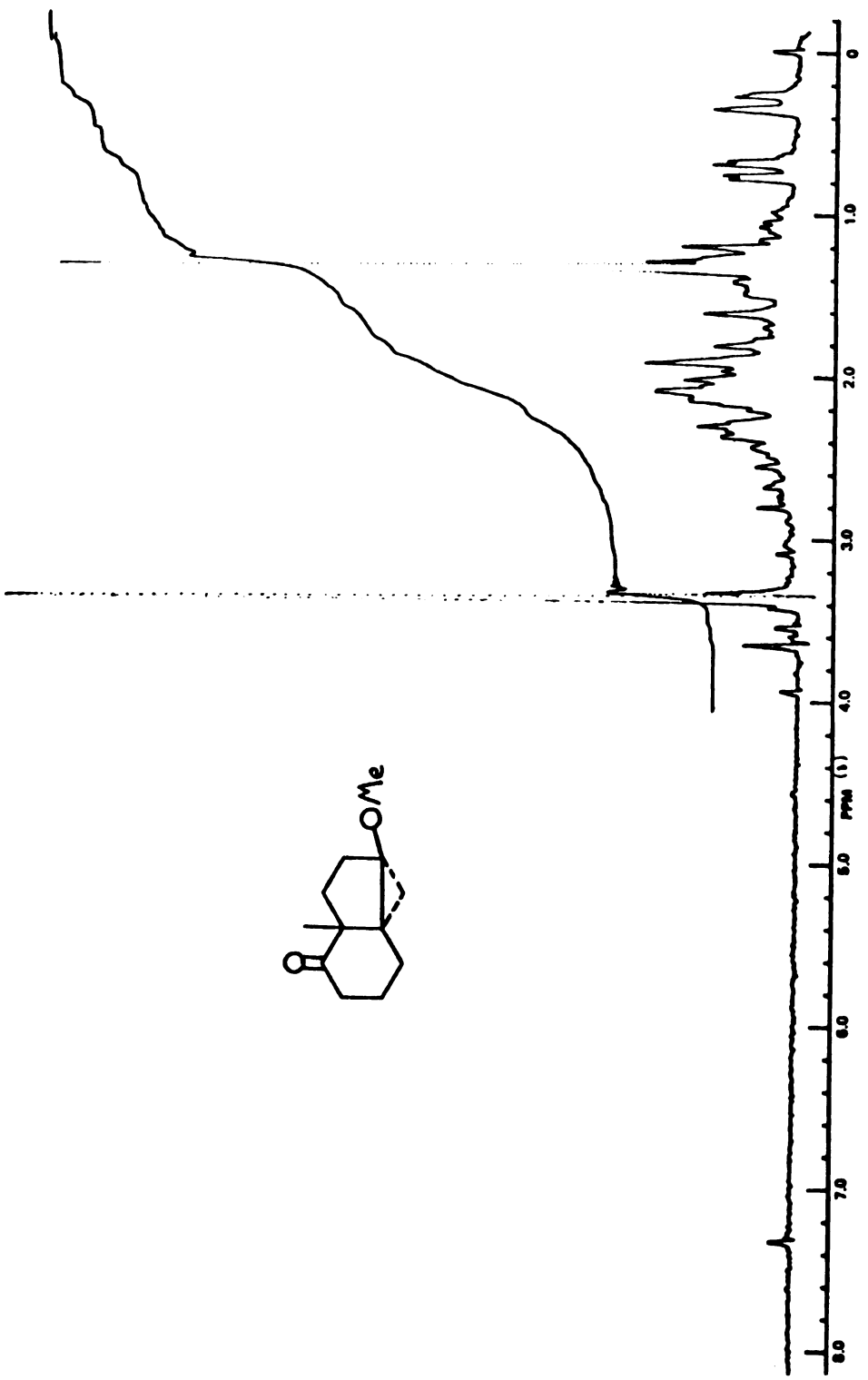


Figure 58. Pmr spectrum of (1S*,3α,6α)-3-methoxy-6-methyltricyclo[4.4.0.0^{1,3}]decan-7-one (91) ($CDCl_3$).

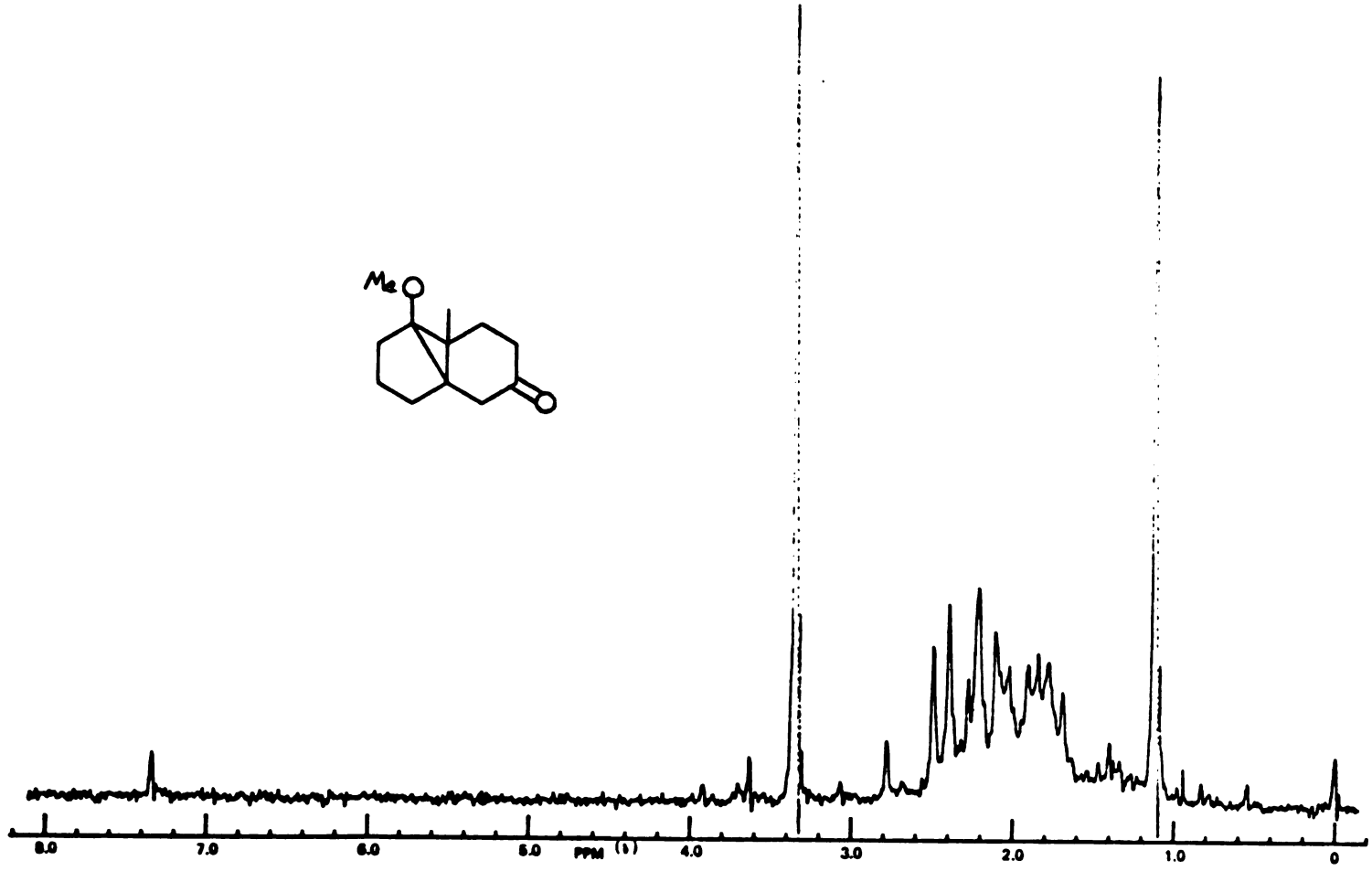


Figure 59. Pmr spectrum of (1R*,5α,6β)-5-methoxy-6-methyltricyclo[4.4.0.0^{1,5}]-decan-9-one (90) ($CDCl_3$)

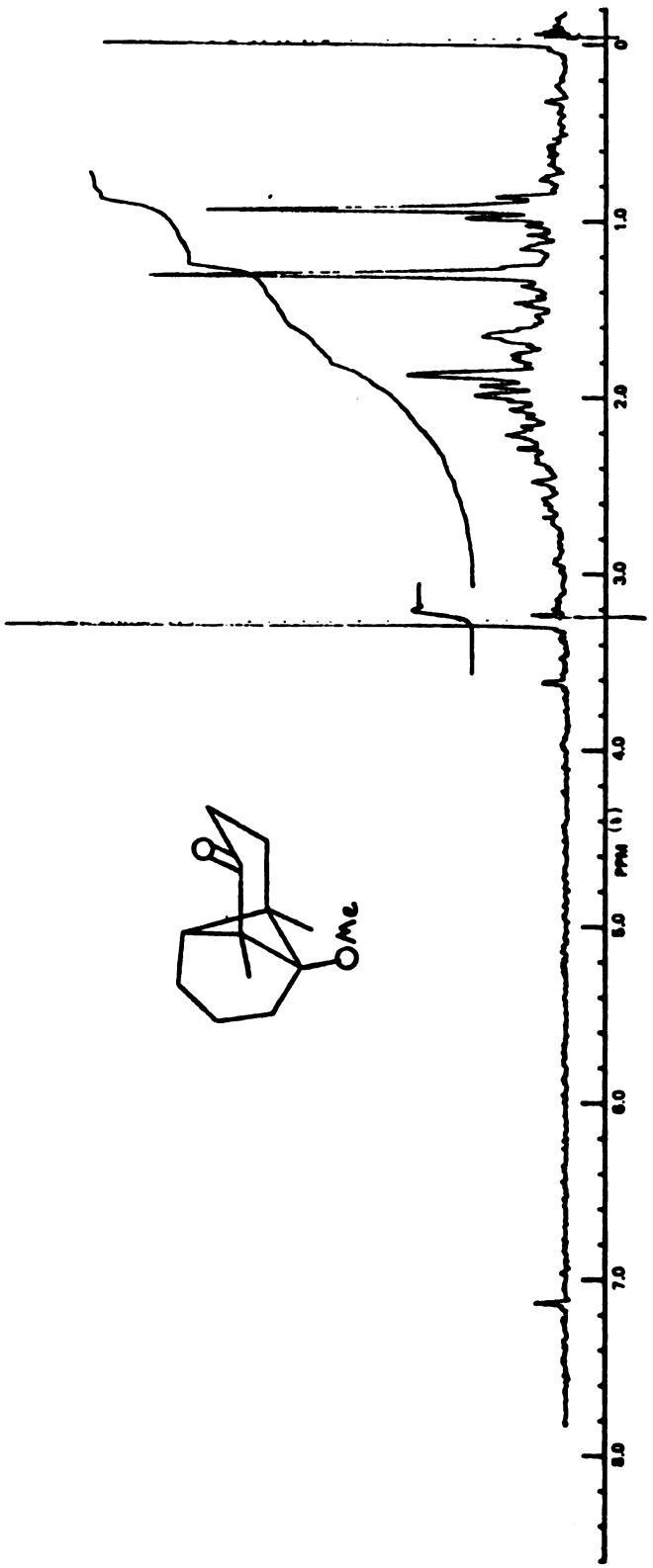


Figure 60. Pmr spectrum of (1R*,2S*,6R*,7R*)-2-methoxy-1,7-dimethyltricyclo-[4.4.0.0^{2},^{7}]decan-8-one (95).

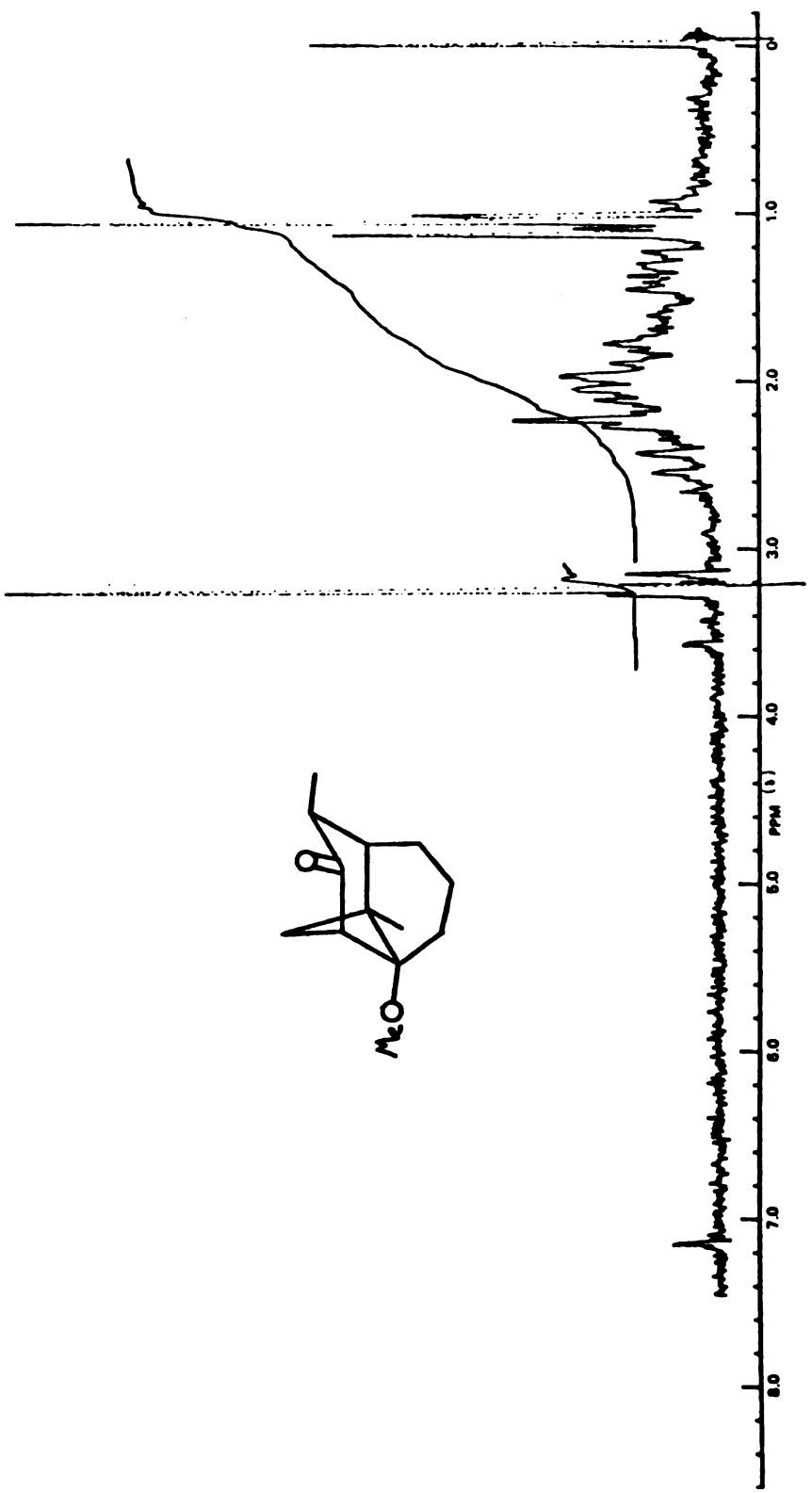


Figure 61. Pmr spectrum of (1R*,2S*,4S*,6S*,7R*)-2-methoxy-1,7-dimethyltricyclo-[4.4.0.0^{2,9}]decan-8-one (96).

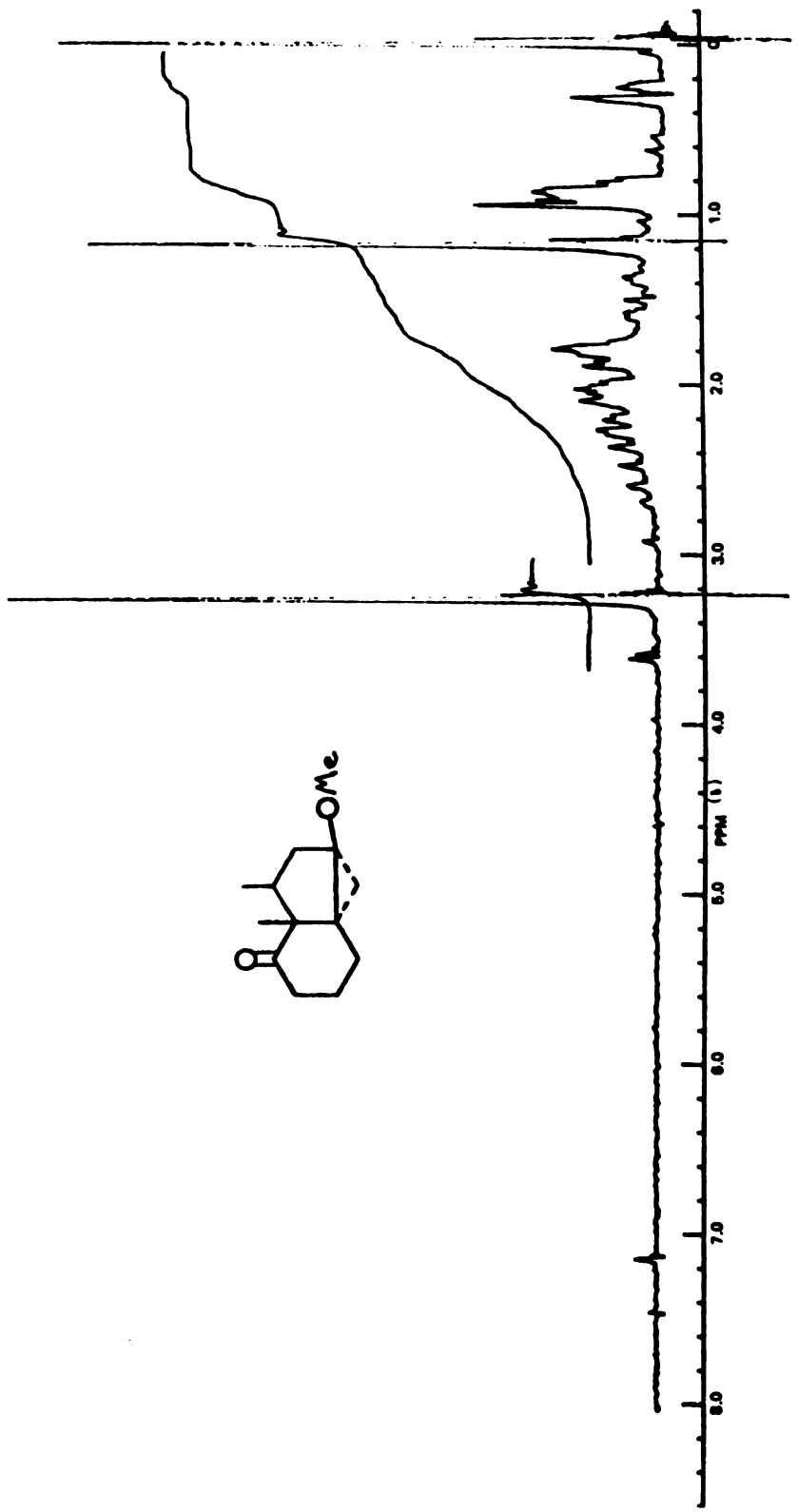


Figure 62. Pmr spectrum of (1S*,3α,5α,6α)-3-methoxy-5,6-dimethyltricyclo-[4.4.0.0^{1,3}]decan-7-one (99) ($CDCl_3$).

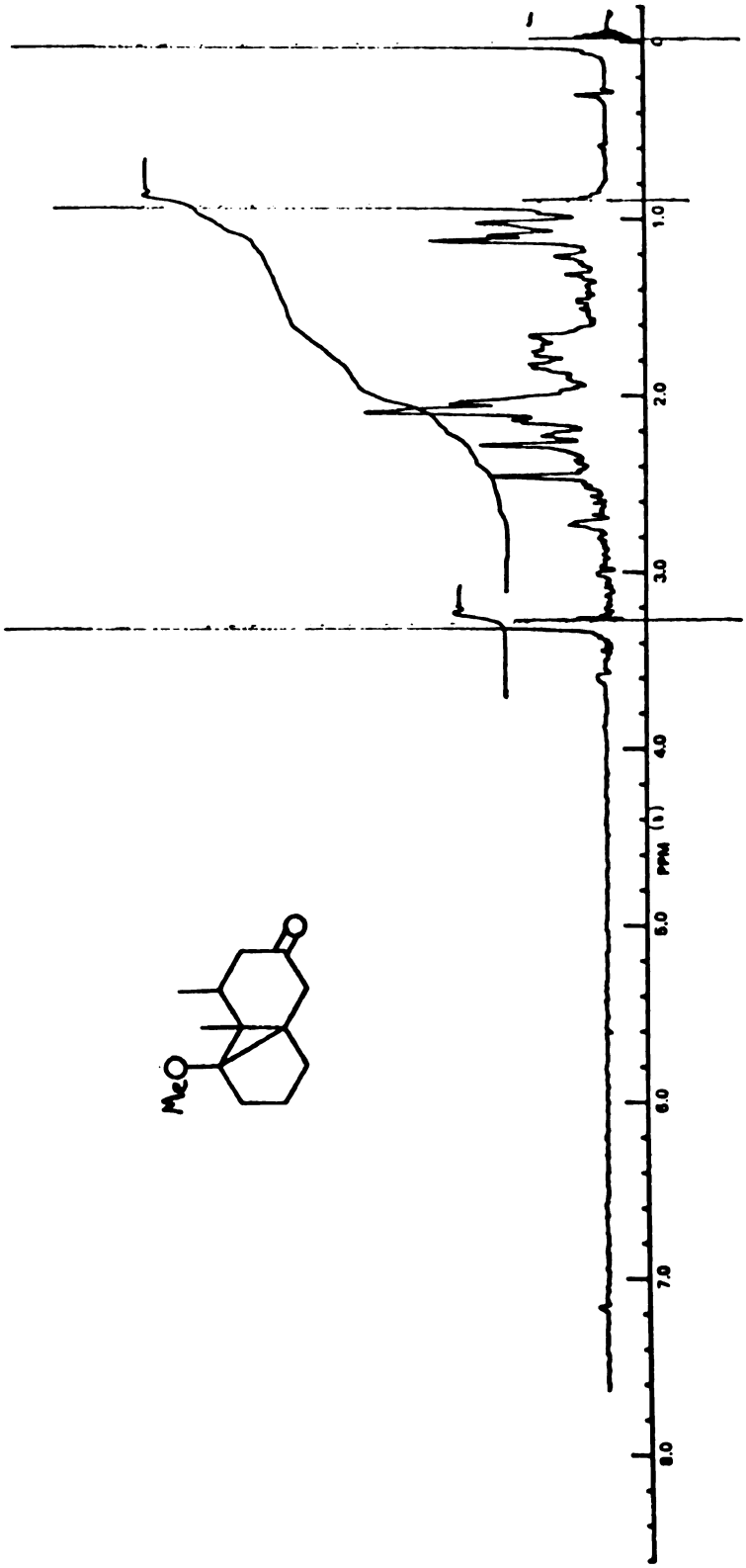


Figure 63. Pmr spectrum of (1R*,5β,6α,7α)-5-methoxy-6,7-dimethyltricyclo-[4.4.0.0^{1,5}]decan-9-one (98) ($CDCl_3$).

