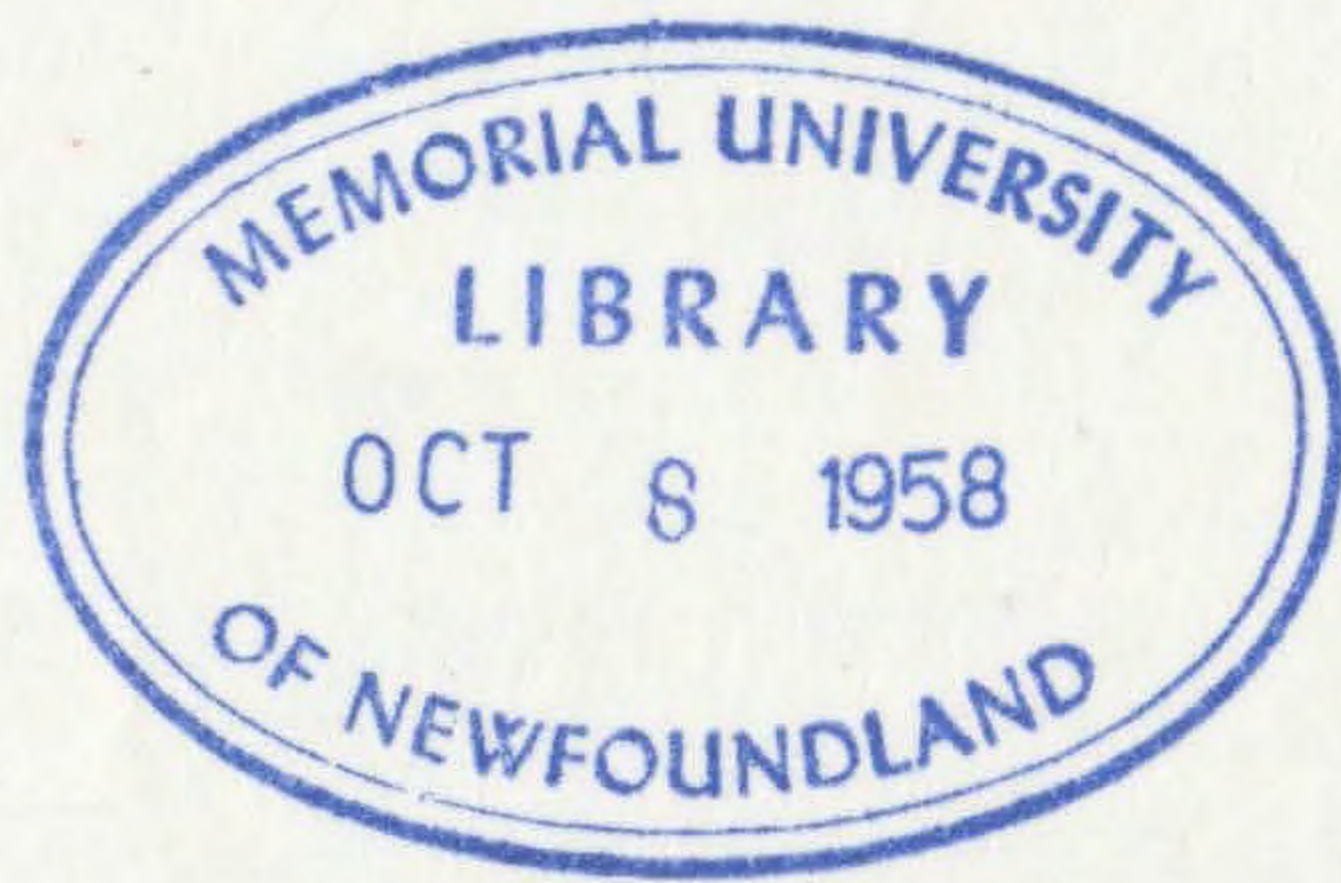THE ULTRAVIOLET ABSORPTION SPECTRA

OF SOME SUBSTITUTED ACETOPHENONES

W. A. MUELLER

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THE ULTRAVIOLET ABSORPTION SPECTRA
OF SOME SUBSTITUTED ACETOPHENONES

A Thesis

By

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Note.

The abbreviation J. A. C. S. used throughout this thesis refers to
the J. Am. Chem. Soc.

<div align="right">W. A. Mueller.</div>

ABSTRACT

In order to investigate more fully the steric
influences in the B-band of the ultraviolet spectrum,
several acetophenones were prepared, giving molecules
in which the angle between the planes of the electron
rich centers varied. It was found that the light
absorption maximum moved to shorter wavelengths
as the amount of hindrance about the carbonyl group
was increased, (i.e., as the interplanar angle
was increased), and that steric hindrance increased
in the order hydrogen atom < ortho-methylene group
of the cyclopentyl ring < ortho-methyl group < ortho-
methylene group of the cyclohexyl ring < an ortho-
methyl group "buttressed" by a methyl group in the
adjacent meta-position.

The carbonyl group becomes less readily access-
ible as steric interference is increased, as shown
by the inability of the highly hindered ketones
to form the ordinary ketone derivatives. In the
highly hindered ketones, conjugation is inhibited
to such an extent that the main peaks closely
correspond to those of the substituted benzenoid
hydrocarbons.

The spatial orientation of the compounds is discussed by interpreting the spectra in terms of the electronic and steric effects of the substituents.

The 2,4-dinitrophenylhydrazones of the unsubstituted compounds, and some of the substituted compounds are included, and it was found that the amount of steric hindrance can sometimes be estimated by color, i.e., as conjugation increases, the colors tend from yellow to red.

A recent example from the literature on the spectra of substituted hydroxybenzoic acids is included, and it was found possible to correlate nicely the observed spectra by means of the theories of steric and electronic effects.

In the experimental part, the syntheses of the ketones are described, along with the reaction of β-chloropropionyl chloride with tetralin, and an attempt to prepare 2,3,5,6-tetraethylbenzene.

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INTRODUCTION

The entire range of electromagnetic radiation
can interact with matter, but that range in the
visible and ultra-violet region of the spectrum
is of particular interest to the chemist, since
interaction in this region is dependent on the
electronic structure of the molecule, and hence is
closely related to chemical reactivity.

Absorption in the ultra-violet and visible region
produces changes intermediate between the high energy
required for complete photo-ionization of the mol-
ecule, and the relatively low energy of the infra-
red region, which gives rise to rotational and vi-
brational changes. Absorption in the ultra-violet
region is ascribed to a change in the electronic
patterns of the non-bonding π electrons, and may
also involve the p-electrons of single atoms.
This type of absorption is found in molecules con-
taining centers of unsaturation, such as the styrenes,
diphenyls, benzamidines, benzaldehydes, etc.

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Acetophenone itself has an intense absorption band at 240 mμ, ϵ = 13,000. Methyl substituents cause rather small wavelength displacements ($\Delta\lambda$ =10 mμ). In the benzaldehyde system, meta- and para- groups cause a small increase in absorption probability (ϵ), while ortho- groups cause a small decrease in ϵ . With acetophenones, meta- and para-substituents produce a similar increase in ϵ , but ortho- groups give rise to a marked decrease. The propiophenones exhibit a like effect. The differences between the aldehyde and ketone are undoubtedly due to the fact that whereas the steric overlap between the ortho-methyl group of the benzene ring and the aldehyde-hydrogen atom is small, replacement of the latter by a methyl group causes appreciable interference.

It is instructive to compare the difference in spectral properties between the acetophenones and the diphenyls. Thus in the case of the diphenyls, ortho-methyl groups cause a considerable hypsochromic shift of the band, together with a pronounced loss in ϵ . This type of effect has been ascribed[1] to transitions involving non-planar ground states and

1.   Braude, E. A., Sondheimer, F., and Forbes, W. F., Nature, <u>173</u>, 117, (1954).

non-planar excited states. In the case of aceto-
phenone, however, the absence of any remarkable
changes in the band means that the transition en-
ergy remains almost unchanged. Transition in this
region corresponds to an energy change of about
80 kcal/mol. The changes in wavelength in the
acetophenone series correspond to an energy differ-
ence of 2-4 kcal/mol, which is approximately that
required for vibrational transitions in a polyatomic
molecule.Therefore, this type of steric effect found
in acetophenones has been postulated as due to the
restriction, caused by steric hindrance, of the
number of ground state molecules having a sufficient-
ly planar configuration permitting transition to a
uniplanar excited state, thereby causing a reduction
in the intensity of absorption.