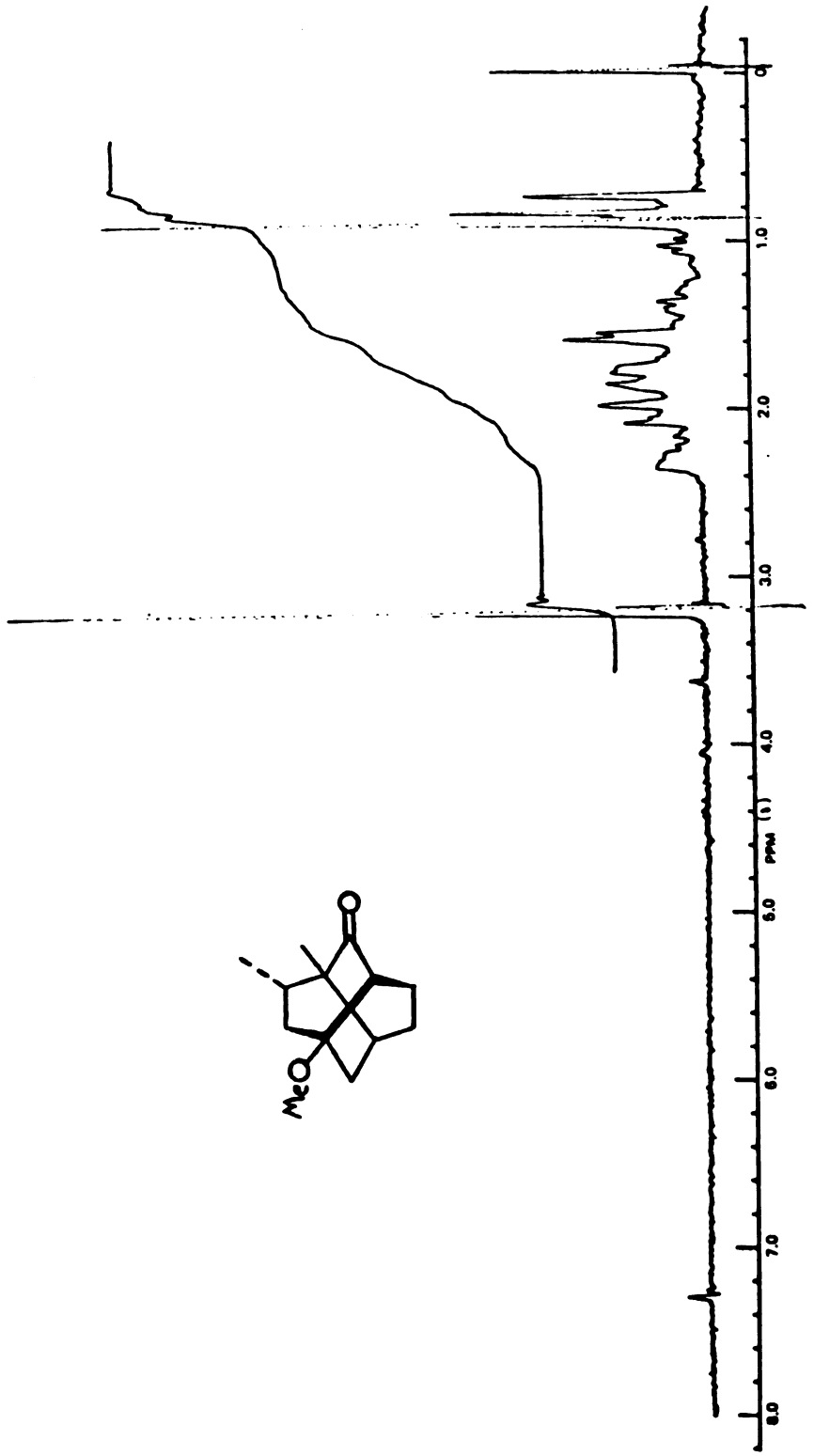


Figure 64. Pmr spectrum of (1R*,3R*,6S*,8R*,10R*)-8-methoxy-1,10-dimethyltricyclo-[4.4.0.0^{3,8}]decan-2-one (10I) ($CDCl_3$).

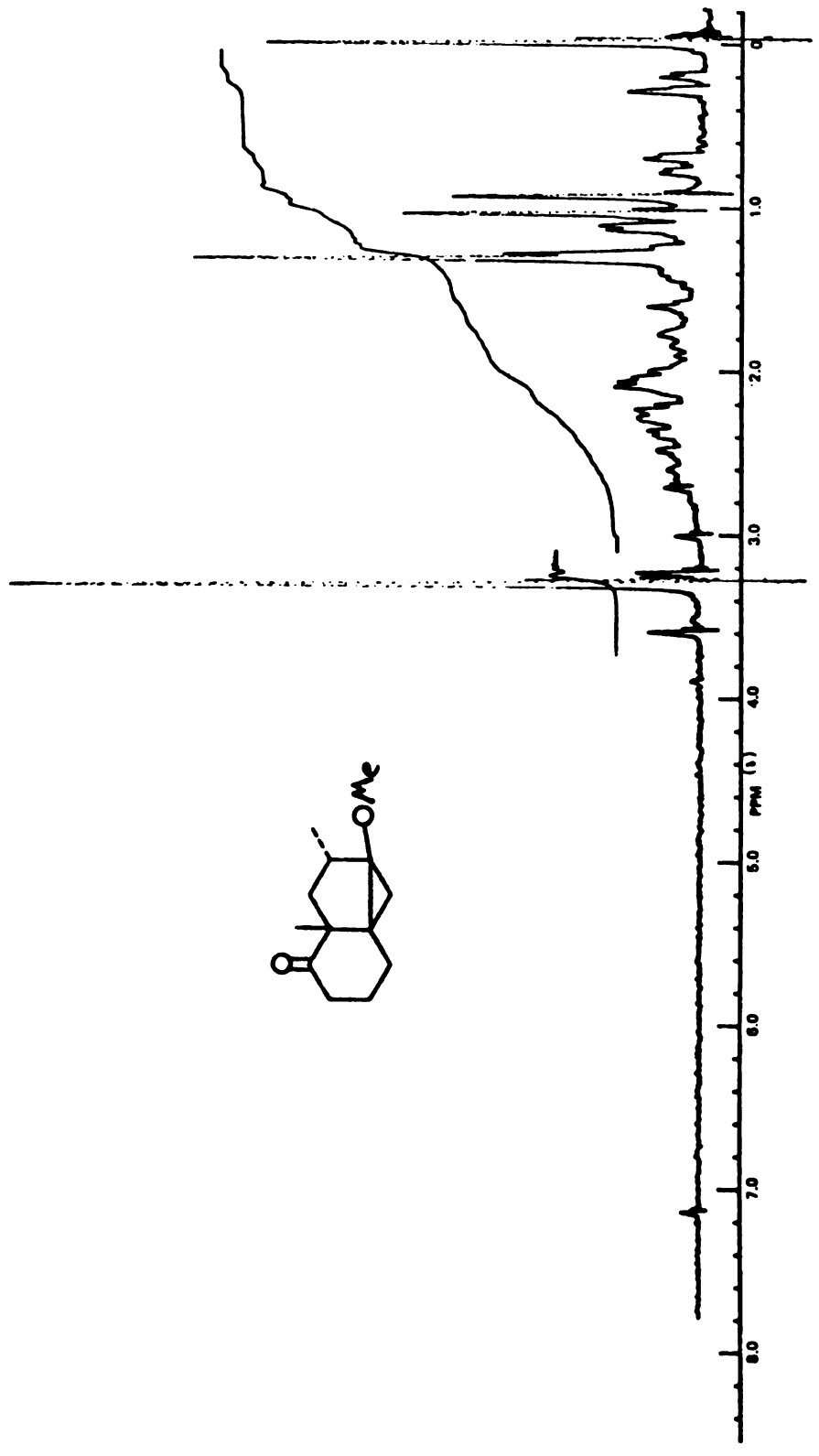


Figure 65. Pmr spectrum of (1S*,3α,4β,6α)-3-methoxy-4,6-dimethyltricyclo-[4.4.0.0^{1,3}]decan-7-one (105) ($CDCl_3$).

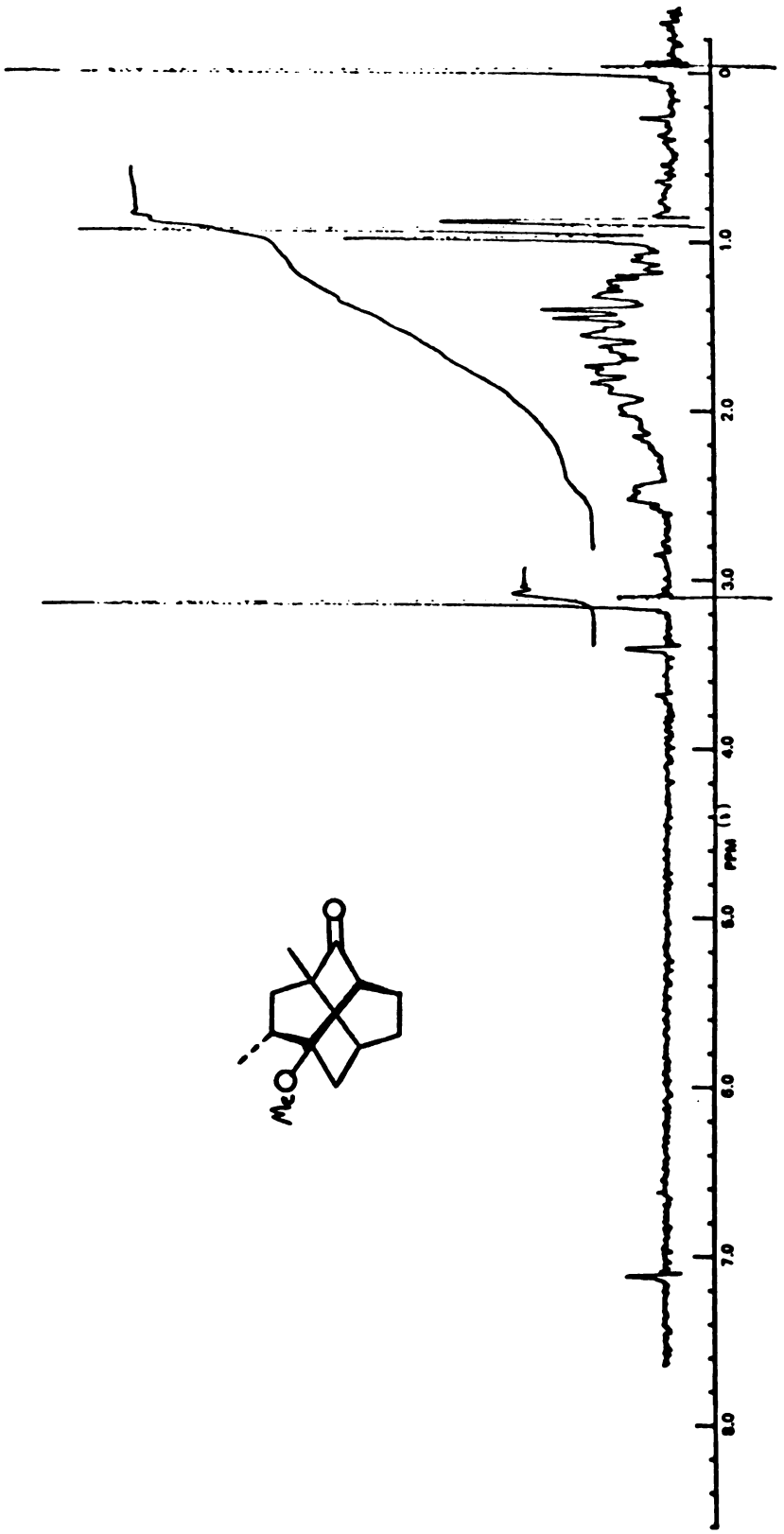


Figure 66. Pmr spectrum of (1R*,3R*,6S*,8R*,9S*)-8-methoxy-1,9-dimethyltricyclo-[4.4.0.0^{3,8}]decan-2-one (106).

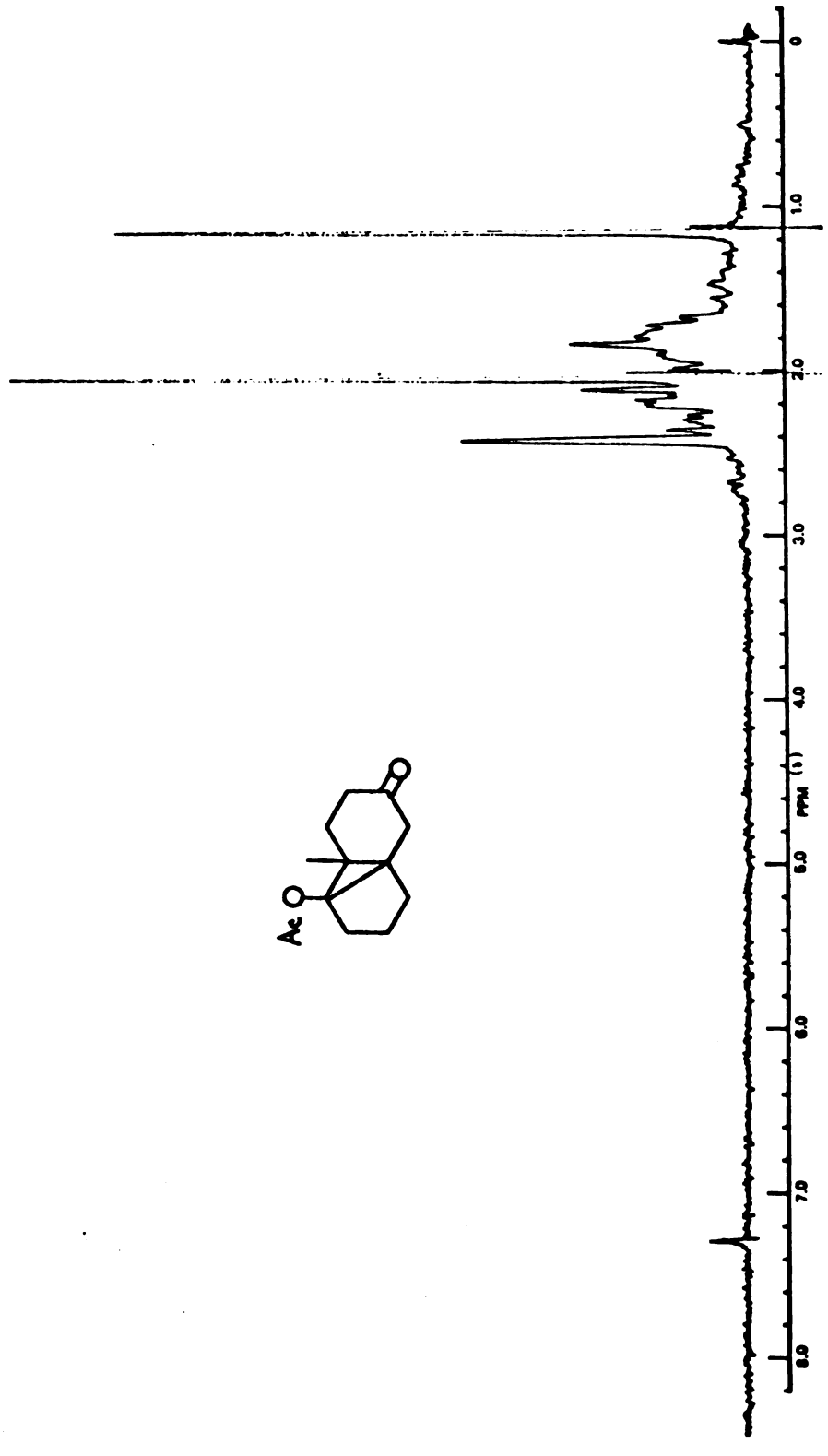


Figure 67. Pmr spectrum of (1R*,5α,6β)-5-acetoxy-6-methyltricyclo[4.4.0.0^{1,5}]decan-9-one (76) ($CDCl_3$).

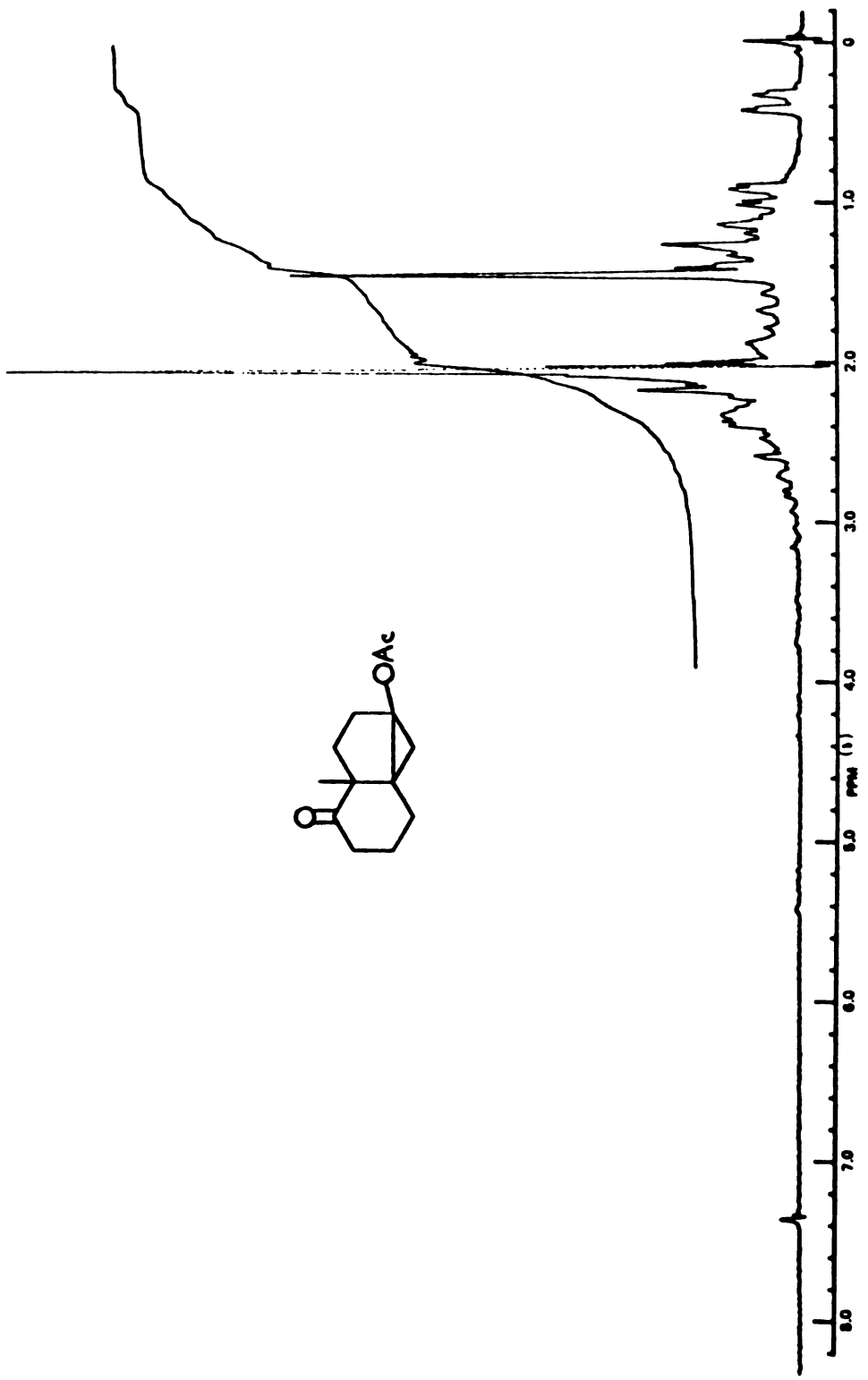


Figure 68. Pmr spectrum of (1S*,3α,6α)-3-acetoxy-6-methyltricyclo[4.4.0.0^{1,3}]-decan-7-one (77) ($CDCl_3$).