In the case of acetophenone the allowed trans-
ition may be represented as a change from a non-
ionic ground state to a polar excited state as
follows:
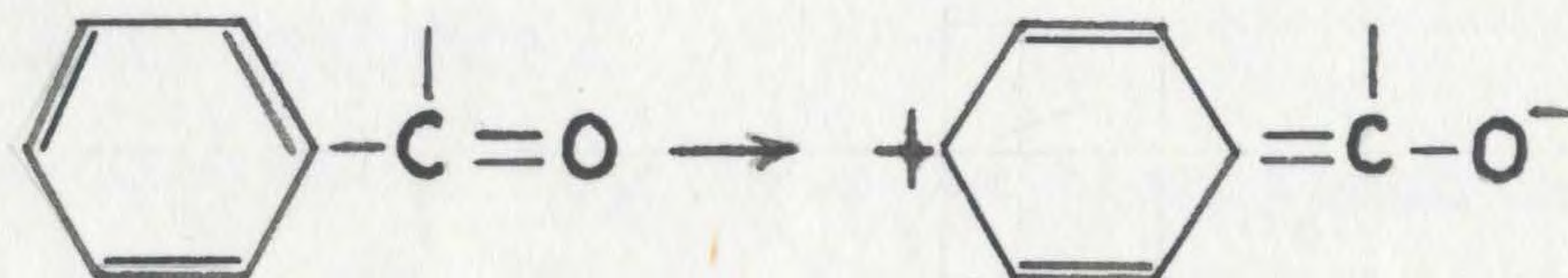
The introduction of an ortho-methyl group will
raise the energy level of the ground state relative
to the unhindered compound, due to the additional

steric strain. In the postulated polar excited state, the phenyl-carbon link will have increased double bond character. Now, due to the fact that considerably more energy is required to twist a double bond than a single bond, and further that since the interplanar angle cannot change during a transition due to the fact that the time required for a transition is much less than that required for a change in configuration (Franck-Condon principle), the increase in energy of the excited state will be raised even more than that of the ground state, thus causing the hypsochromic shift of the band. Transitions of this type may be ascribed to changes between non-planar ground states and planar excited states, and have been shown to exist in conjugated systems, where one unhindered or weakly hindered configuration is possible.

ULTRAVIOLET ABSORPTION SPECTRA

Unsubstituted Ketones

Benzaldehyde has an intense absorption band at 244 mμ, $\epsilon = 13,000$, which is typical of $\pi - \pi$ conjugation. Acetophenone, as compared with benzaldehyde, absorbs at a slightly shorter wavelength

with slightly less intensity. In this case the re-
placement of the aldehyde-hydrogen atom by the
larger methyl group causes a slight increase in
steric hindrance. This trend continues with propio-
phenone, since the larger ethyl group would be ex-
pected to give rise to a slight additional strain
as compared to the methyl group. n-Butyrophenone
has a spectrum similar to that of propiophenone,
which is to be expected, since the additional methyl
group is presumably too far removed to give rise
to any additional hindrance. The spectrum of iso-
butyrophenone indicates a slight additional amount
of strain. This is explained by the fact that the
replacement of two hydrogen atoms of the acetophenone
methyl group by two methyl groups would be expected
to set up an increasing order of steric interference.

Substituted Ketones

Molecular Configuration of 2-methylacetophenone
and 2-methylpropiophenone.

Upon examining the spectra, it will be noticed
that the change in spectral properties between 4-
methyl- and 2-methylacetophenone is almost identical
with the change observed between 4-methyl- and 2-
methylpropiophenone. For the first pair, there is

a bathochromic shift of 10 mμ, and the ratio of

extinction coefficients if 0.57 (8500/15,000).

For the second pair, the bathochromic shift is 9

mμ, and the ratio is also 0.57 (9000/14,000).