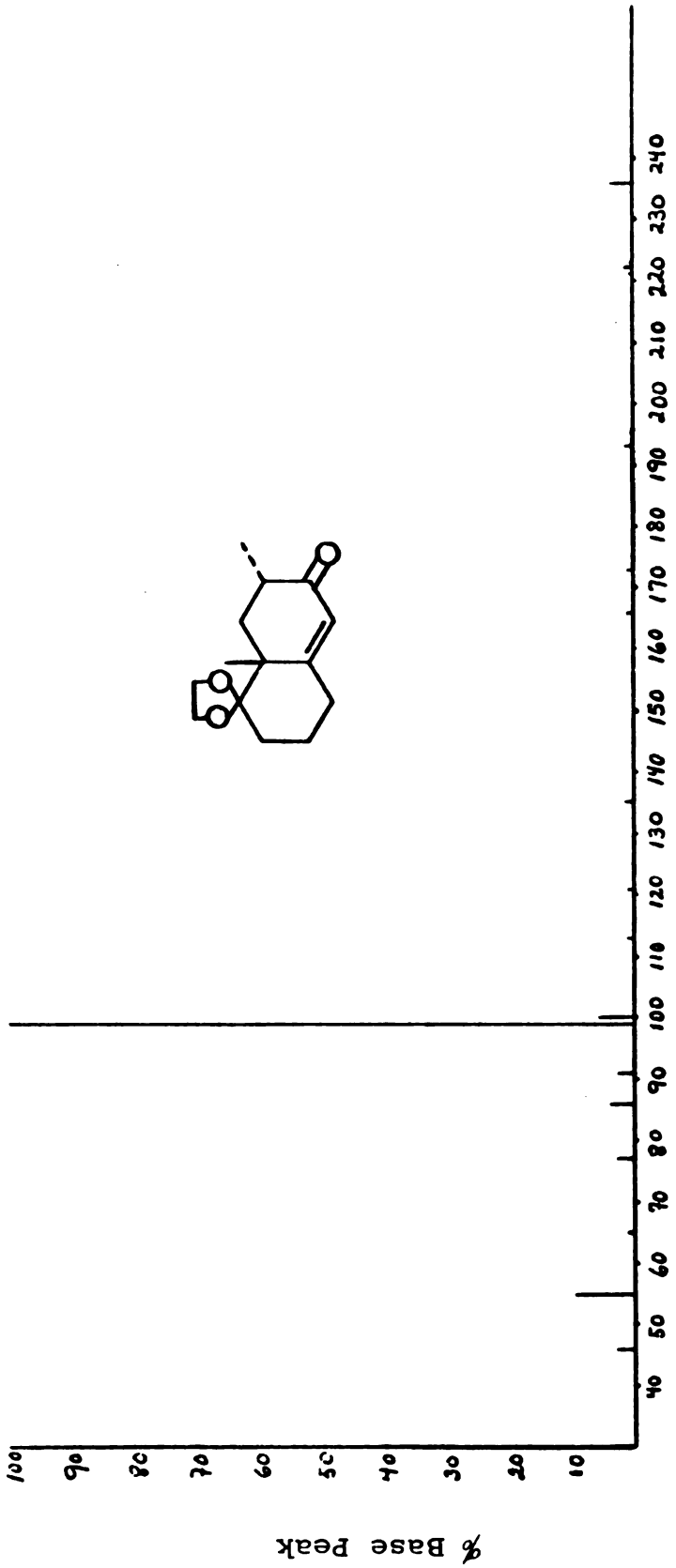


Figure 69. Mass spectrum of trans-1,9-dimethylbicyclo[4.4.0]dec-6-ene-2,8-dione 2-ethylene ketal (60).

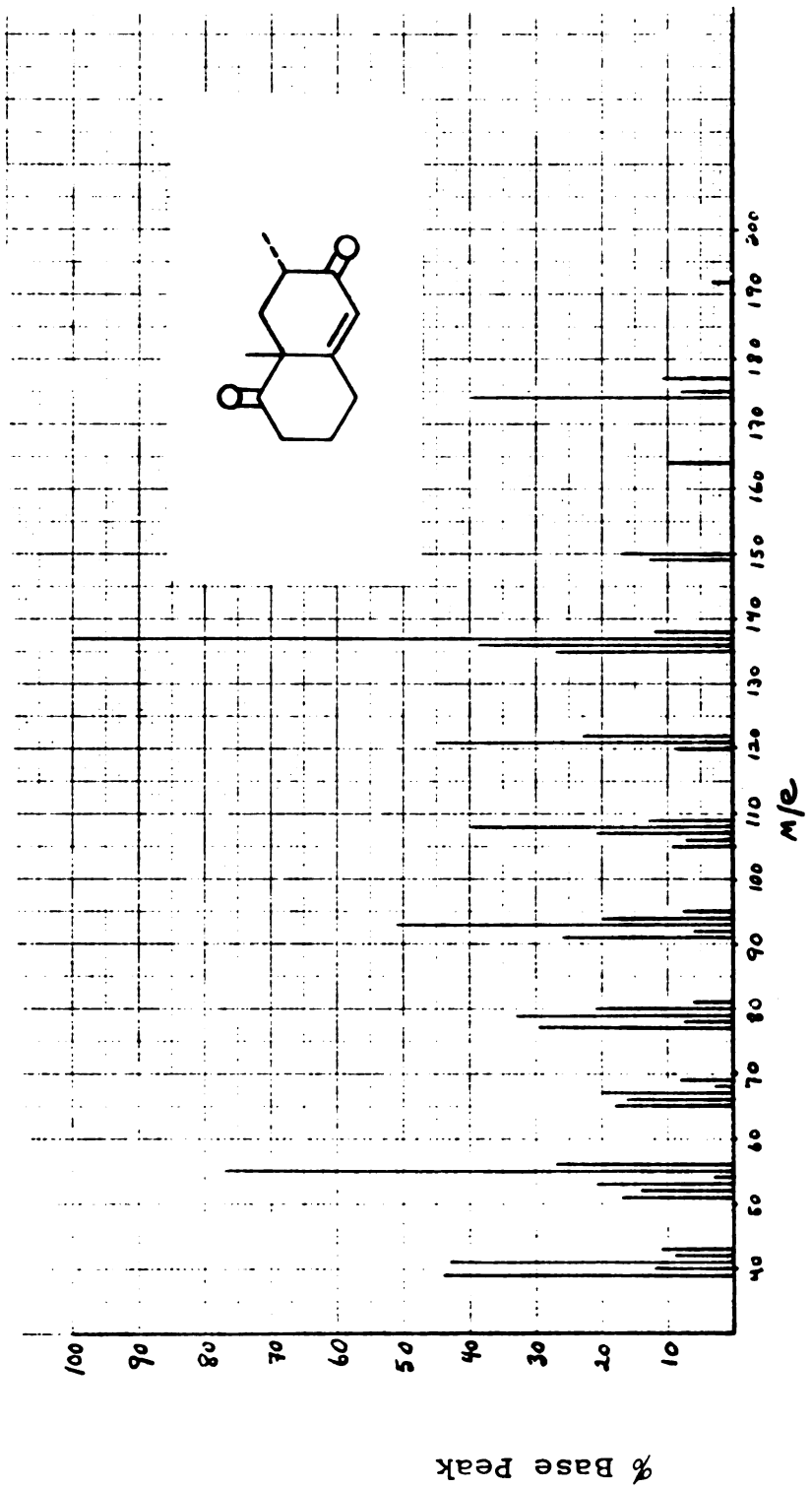


Figure 70. Mass spectrum of trans-1,9-dimethylbicyclo[4.4.0]dec-6-ene-2,8-dione (56).

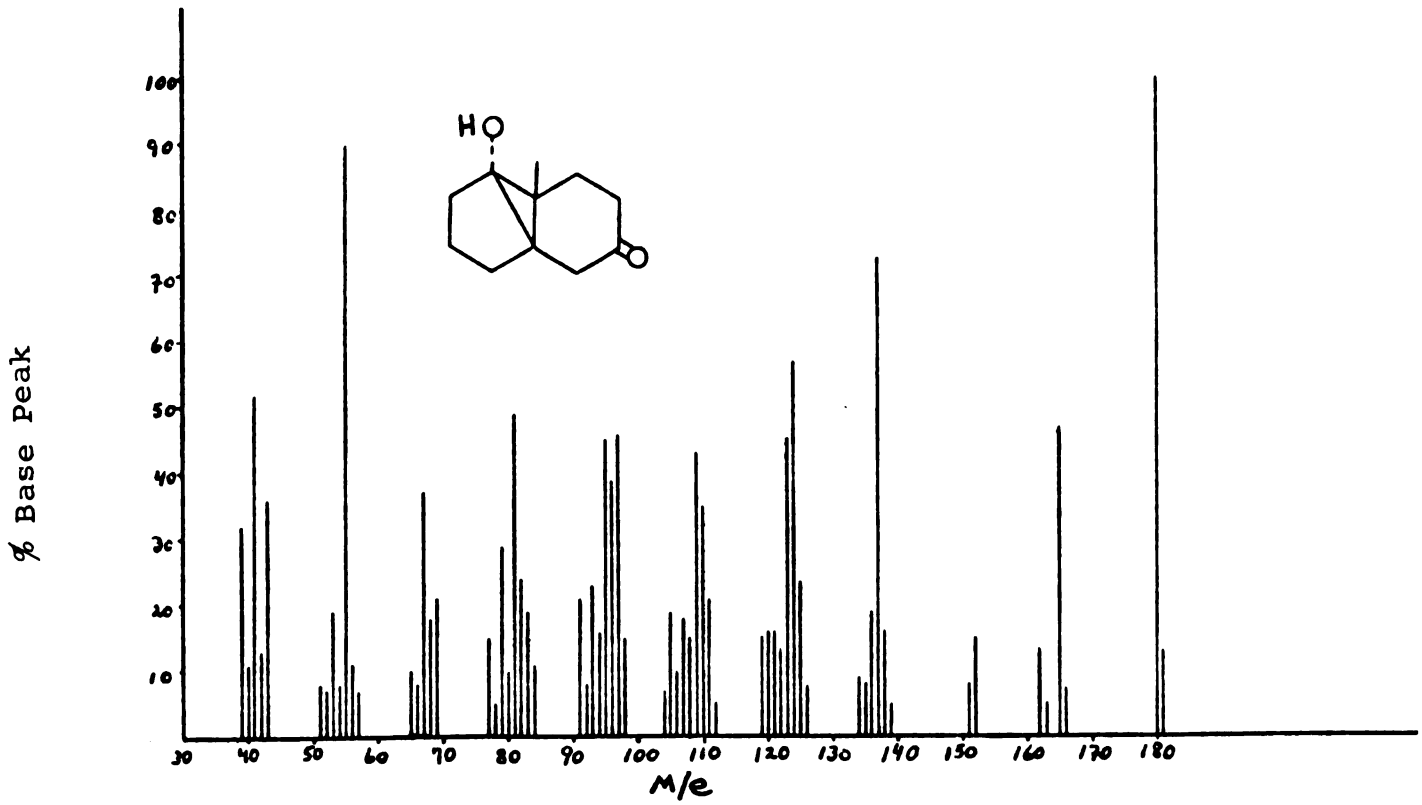


Figure 71. Mass spectrum of (1R*,5α,6β)-5-hydroxy-6-methyltricyclo-[4.4.0.0^{1,5}]decan-9-one (4).

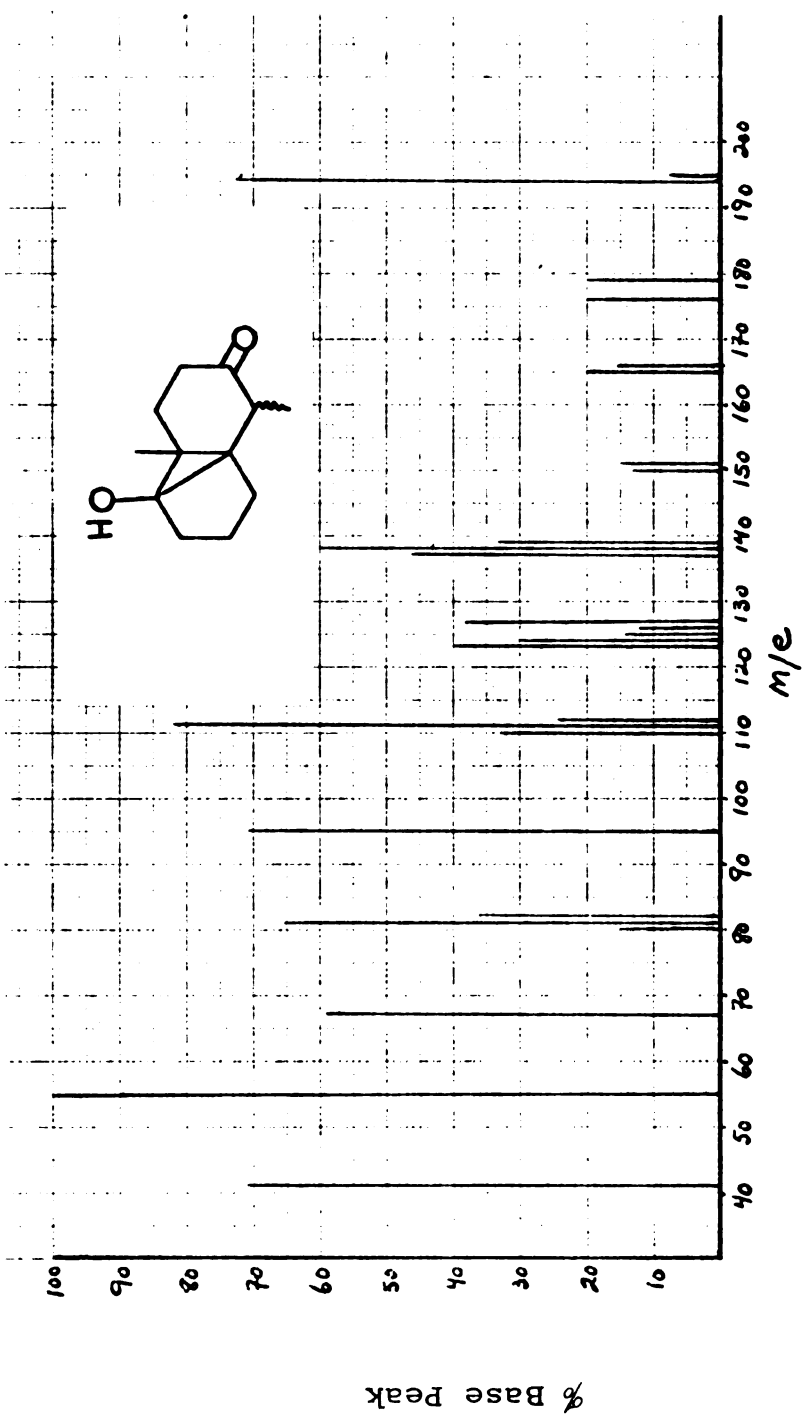


Figure 72. Mass spectrum of (1R*,5α,6E,10E)-5-hydroxy-6,10-dimethyltricyclo-[4.4.0.0^{1,5}]decan-9-one (62).

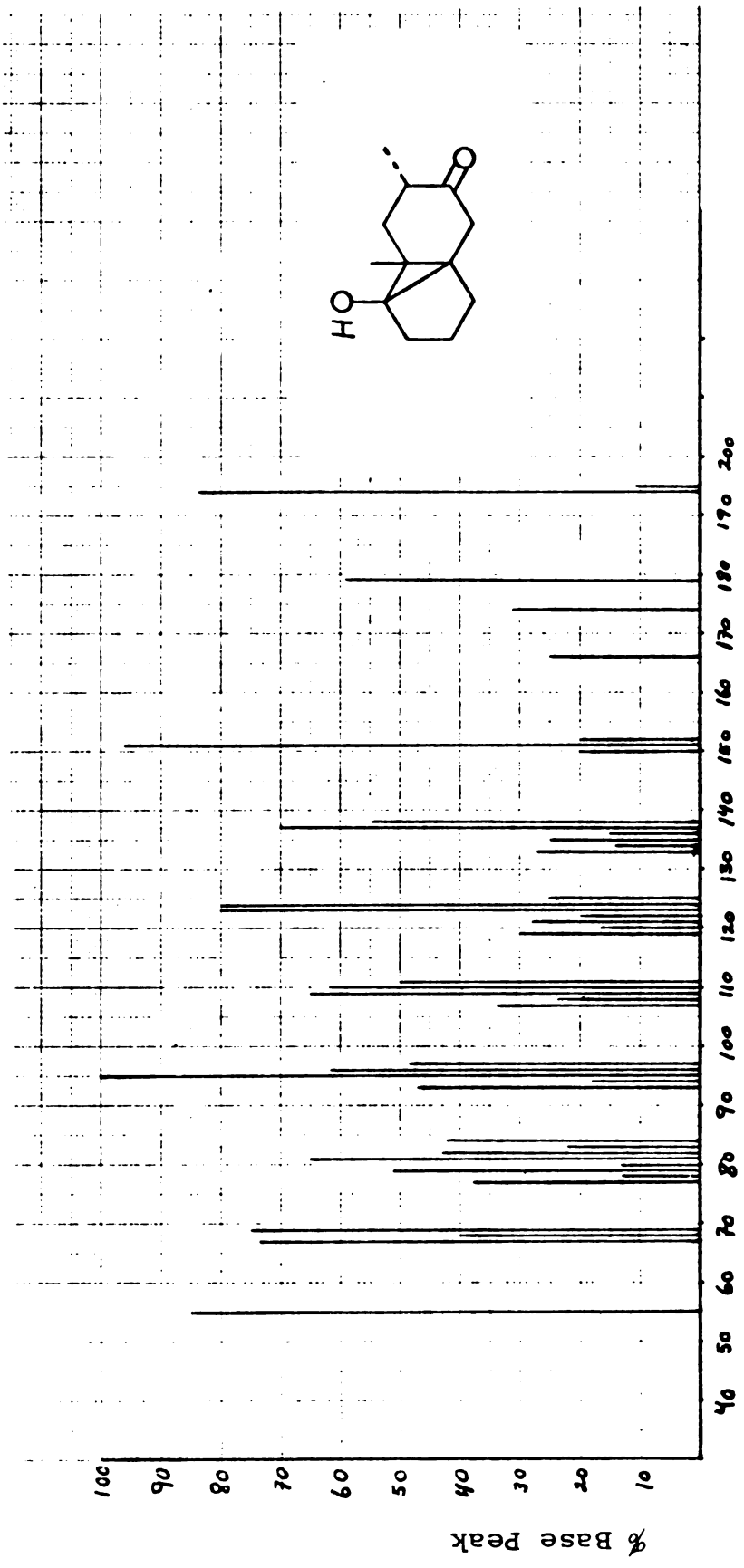


Figure 73. Mass spectrum of (1R*,5α,6β,8α)-5-hydroxy-6,8-dimethyltricyclo-[4.4.0.0^{1,5}]decan-9-one (64).

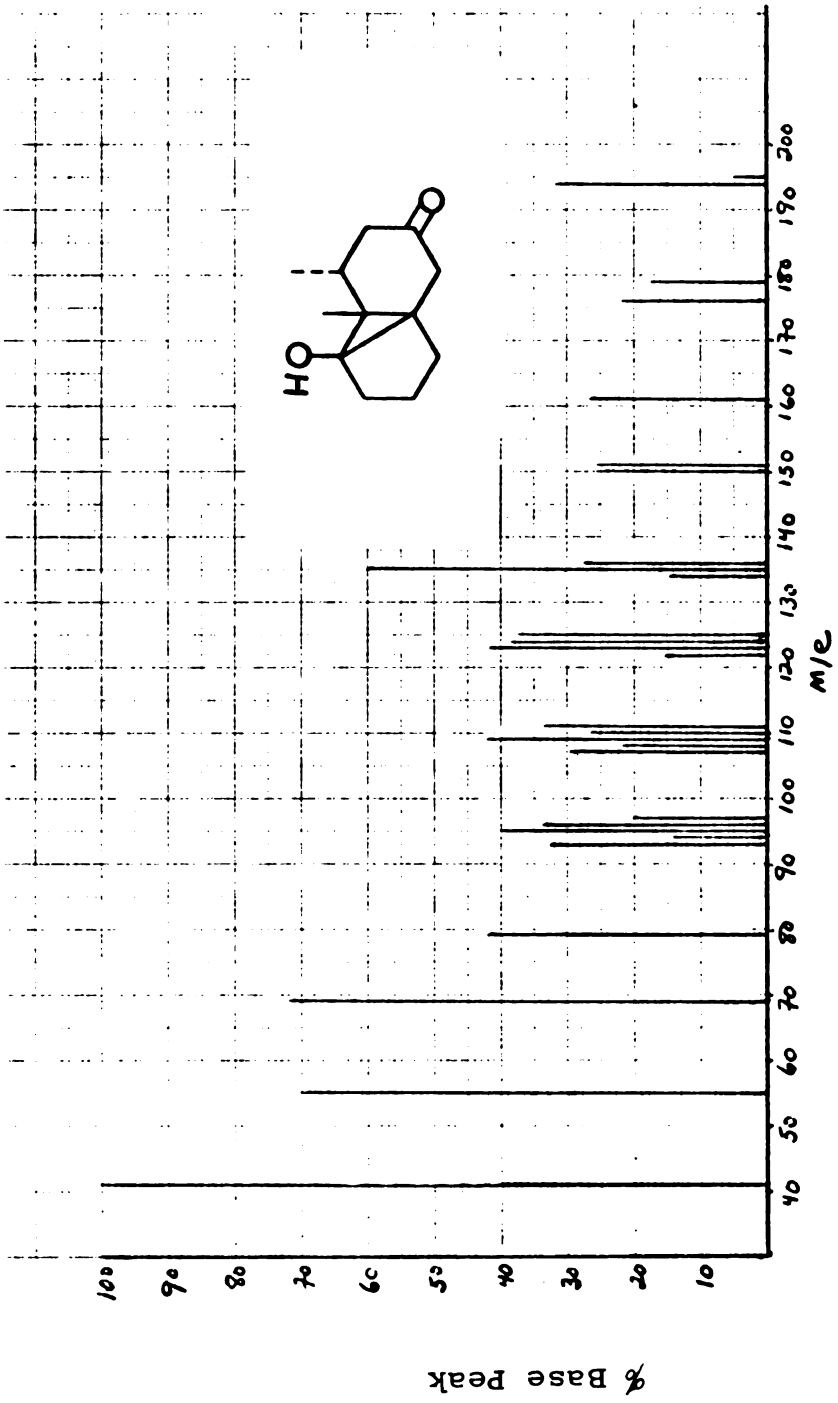


Figure 74. Mass spectrum of (1R*,5α,6ε,7α)-5-hydroxy-6,7-dimethyltricyclo-[4.4.0.0^{1,5}]decan-9-one (50).