This points to the fact that the geometrical con-

fifuration of the two molecules is similar, since

the replacement of the methyl group in acetophenone

by the ethyl group in propiophenone would increase

the hindrance, thus giving rise to a greater diff-

erence in the shift between the two. Thus we may

conclude that the preferred configuration is IA

IA   IB
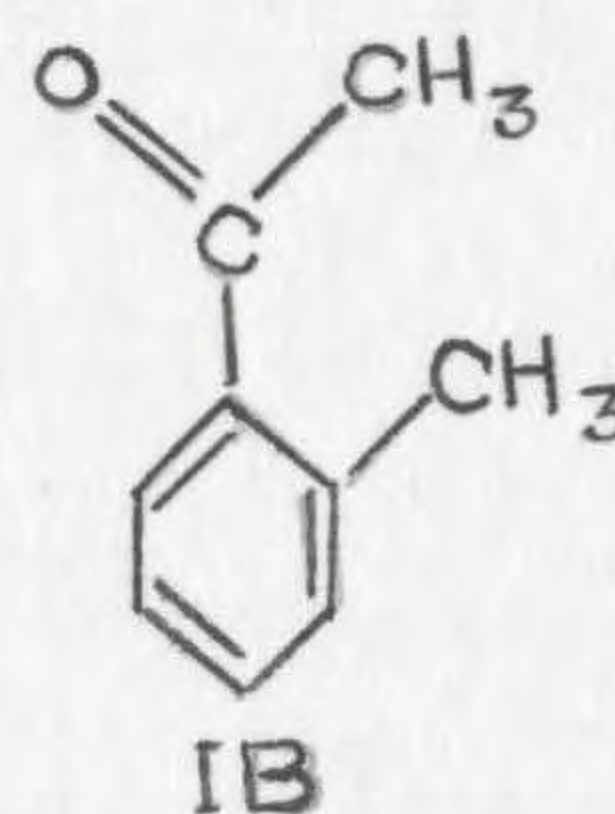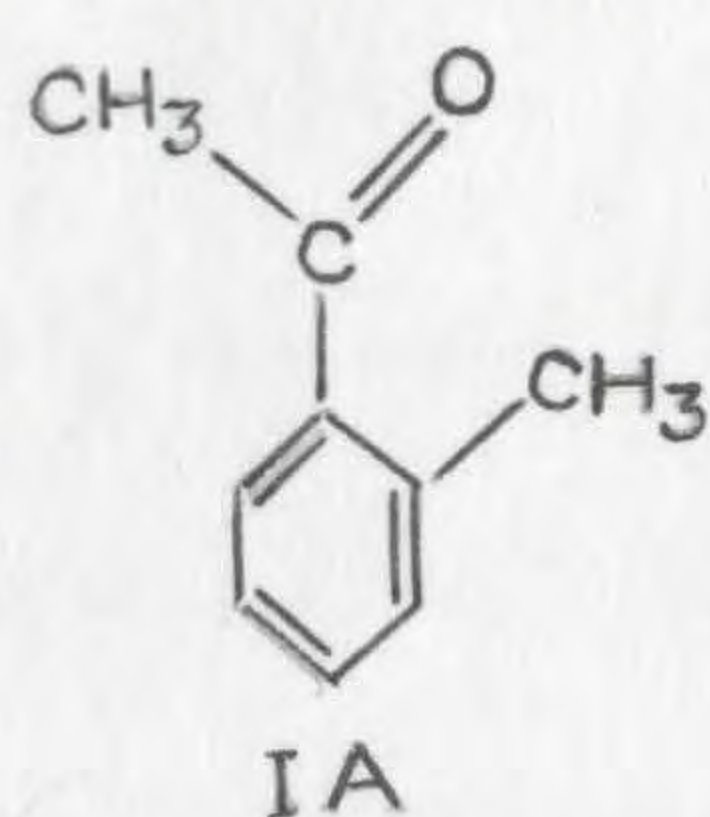
rather than IB. Examination of the spectra of penta-

methyl- and pentaethylacetophenones indicates that

the replacement of the methyl group by the more

bulky ethyl group does cause additional steric effect,

thus fortifying the argument.