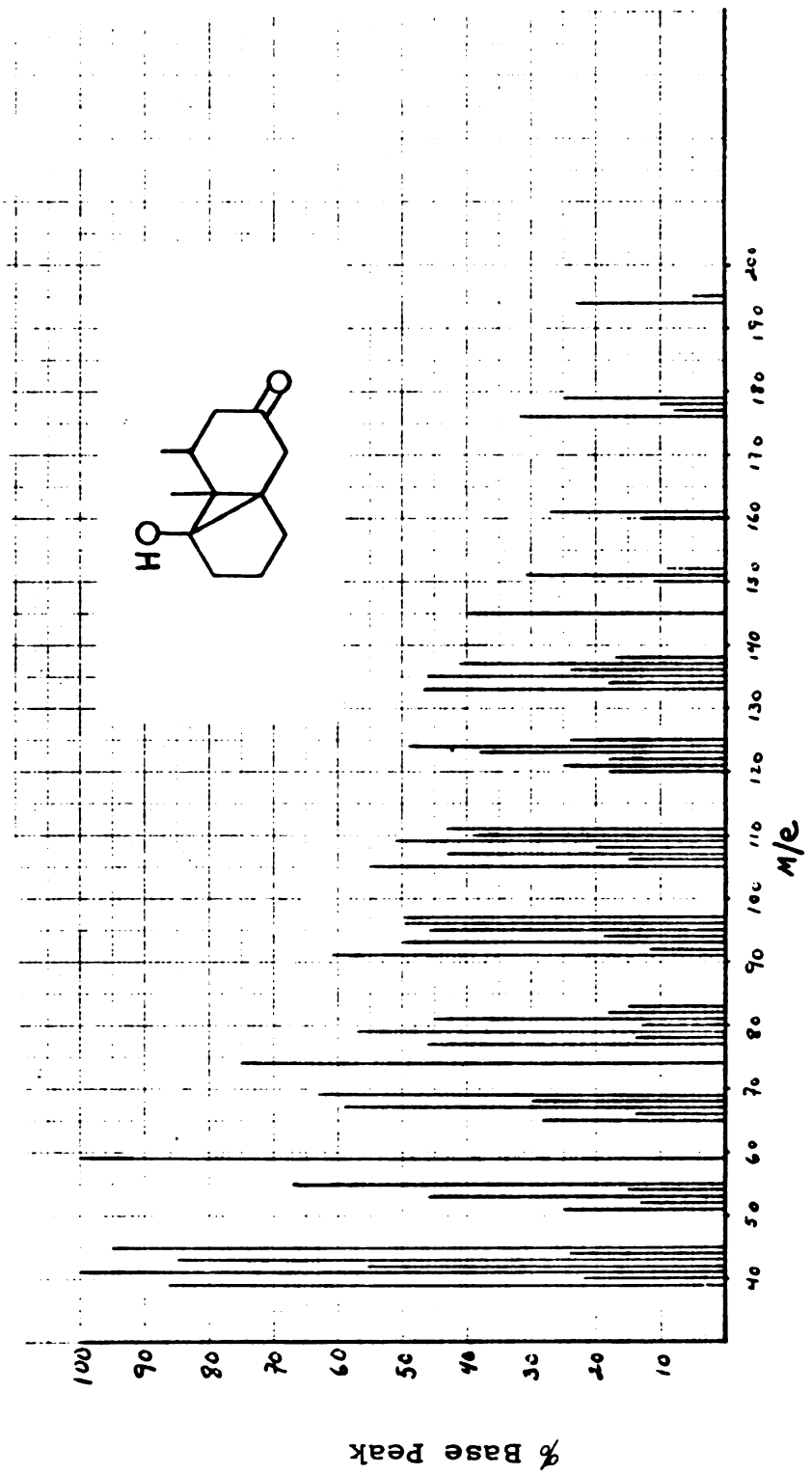


Figure 75. Mass spectrum of (1R*,5β,6α,7α)-5-hydroxy-6,7-dimethyltricyclo-[4.4.0.0^{1,5}]decan-9-one (63).

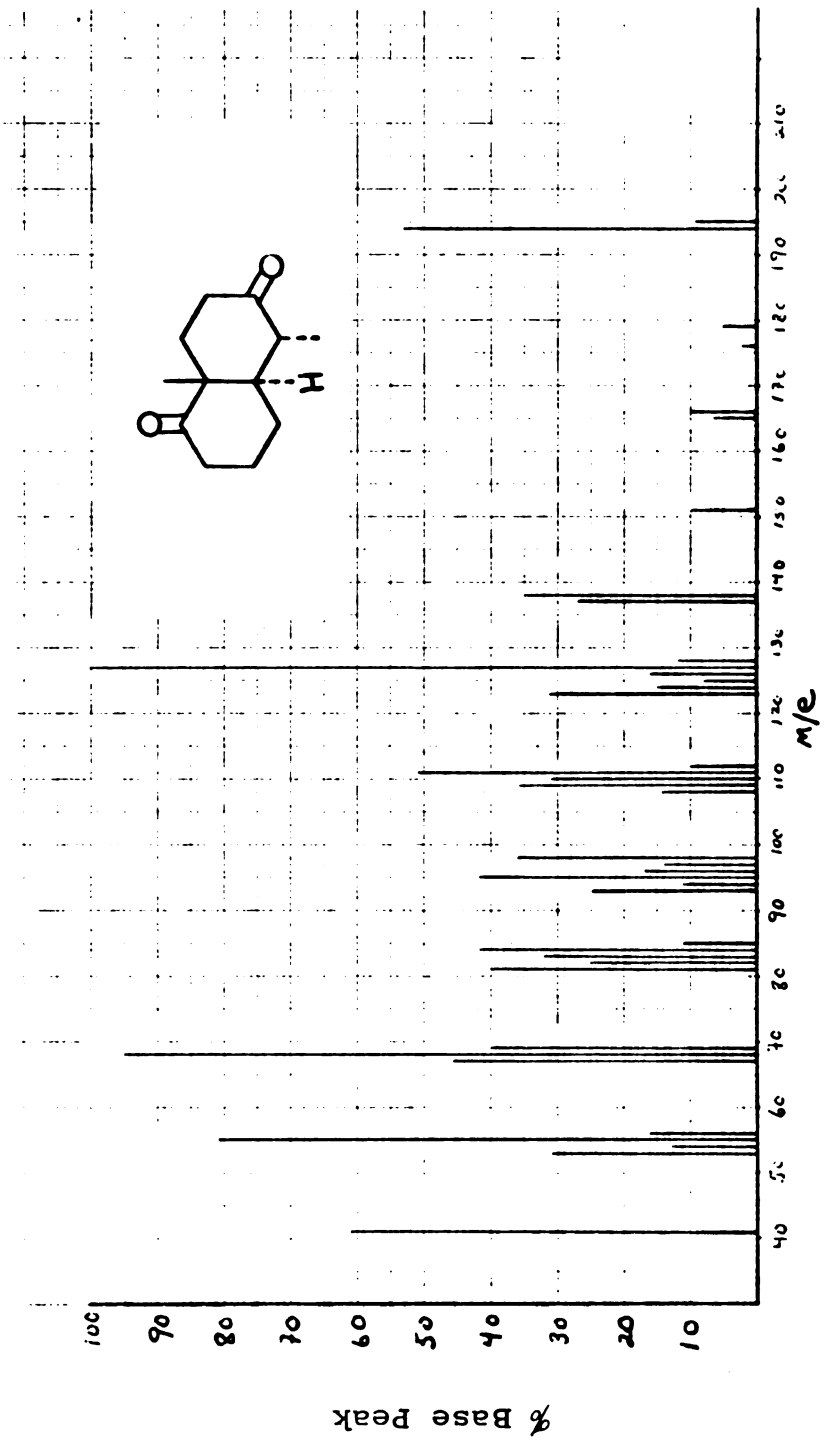


Figure 76. Mass spectrum of (1β,6α, 7α)-1, 7 -dimethylbicyclo[4.4.0]decan-2,8-dione (65).

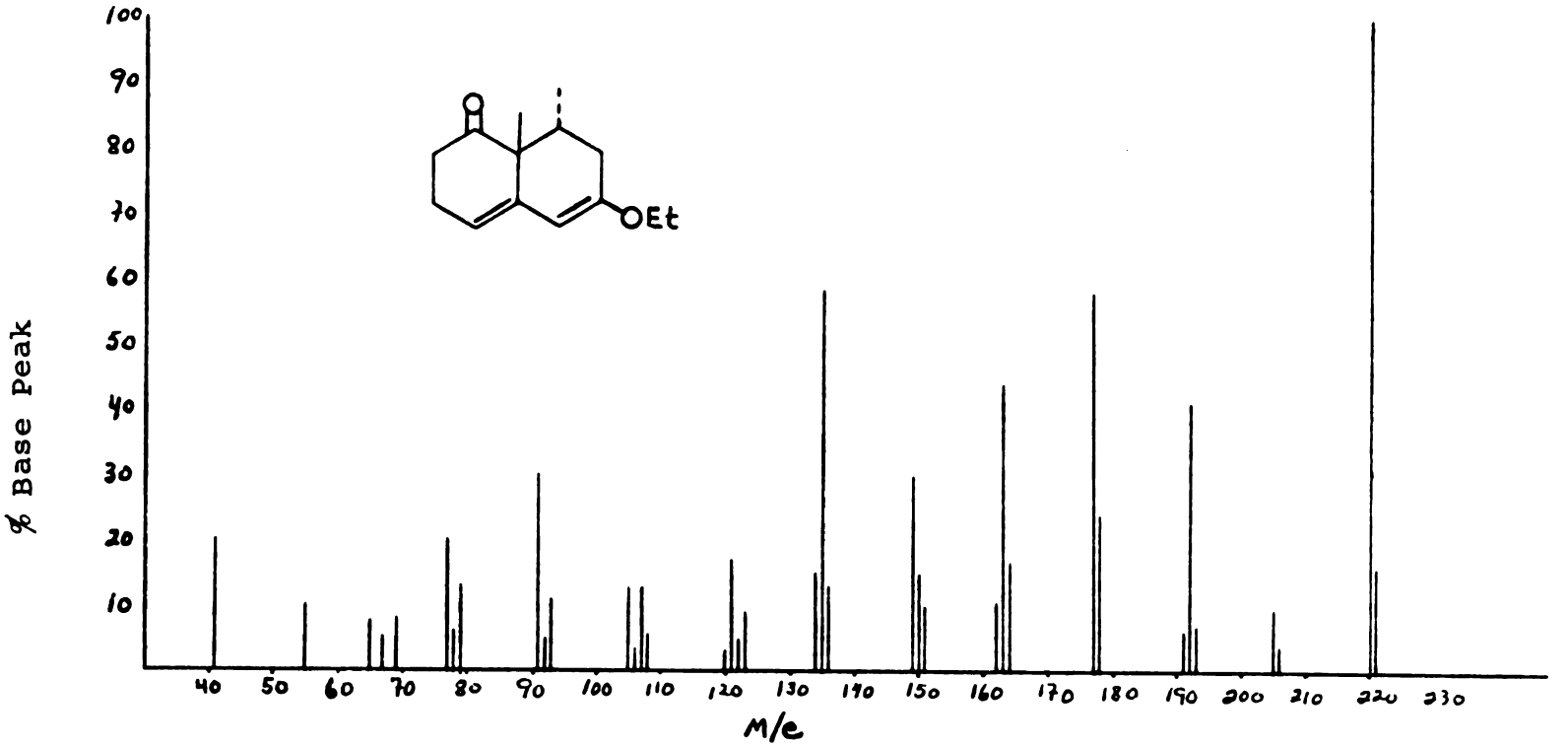


Figure 77. Mass spectrum of 8-ethoxy-trans-1,10-dimethylbicyclo[4.4.0]dec-5,7-diene-2-one (58).

Figure 78. Mass spectrum of (5α,6β,7α)-7-hydroxy-5,6-dimethylbicyclo[4.4.0]-dec-1-ene-3-one (67).

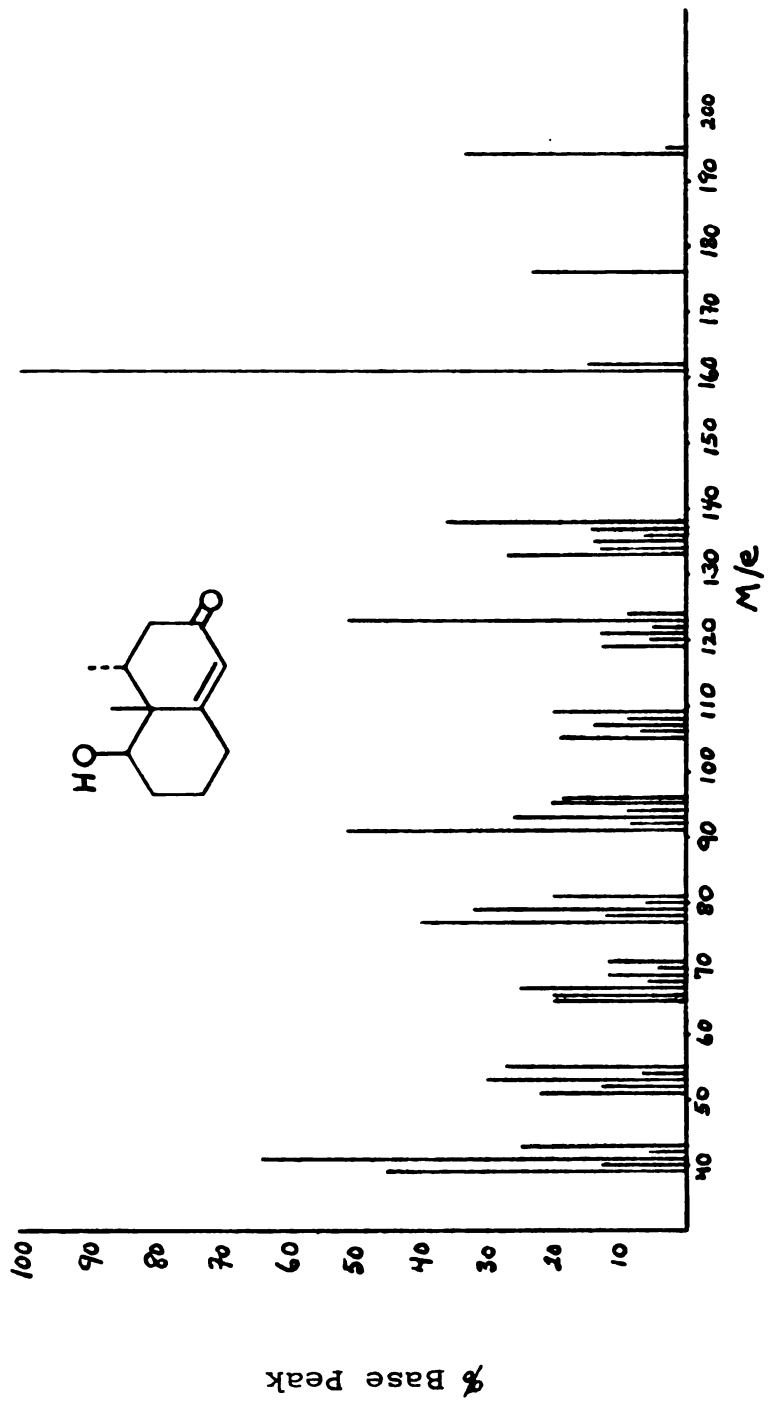


Figure 79. Mass spectrum of (5β,6α,7α)-7-hydroxy-5,6-dimethylbicyclo[4.4.0]-dec-1-ene-3-one (68).

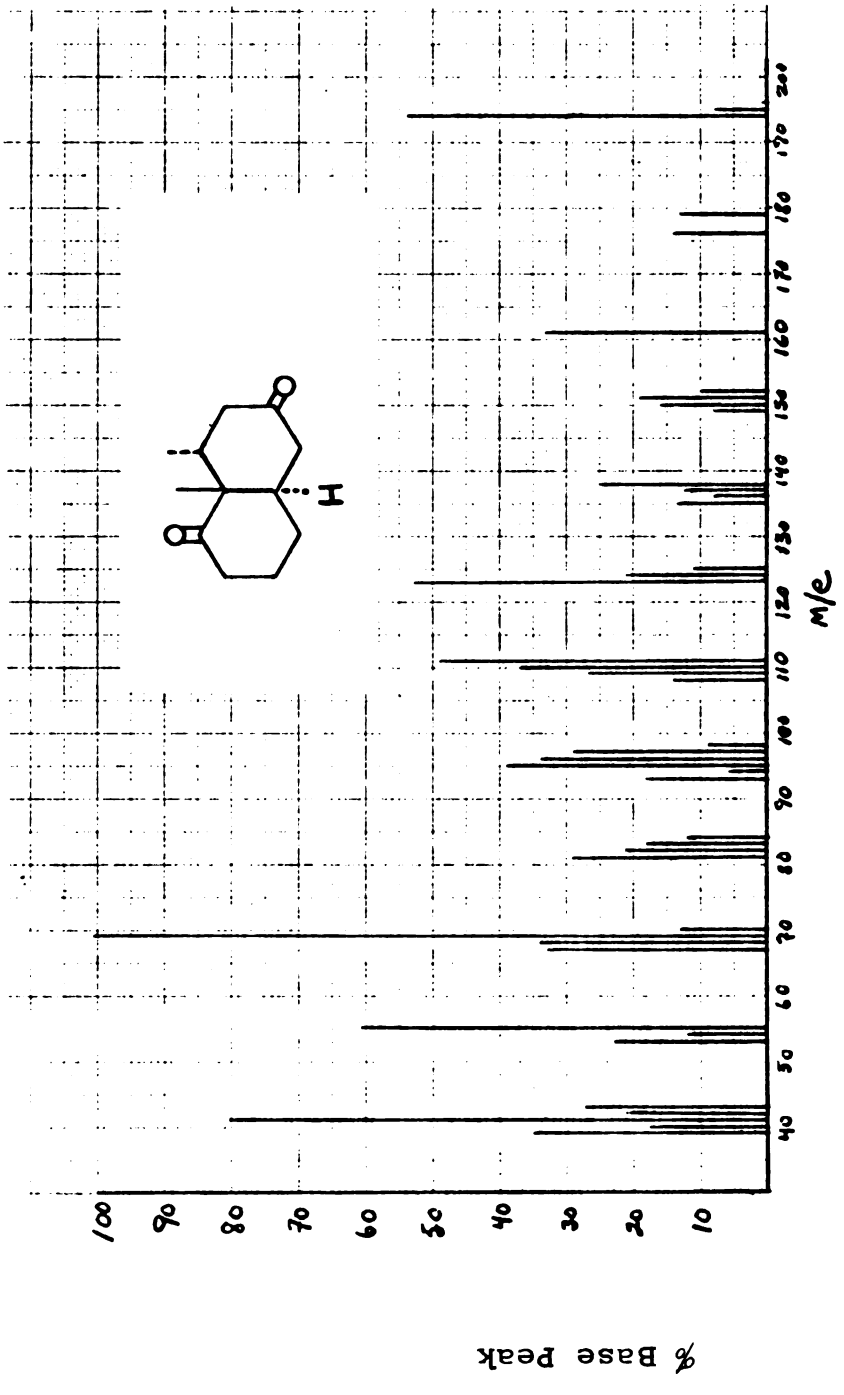


Figure 80. Mass spectrum of (1β,6α,10α)-1,10-dimethylbicyclo[4.4.0]decan-2,8-dione (66).

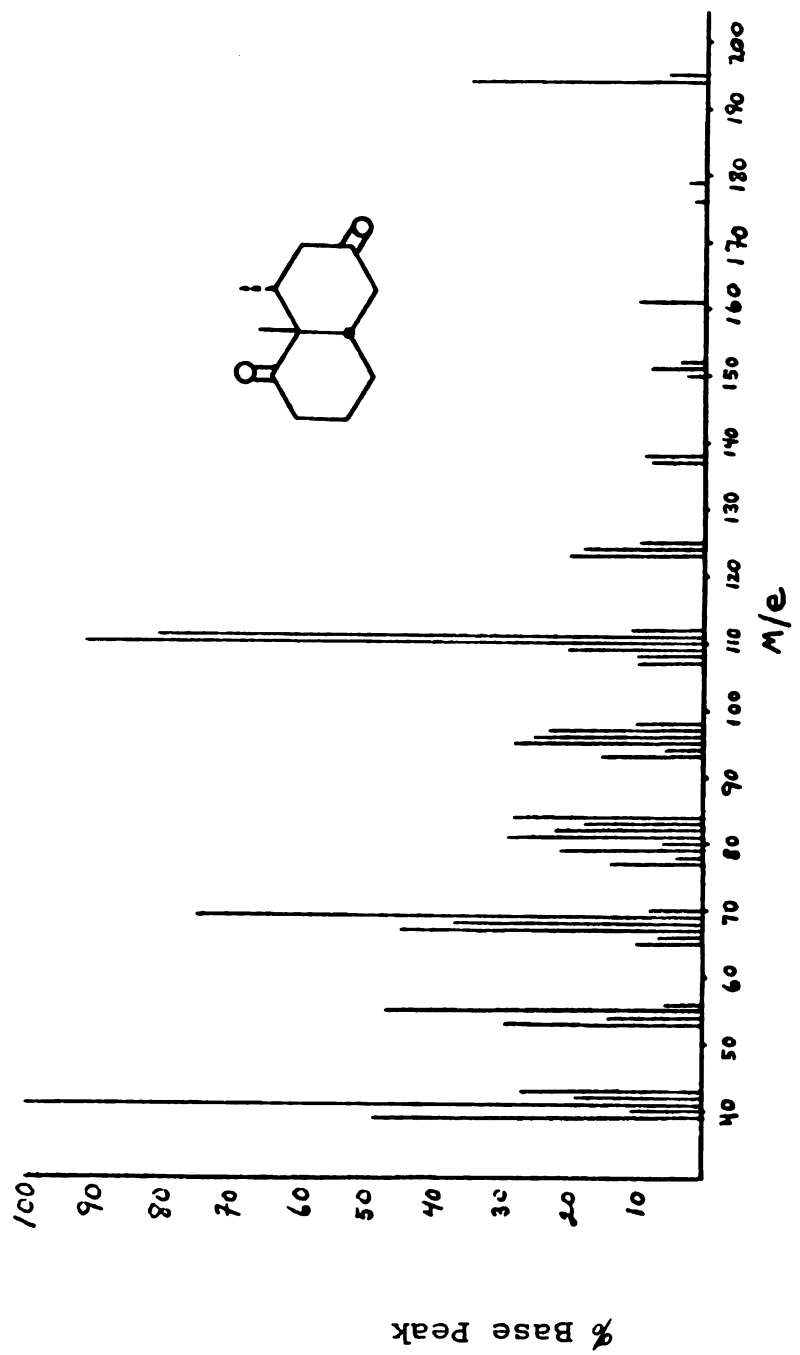


Figure 81. Mass spectrum of (1α,6α,10β)-1,10-dimethylbicyclo[4.4.0]decan-2,8-dione (69).

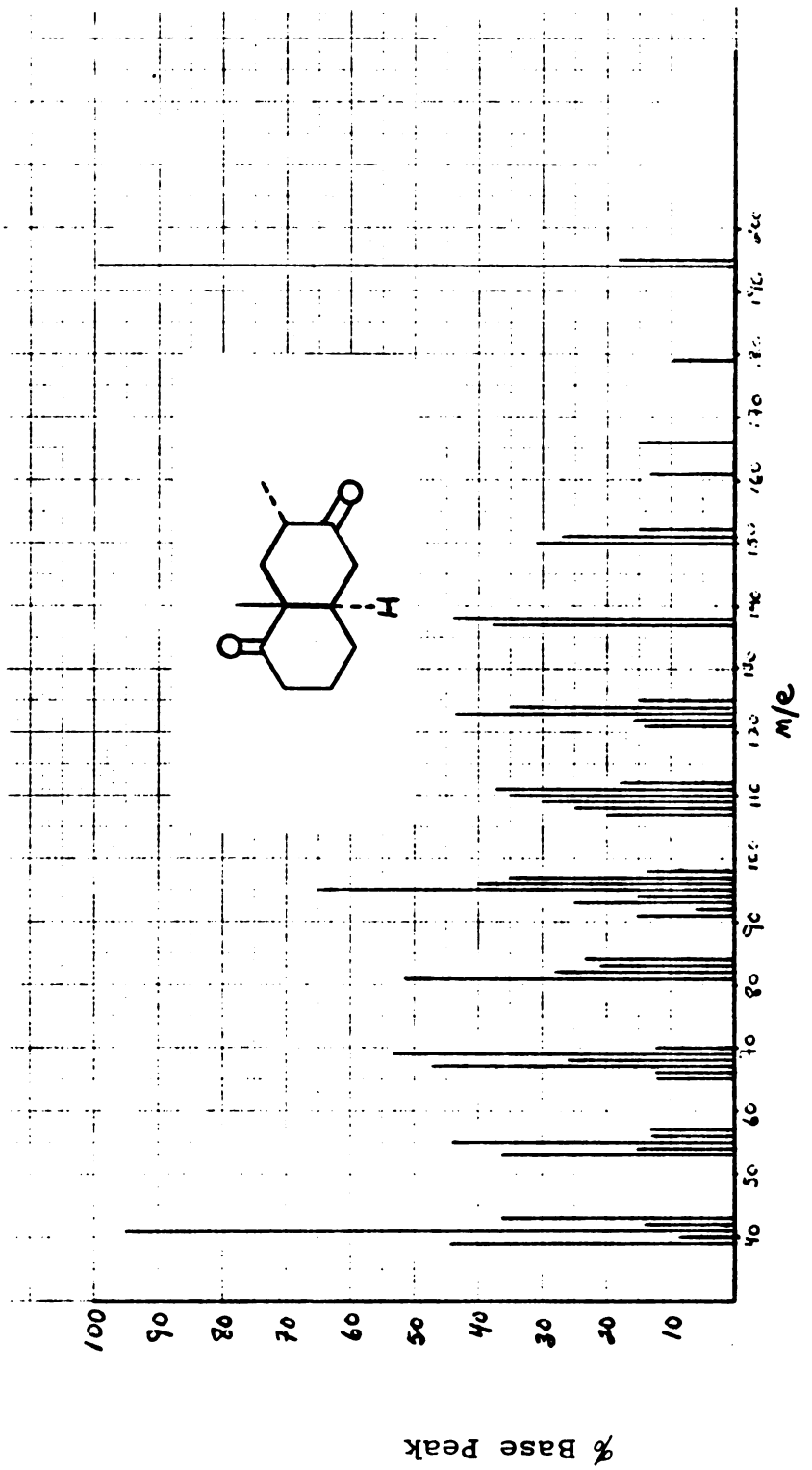


Figure 82. Mass spectrum of (1β,6α,9α)-1,9-dimethylbicyclo[4.4.0]decan-2,8-dione (110).

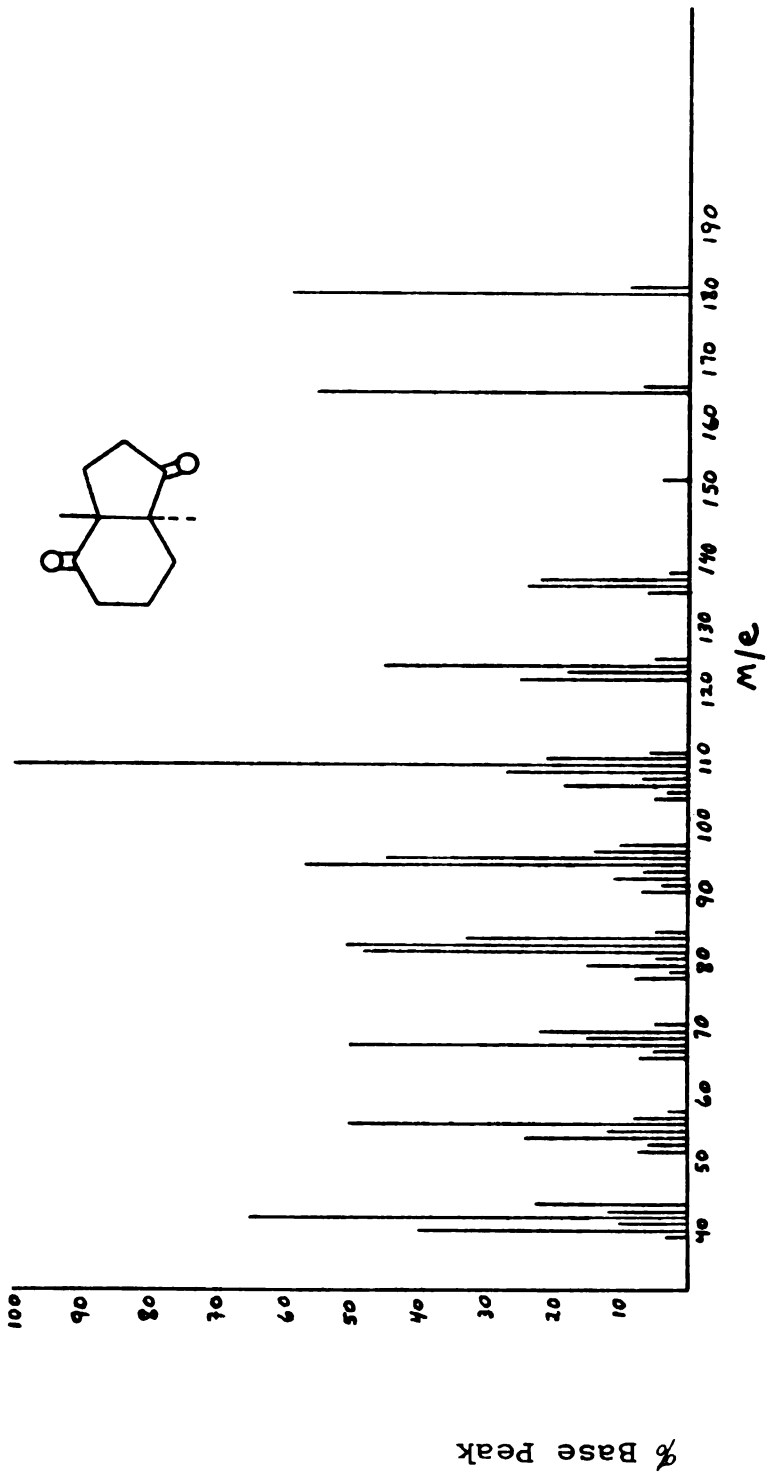


Figure 83. Mass spectrum of trans-1,6-dimethylbicyclo[4.3.0]nona-2,7-dione (46).

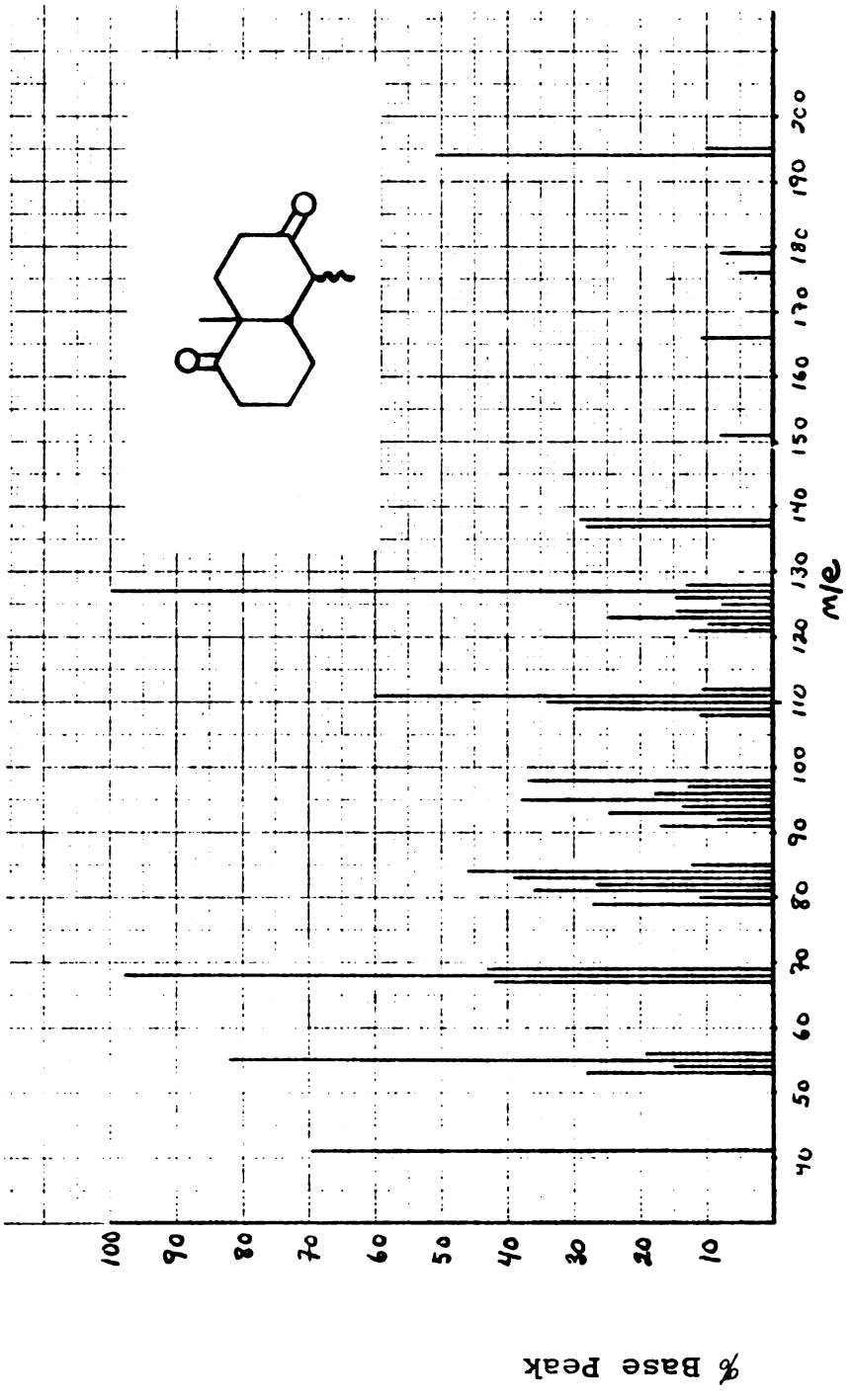


Figure 84. Mass spectrum of (1α,6α,7ξ)-1,7-dimethylbicyclo[4.4.0]decan-2,8-dione (92 and 93).

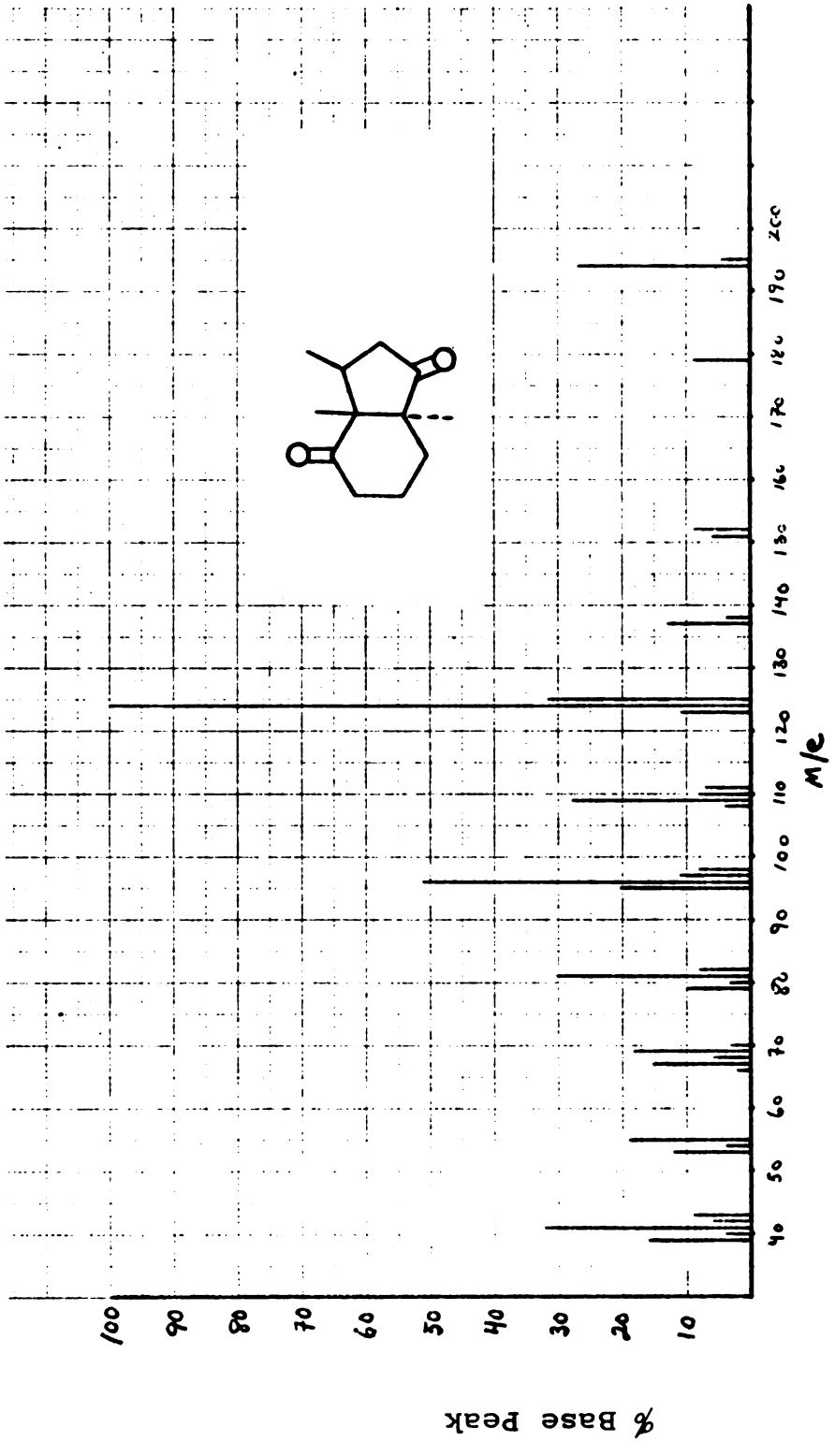


Figure 85. Mass spectrum of (1α,6β,9α)-trimethylbicyclo[4.3.0]nona-2,7-dione (97).

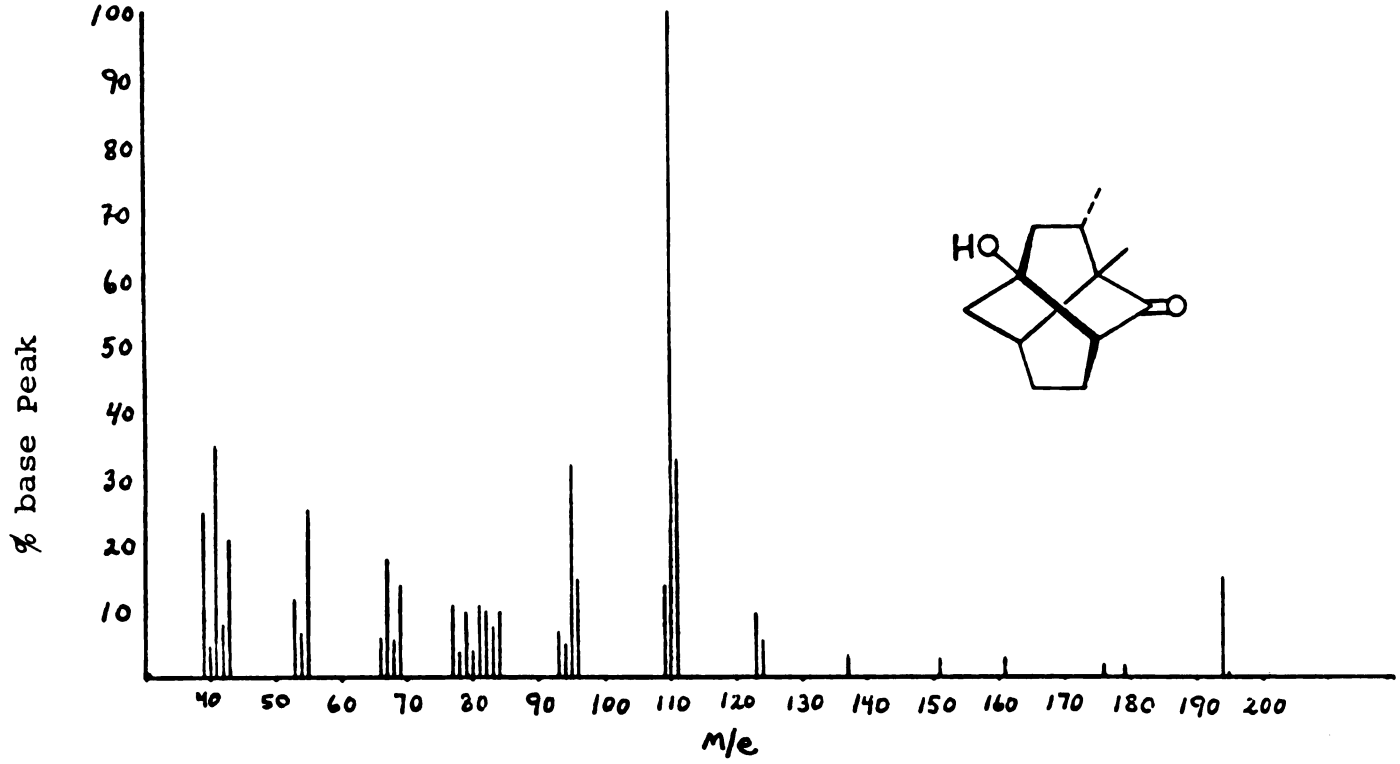


Figure 86. Mass spectrum of (1R*,3R*,6S*,8R*,10R*)-8-hydroxy-1,10-dimethyltricyclo[4.4.0.0^{3,8}]decan-2-one (100).