The Electronic Effect of Substituents

Examination of the sata show the 4-methyl- and

2-methylbenzaldehyde absorb at identical wavelengths,

TABLE I

ABSORPTION SPECTRA OF ORTHO-SUBSTITUTED ACETOPHENONES

AND RELATED COMPOUNDS IN ABSOLUTE ETHANOL

Wave-lengths and intensities of the main maxima
(Underlined values represent inflections)

Compound	λ max mμ	ϵ max	λ max mμ	ϵ max
Benzaldehyde	244	13,000	279	950
Acetophenone	240	12,500	276	1000
Propiophenone	240	12,000	276	1000
n-Butyrophenone	240	11,500	276	1000
Isobutyrophenone	240	10,500	276	850
4-Methylbenzaldehyde (1)	251	15,000	–	–
2-Methylbenzaldehyde (1)	251	13,000	–	–
2-Methylacetophenone (1)	242	8500	283	1250
4-Methylacetophenone (1)	252	15,000	278	850
2,4-Dimethylacetophenone (1)	251	13,000	282	1250
2,6-Dimethylacetophenone (2)	241	2100	–	–
2,4,6-Trimethylacetophenone (2)	245	2300	–	–
2,3,5,6-Tetramethylacetophenone	212	11,500	277	850
2,3,4,5,6-Pentamethylacetophenone	216	12,000	280	600
2,3,4,5,6-Pentaethylacetophenone	218	14,000	280	500
4-Methylpropiophenone	249	14,000	–	–
2-Methylpropiophenone	240	8000	282	1200
4-Acetylhydrindacene (II)	252	7000	308	3000

TABLE I (cont'd)

Compound	λ_{max} mμ	ϵ_{max}	λ_{max} mμ	ϵ_{max}
4-Acetyl-5,6-dimethylindane (III)	246	3000	280	1700
9-Acetyloctahydroanthracene (IV)	220	10,000	282	1500
5-Acetyl-6,7-dimethyltetralin (V)	218	11,000	278	1100
2,3,5,6-Tetramethylbenzene	214	8500	268	600

2. Schwartzman, L. H., and Corson, B. B., J.A.C.S. 76, 781, (1954).
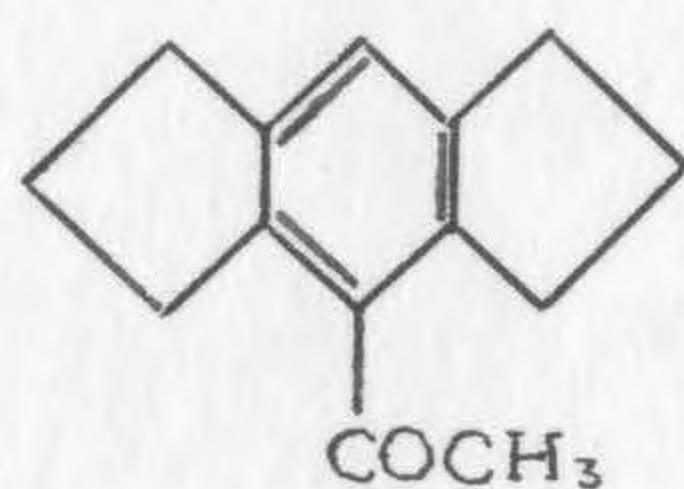
II
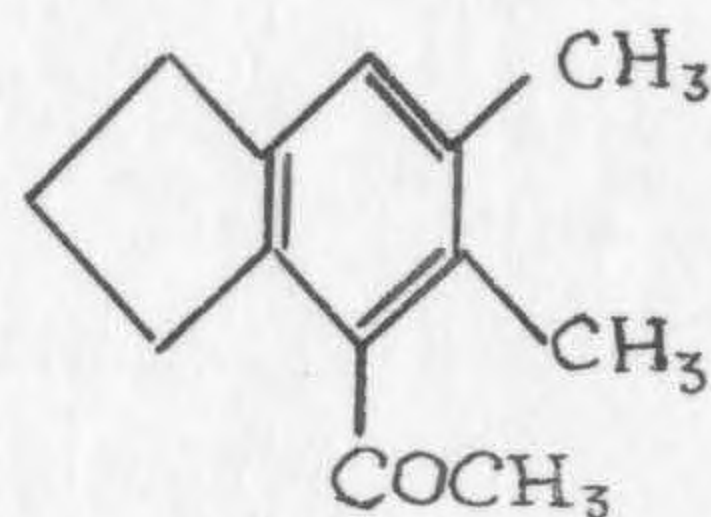
III