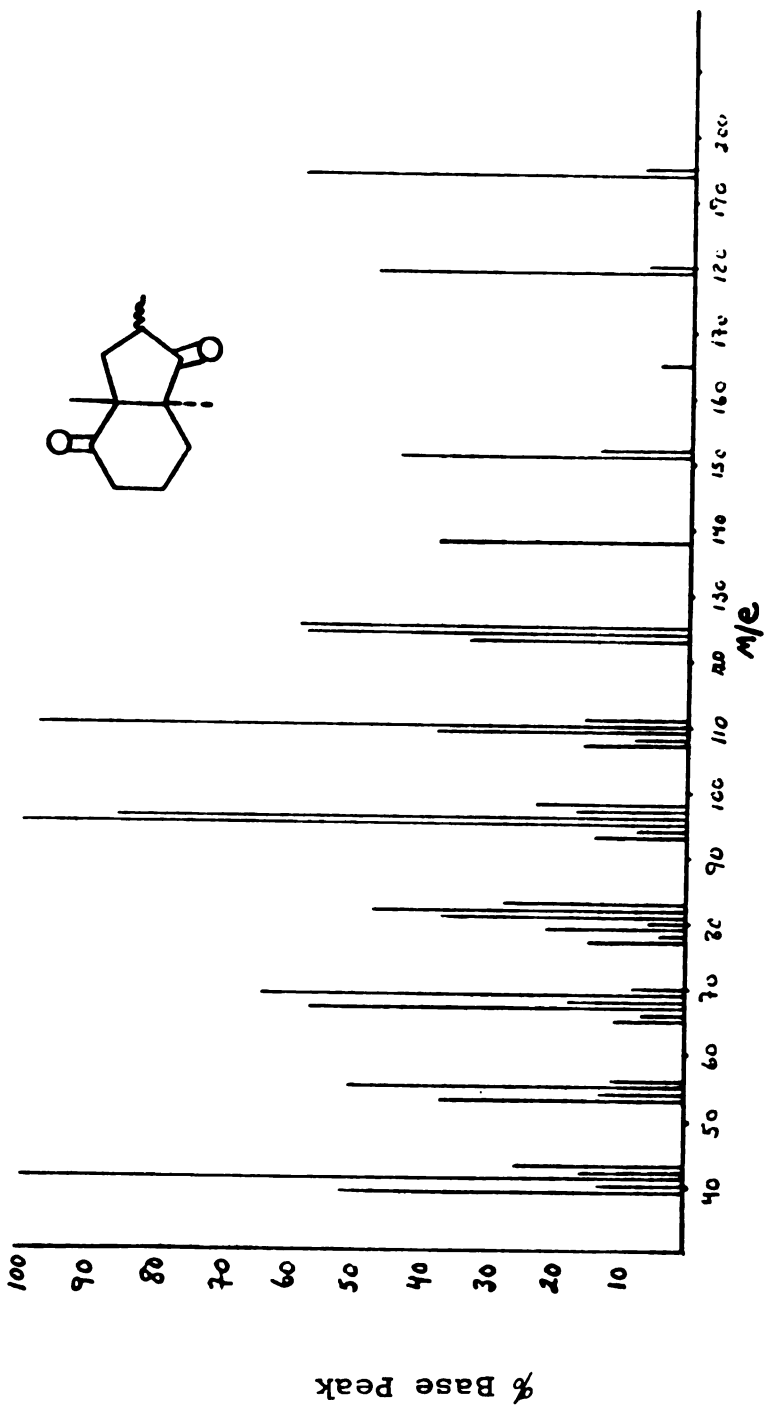


Figure 87. Mass spectrum of (1α,6β,8ξ)-1,6,8-trimethylbicyclo[4.3.0]nona-2,7-dione (102).

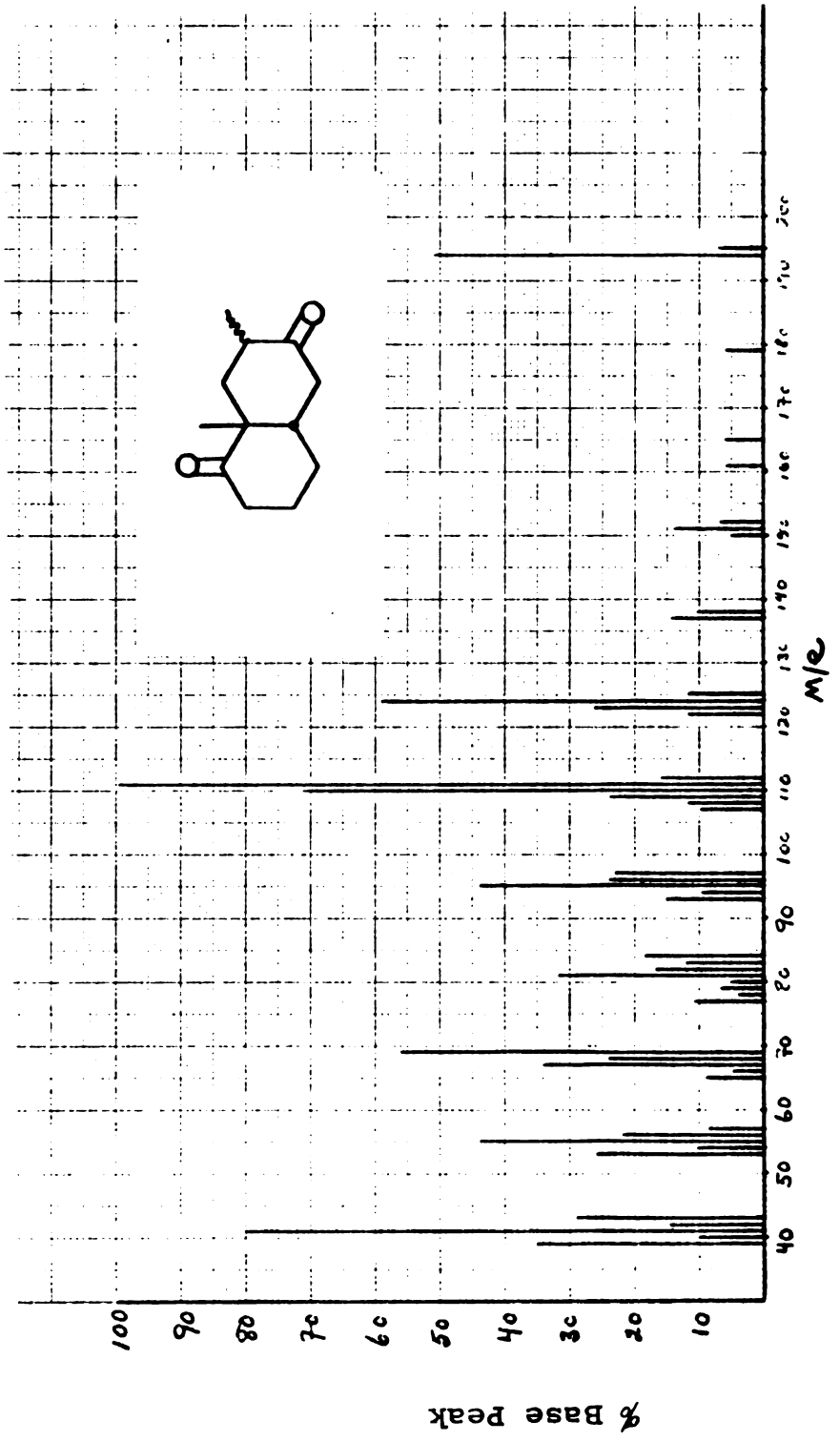


Figure 88. Mass spectrum of (1α,6α,9ξ)-1,9-dimethylbicyclo[4.4.0]decan-2,8-dione (103 and 104).

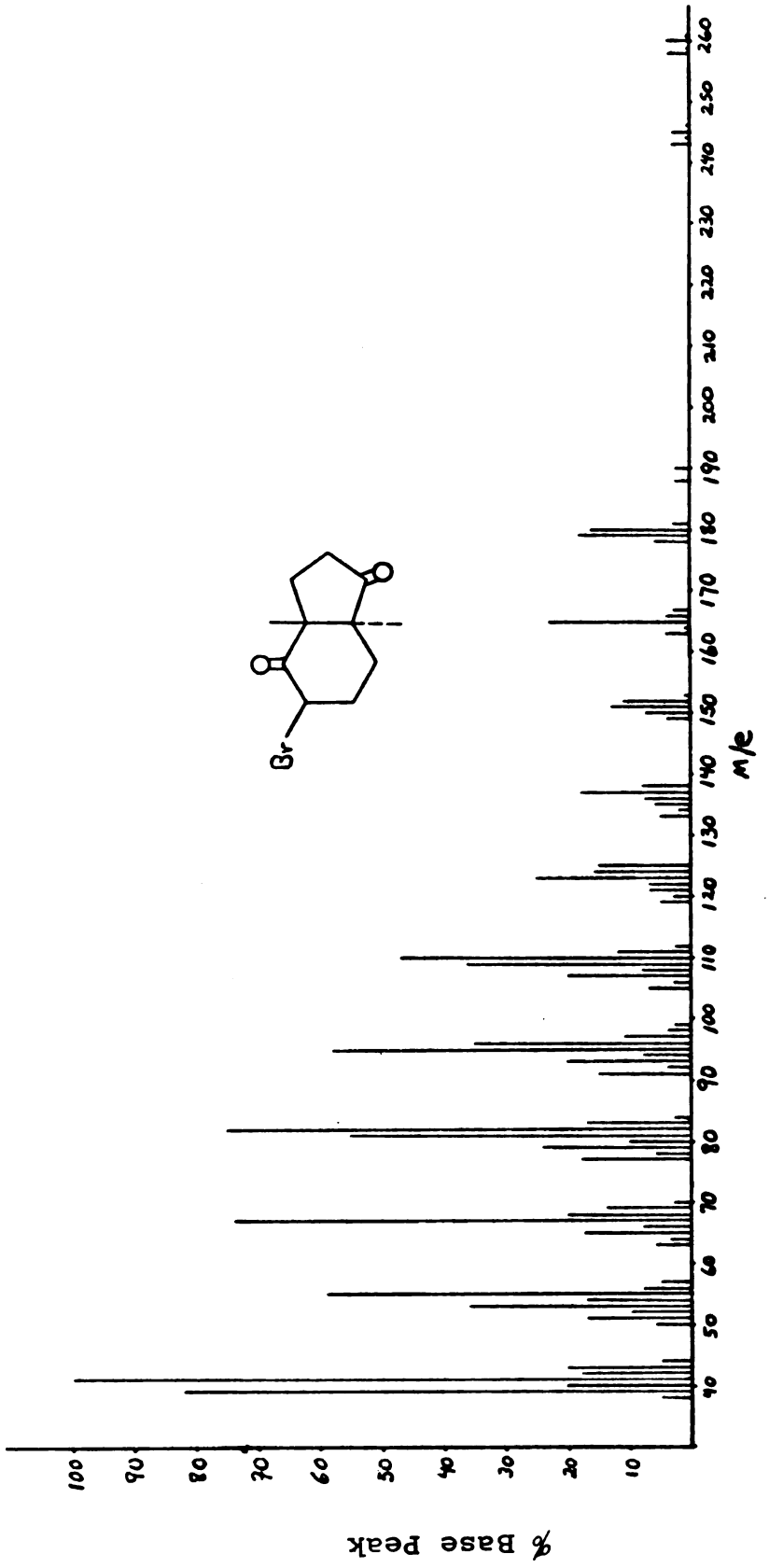


Figure 89. Mass spectrum of (1α,3α,6β)-3-bromo-1,6-dimethylbicyclo[4.3.0]nona-2,7-dione (Figure 1).

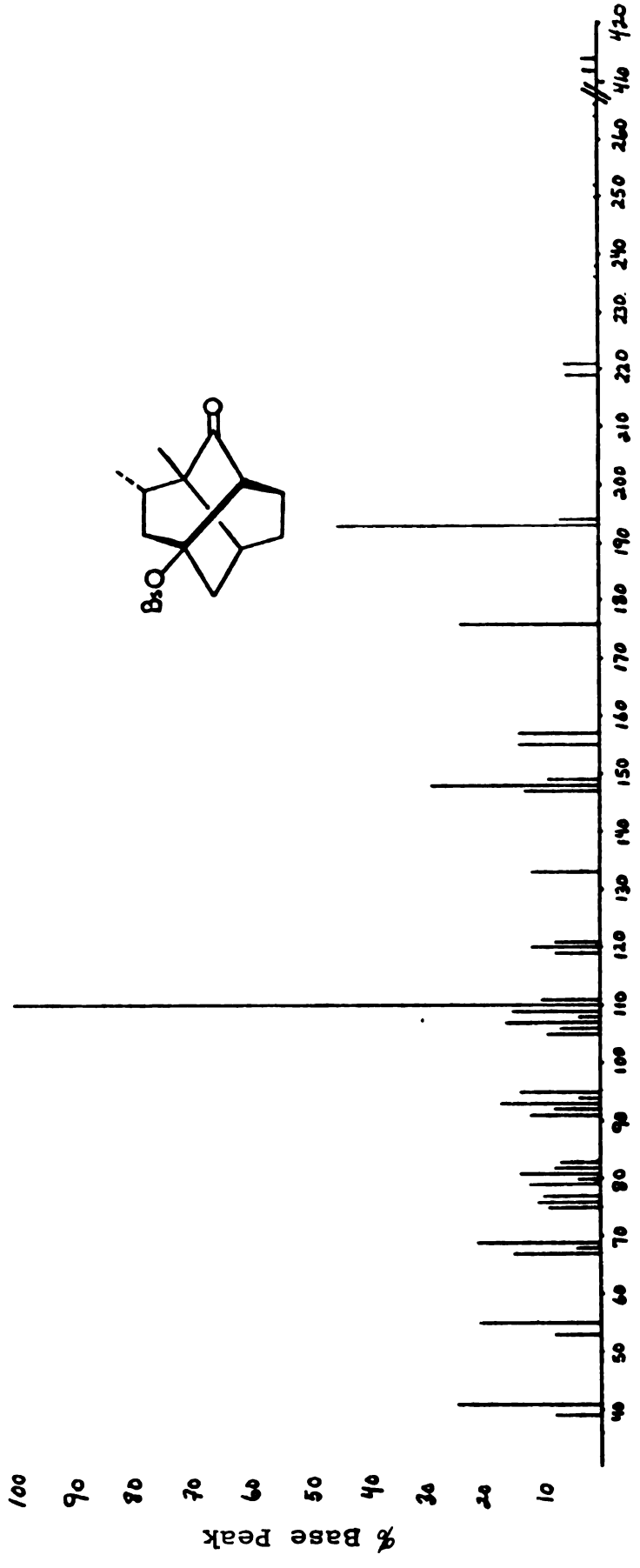


Figure 90. Mass spectrum of (1R*,3R*,6S*,8R*,10R*)-8-(p-bromobenzenesulfonoxy)-1,10-dimethyltricyclo[4.4.0.0^{3,8}]decan-2-one (Figure 2).

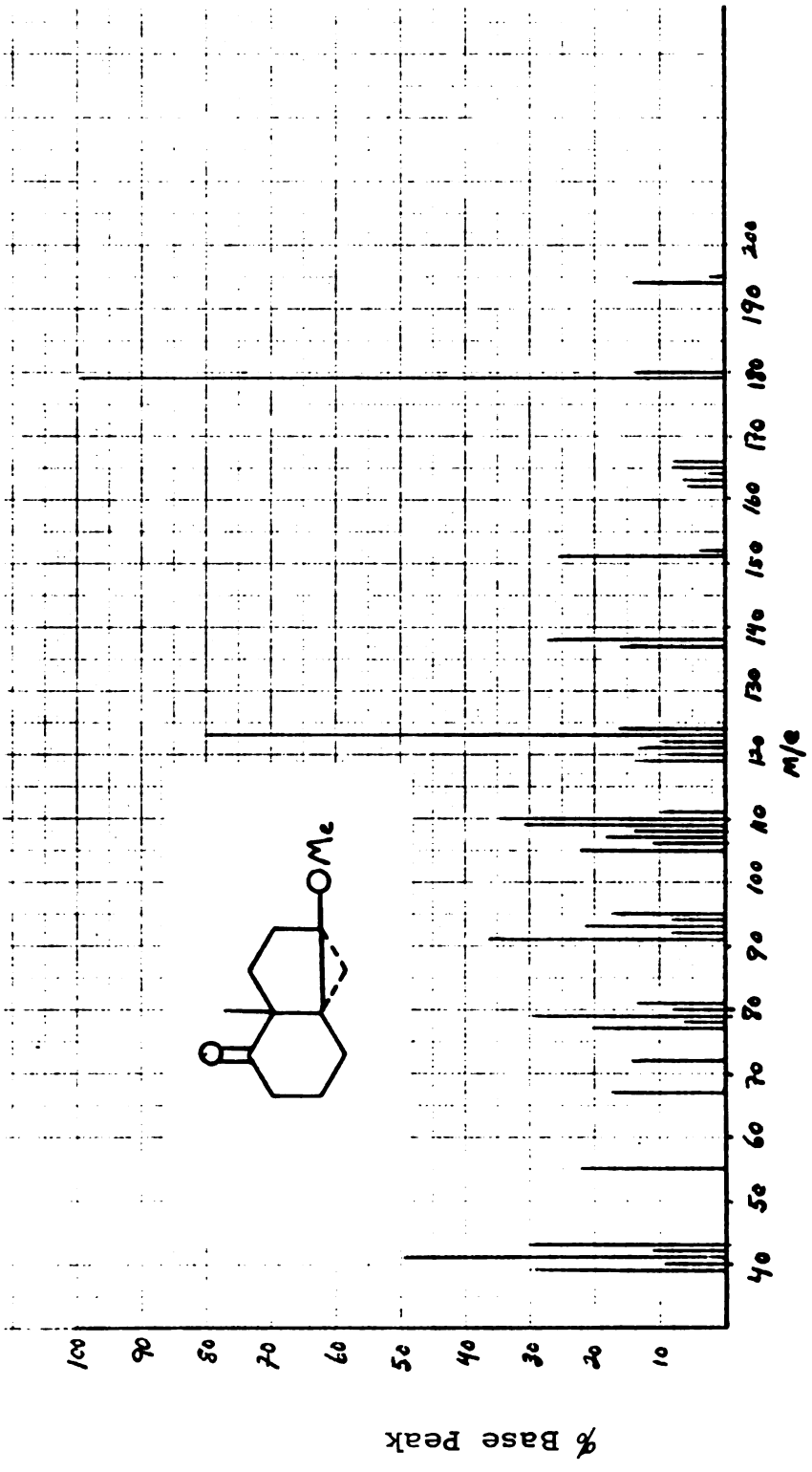


Figure 91. Mass spectrum of (1S*,3α,6α)-3-methoxy-6-methyltricyclo[4.4.0.0^{1,3}]-decan-7-one (91).

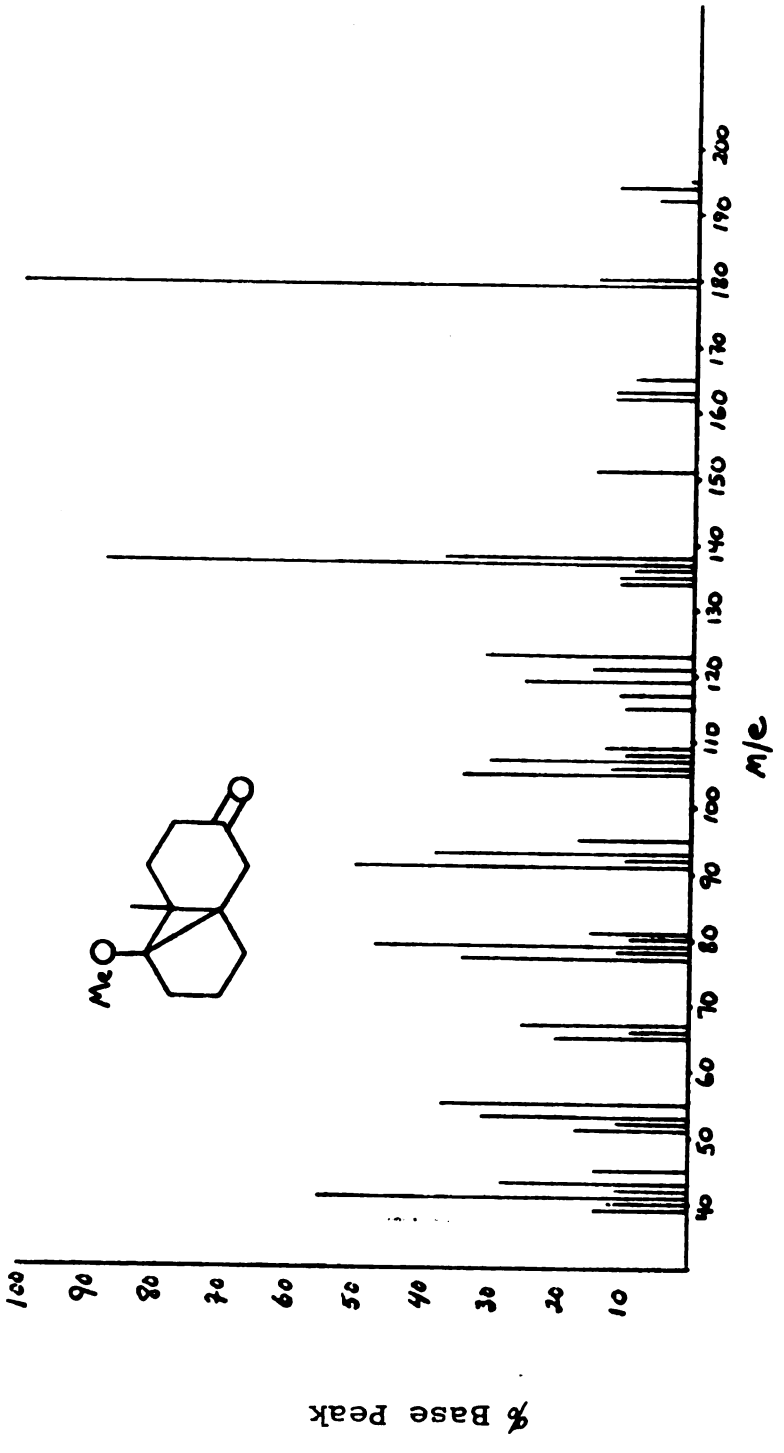


Figure 92. Mass spectrum of (1R*,5α,6β)-5-methoxy-6-methyltricyclo[4.4.0.0^{1,5}]-decan-9-one (90).

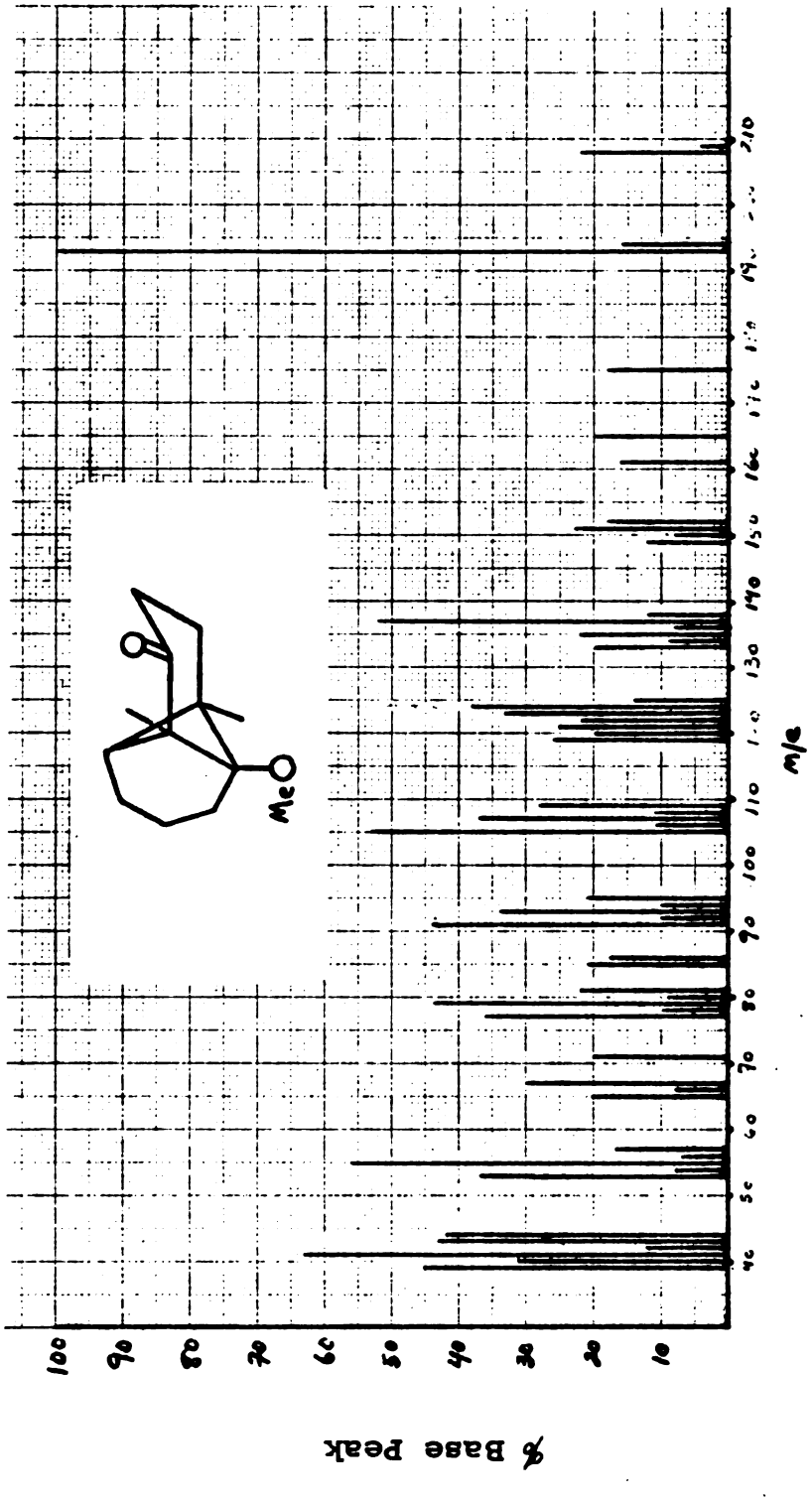


Figure 93. Mass spectrum of (1R*,2S*,6R*,7R*)-2-methoxy-1,7-dimethyltricyclo-[4.4.0.0^{2},^{7}]decan-8-one (95).

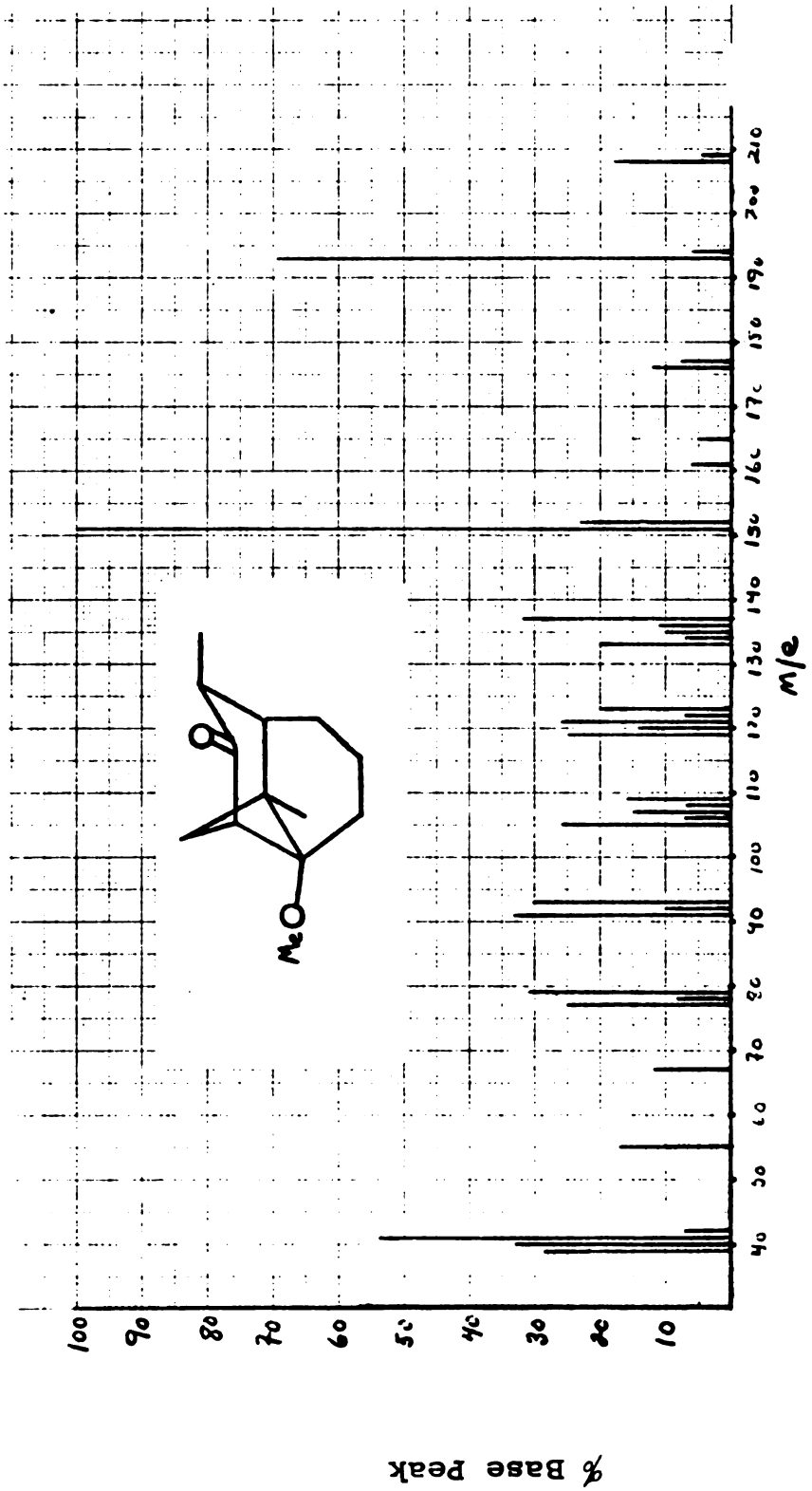


Figure 94. Mass spectrum of (1R*,2S*,4S*,6S*,7R*)-2-methoxy-1,7-dimethyltricyclo[4.4.0.0^{2,9}]decan-8-one (96).

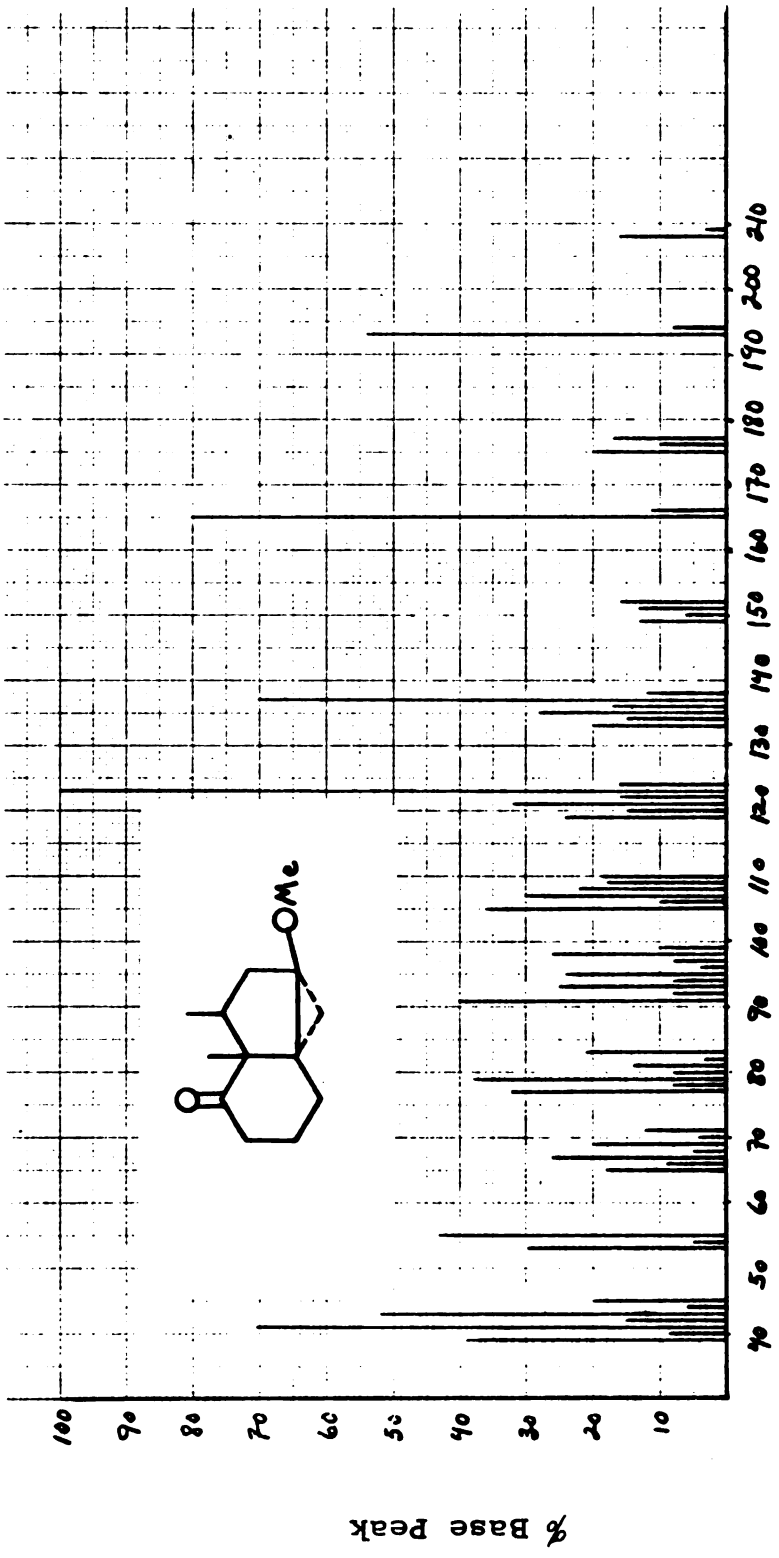


Figure 95. Mass spectrum of (1S*,3α,5α,6α)-3-methoxy-4,5-dimethyltricyclo-[4.4.0.0^{1,3}]decan-7-one (99)

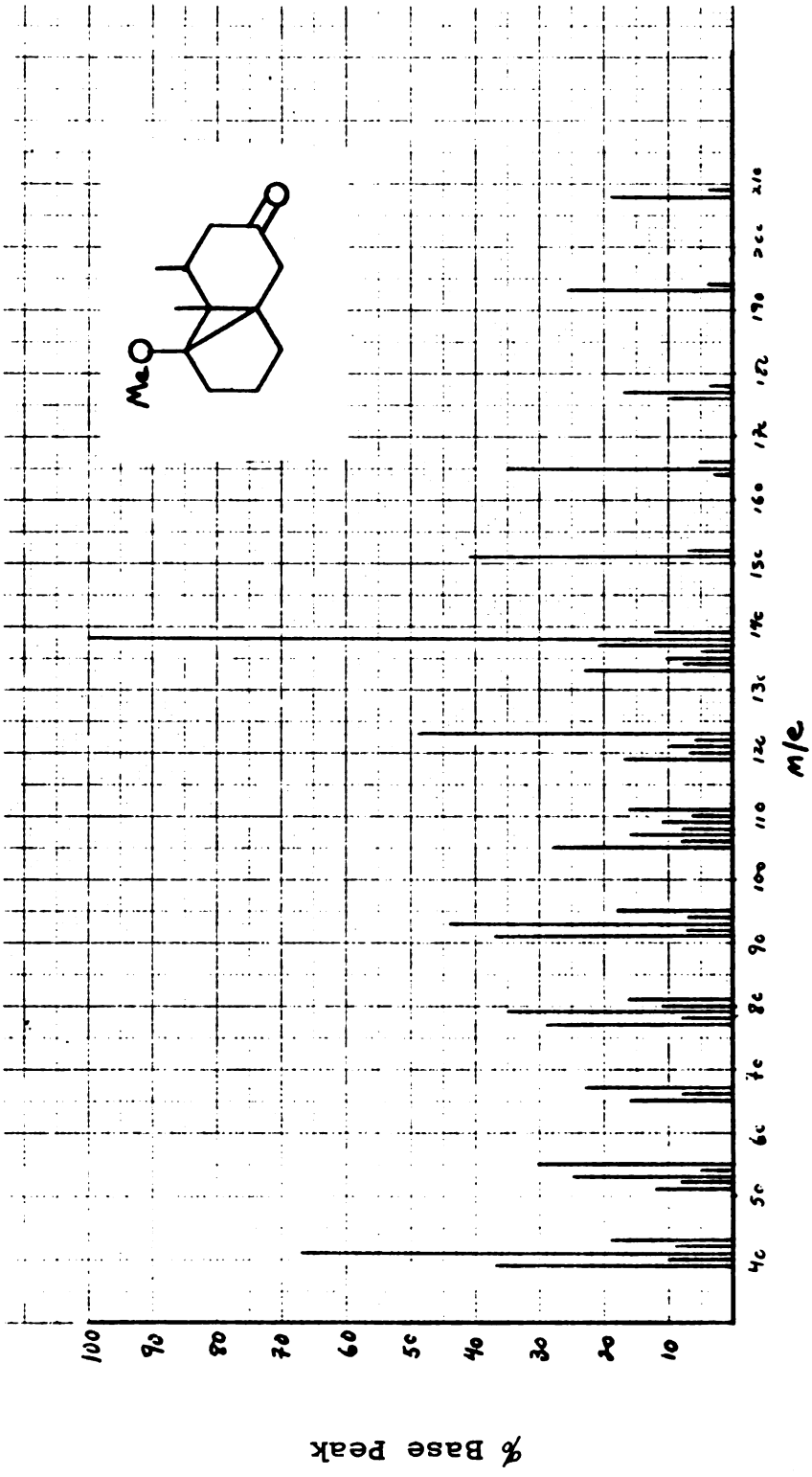


Figure 96. Mass spectrum of (1R*,5β,6α,7α)-5-methoxy-6,7-dimethyltricyclo-[4.4.0.0^{1,5}]decan-9-one (98).

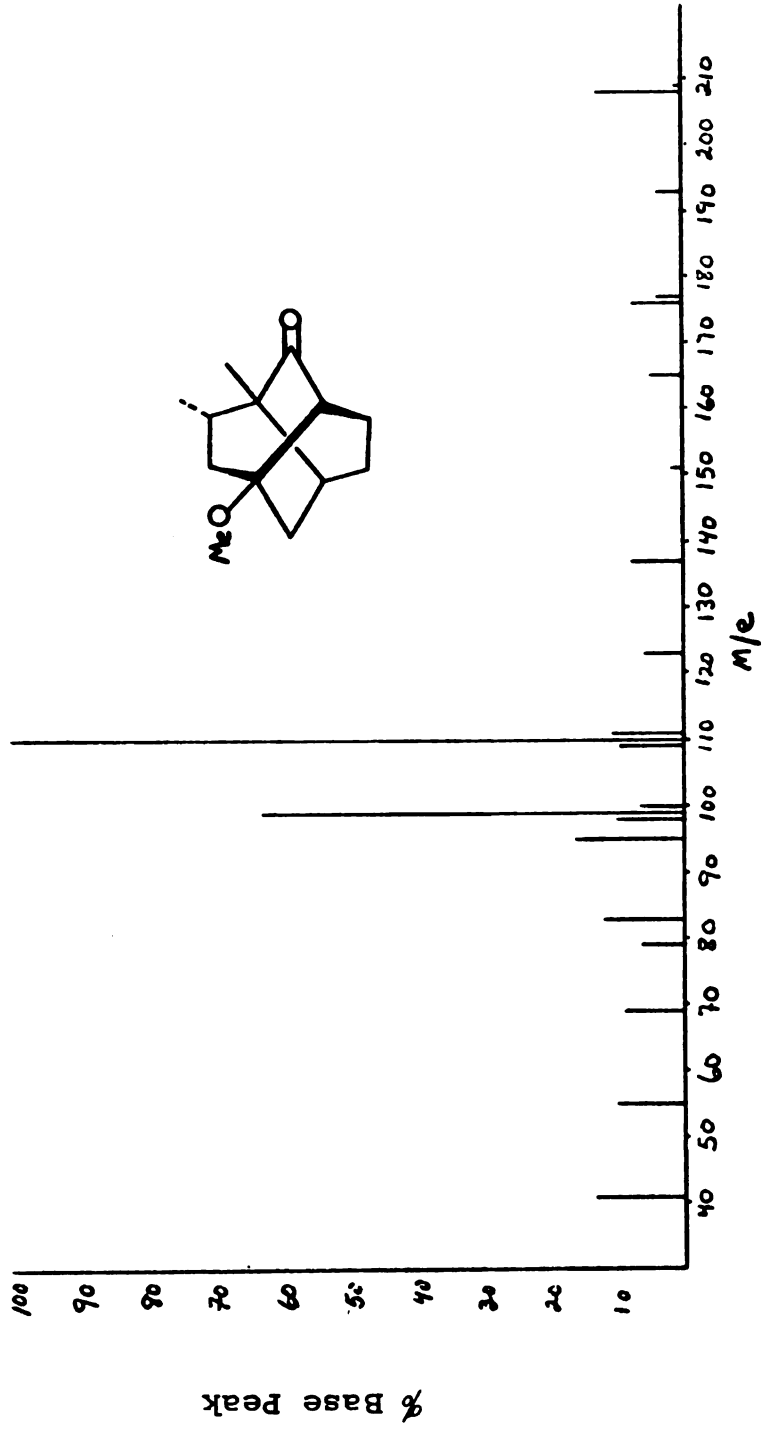


Figure 97. Mass spectrum of (1R*,3R*,6S*,8R*,10R*)-8-methoxy-1,10-dimethyltricyclo[4.4.0.0^{3},^{8}]decan-2-one (101).

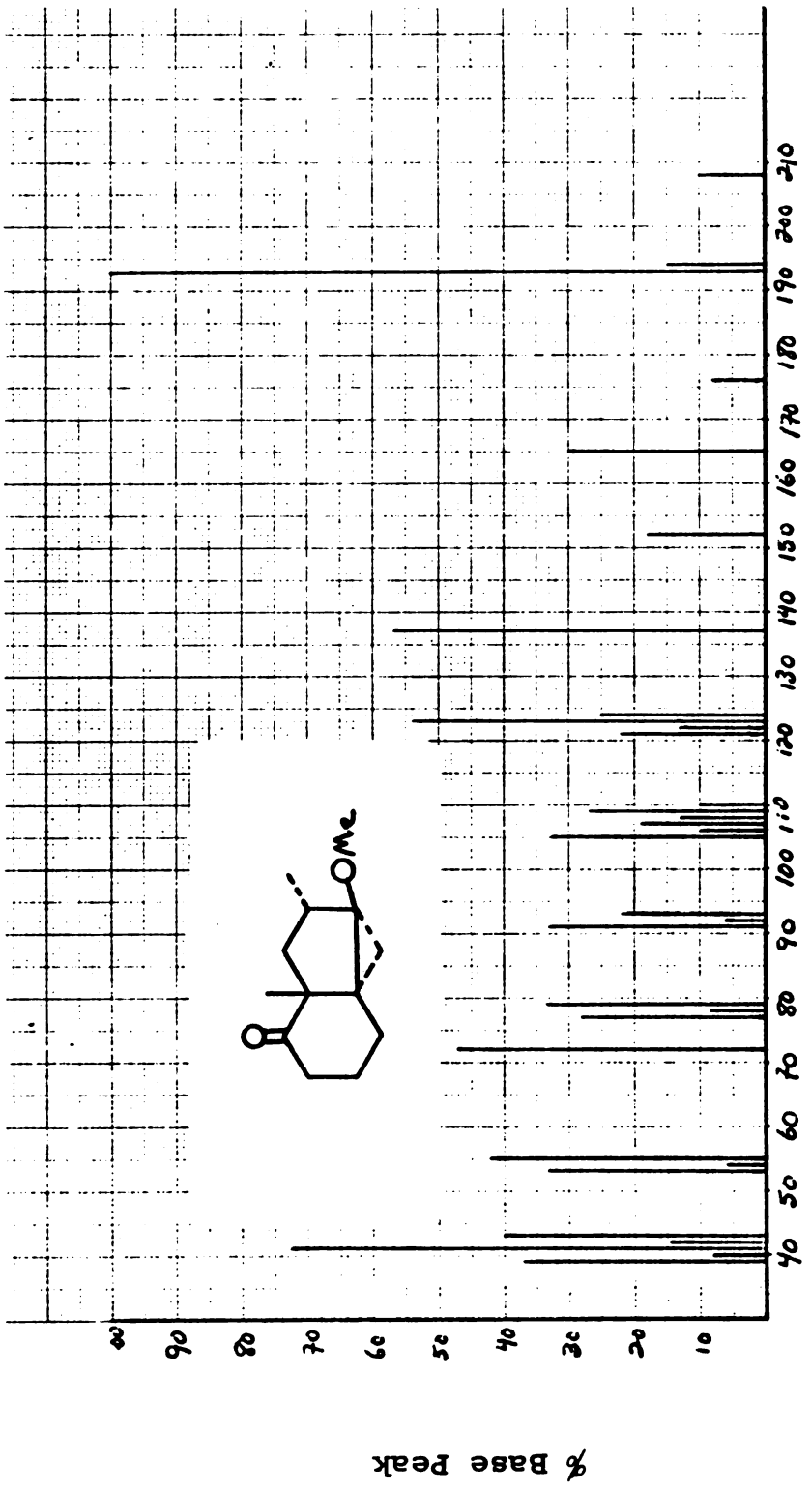


Figure 98. Mass spectrum of (1S*,3α,4β,6α)-3-methoxy-4,6-dimethyltricyclo-[4.4.0.0^{1,3}]decan-7-one (105).

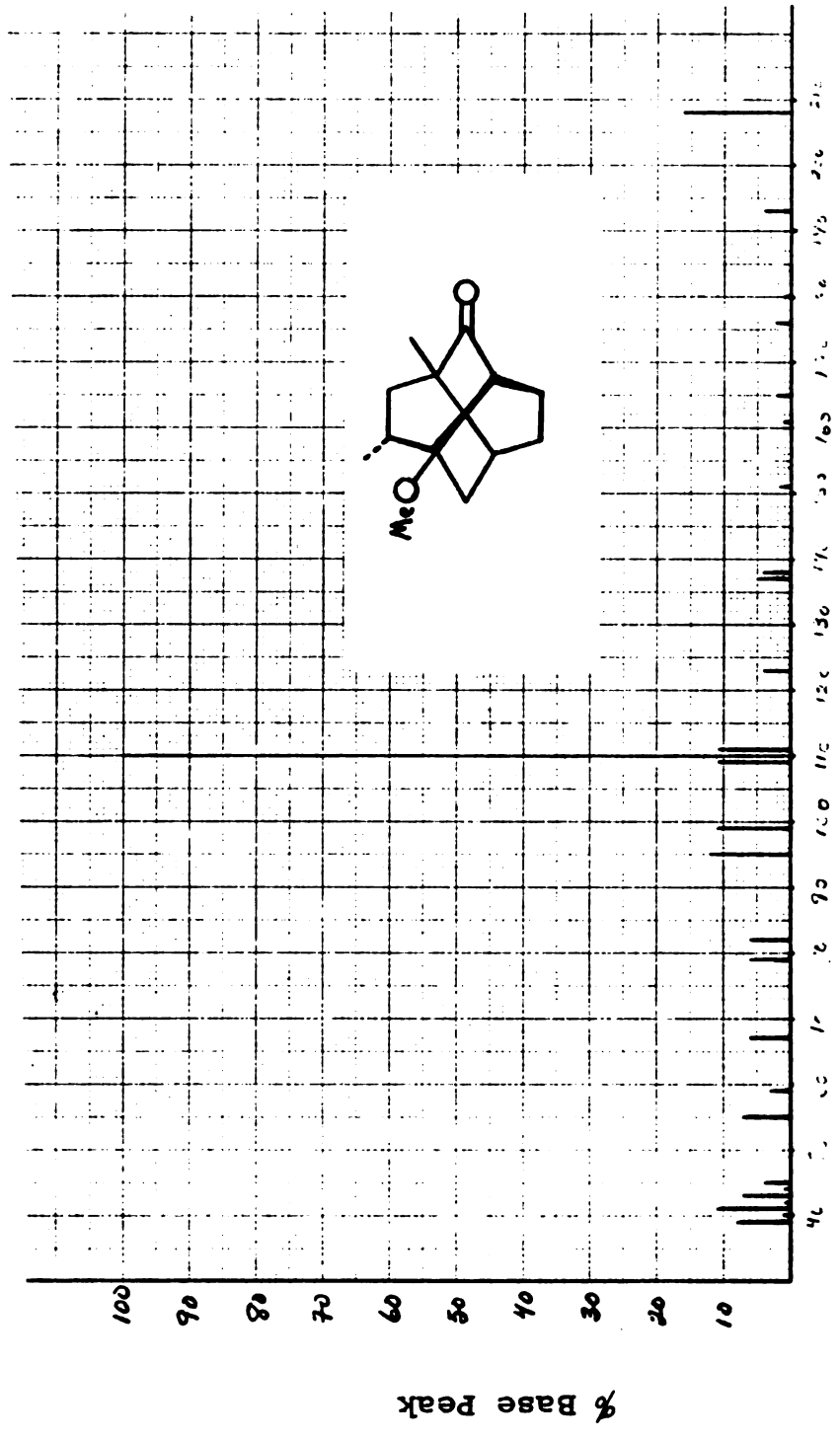


Figure 99. Mass spectrum of (1R*,3R*,6S*,8R*,9S*)-8-methoxy-1,9-dimethyltricyclo[4.4.0.0^{3,8}]decan-2-one (106).

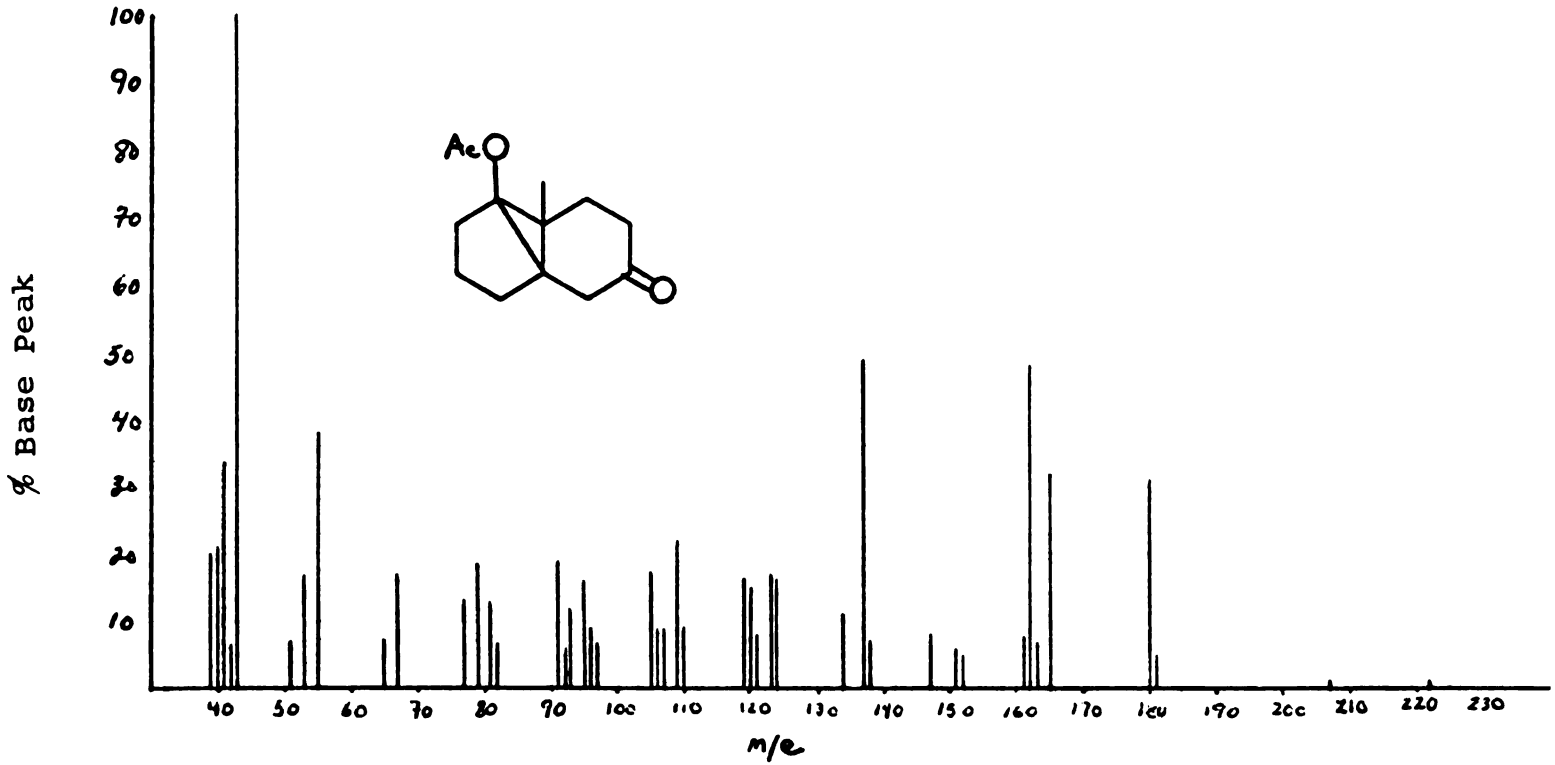


Figure 100. Mass spectrum of (1R*,5α,6β)-5-acetoxy-6-methyltricyclo-[4.4.0.0^{1,5}]decan-9-one (76).

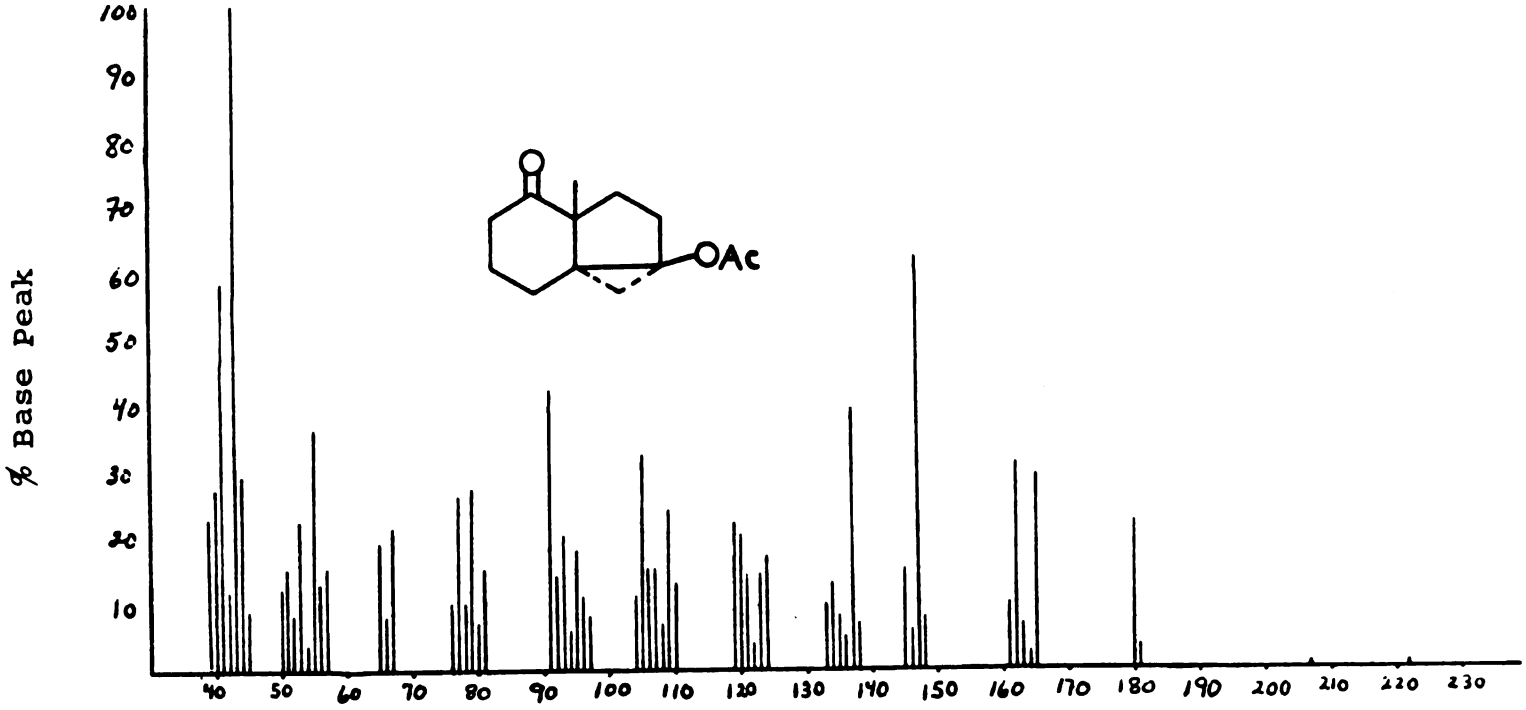


Figure 101. Mass spectrum of (1S*,3α,6α)-3-acetoxy-6-methyltricyclo-[4.4.0.0^{1,3}]decan-7-one (77).

APPENDIX B

NOMENCLATURE

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Kurt L. Loening
Nomenclature Director

April 17, 1974

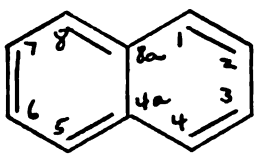
Dr. John D. Yordy
Chemistry Department
Michigan State University
East Lansing, Michigan 48824

Dear Dr. Yordy:

Please excuse the delay in replying to your letter of March 26. It arrived while I was at the ACS meeting in Los Angeles, and I am still trying to catch up with my correspondence.

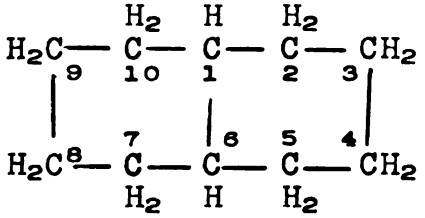
In answer to your query, Chemical Abstracts names most of the ring systems involved in your compounds as ortho- and ortho-peri-fused systems rather than as von Baeyer rings. The IUPAC rules of organic nomenclature allow both methods. Thus, listing both methods, the fundamental ring systems involved in your six compounds[1] are named, numbered, and oriented as shown below.

A:



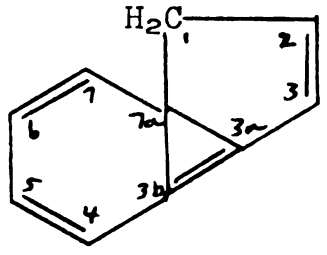
Naphthalene

or



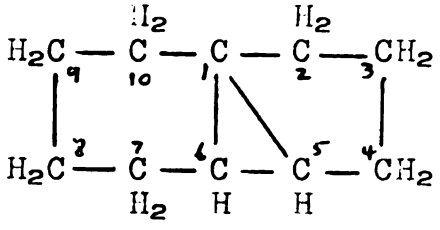
Bicyclo[4.4.0]decane

B:



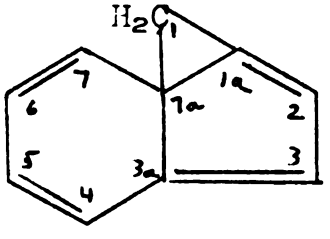
1H-Cyclopenta[1,3]cyclopropa[1,2]benzene

or



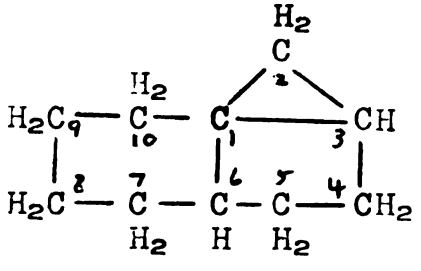
Tricyclo[4.4.0.$0^{1,5}$]decane

C:



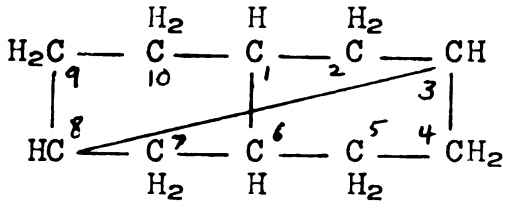
1H-Cycloprop[c]indene

or



Tricyclo[4.4.0.$0^{1,3}$]decane

D:



Tricyclo[4.4.0.0^{3,8}]decane

Thus, disregarding stereochemistry for the moment, your compounds[1] are named as follows:

(1): 3,4,8,8a-Tetrahydro-8,8a-dimethyl-1,6(2H,7H)-naphthalenedione

or

1,10-Dimethylbicyclo[4.4.0]dec-6-ene-2,8-dione (1)

(2): Octahydro-5-hydroxy-4,4a-dimethyl-2(1H)-naphthalenone

or

7-Hydroxy-5,6-dimethylbicyclo[4.4.0]decan-3-one (2)

(3): Hexahydro-3a-hydroxy-3b,4-dimethyl-1H-cyclopenta[1,3]cyclopropa[1,2]benzen-6(7H)-one

or

5-Hydroxy-6,7-dimethyltricyclo[4.4.0.0^{1,5}]decan-9-one (3)

(4): Hexahydro-1a-hydroxy-3,3a-dimethyl-1H-cycloprop[c]inden-4(5H)-one

or

3-Hydroxy-5,6-dimethyltricyclo[4.4.0.0^{1,3}]decan-7-one (4)

(5): same as 4 except for stereochemistry (5)

(6): 8-Hydroxy-1,10-dimethyltricyclo[4.4.0.0^{3,8}]decan-2-one (6)

As for stereochemistry, I enclose a copy of the IUPAC tentative rules for fundamental stereochemistry.[2] According to these rules, if the absolute configurations of your compounds are known, the Cahn-Ingold-Prelog sequence-rule symbols are used for the chiral

centers. For the designation of relative configuration the R*,S* system (rule E-5.10) is suggested.

On the other hand, Chemical Abstracts, for the present collective-index period, has developed its own system of stereodescriptors to be prefixed to the non-stereospecific names of compounds. This system is a combination of the R,S system and the α,β system and is summarized in §203 of the Volume 76 (1972) introduction to the CA Index Guide (copy enclosed). Applying this system, the stereo-designations for the relative configurations of your compounds are

(1): trans (for both the naphthalene and von Baeyer names)

(2): (4α,4aβ,5α,8aα)
or
(1α,5α,6β,7α) for the von Baeyer name

(3): (3aα,3bβ,4α,7aR*)
or
(1R*,5α,6β,7α) for the von Baeyer name

(4): (1aα,3β,3aα,7aS*)
or
(1S*,3α,5β,6α) for the von Baeyer name

(5): (1aα,3α,3aβ,7aS*)
or
(1S*,3α,5α,6β) for the von Baeyer name

(6): (1R*,3R*,6S*,8R*,10R*)

If the absolute configurations of your compounds are known, then the absolute configuration of the reference center for each of your compounds should be cited in front of the corresponding relative description.

I hope you find this information helpful. Please do not hesitate to let me know if I can be of further assistance.

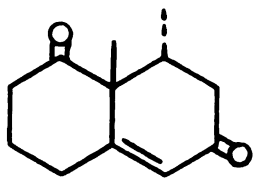
Sincerely,

Kurt L. Loening

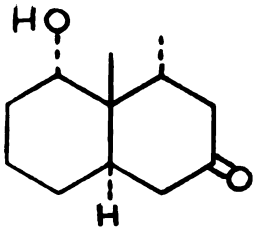
Kurt L. Loening
Director of Nomenclature

KLL/bc
Enclosures

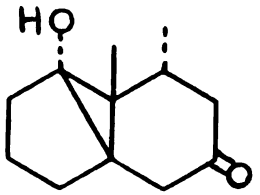
[1]These compounds are the following:



1



2



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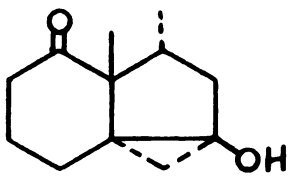

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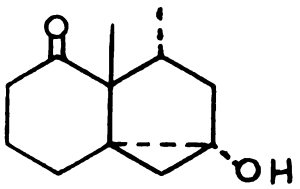

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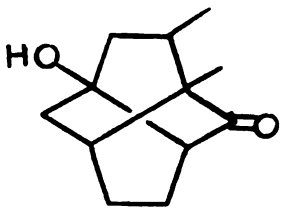

6

[2]Biochimica et Biophysica Acta, 208, 1 (1970).