IV

V

IIIA

IIIB

VA
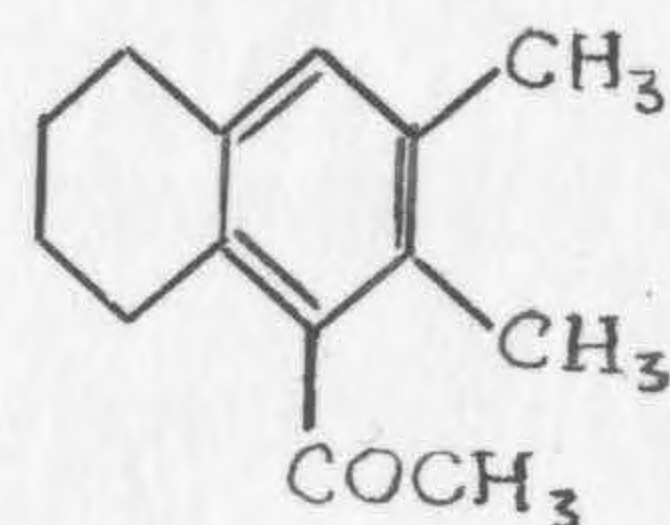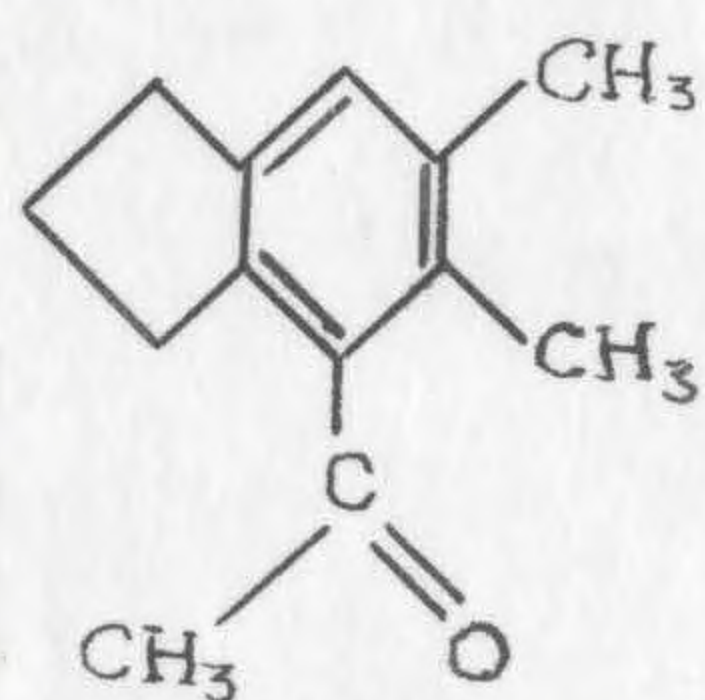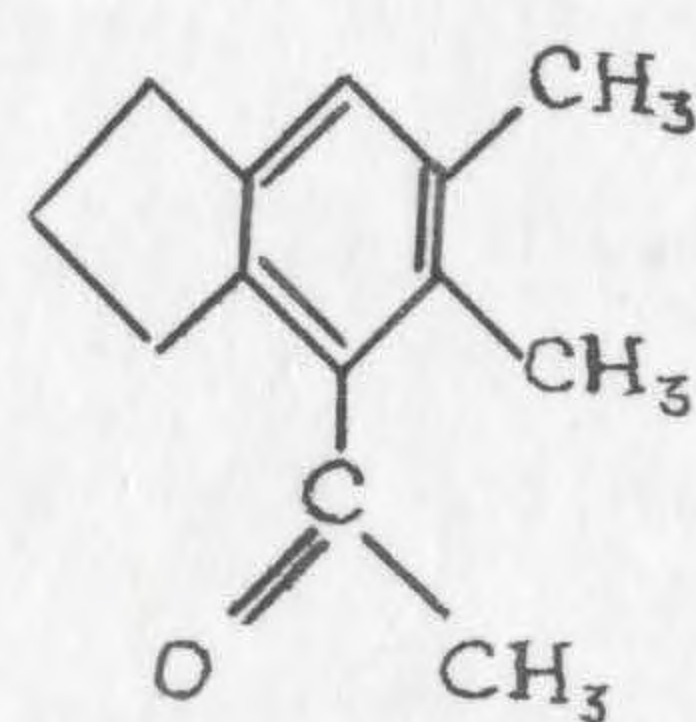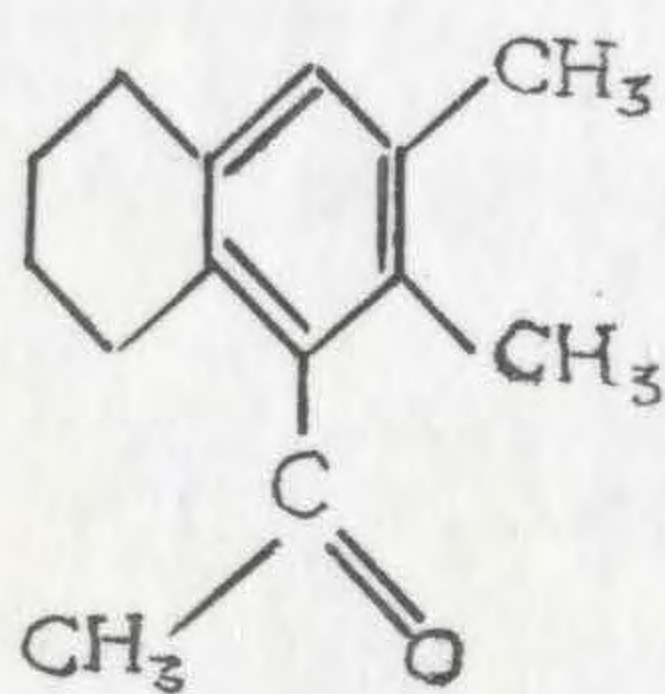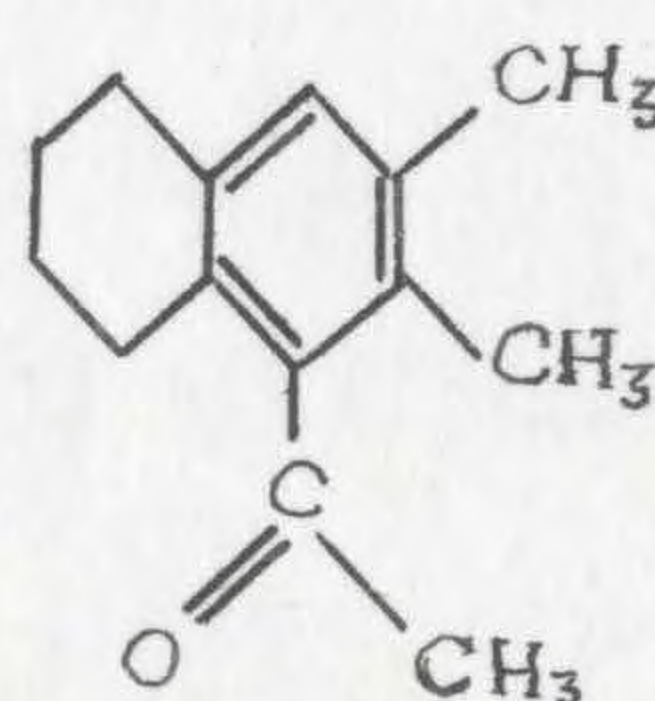
VB

and that the ratio of extinction coefficients is 0.87 (13,000/15,000). Thus in aceto- and propiophenone the intensity is almost halved by the introduction of an <u>ortho</u>-methyl group, whereas in benzaldehyde it remains almost constant. In <u>o</u>-methylbenzaldehyde a bathochromic shift of 7 mμ is observed, while in acetophenone the corresponding shift is only 1 mμ. In addition, the shift between benzaldehyde and 2-methylbenzaldehyde is almost indentical with that between benzaldehyde and 4-methylbenzaldehyde. In the later case, there is little steric strain, and the shift is clearly caused by the electronic influence of the substituent. It may also be noted that 4-methylbenzaldehyde, 4-methylacetophenone, and 4-methylpropiophenone all show substantially similar spectral properties.

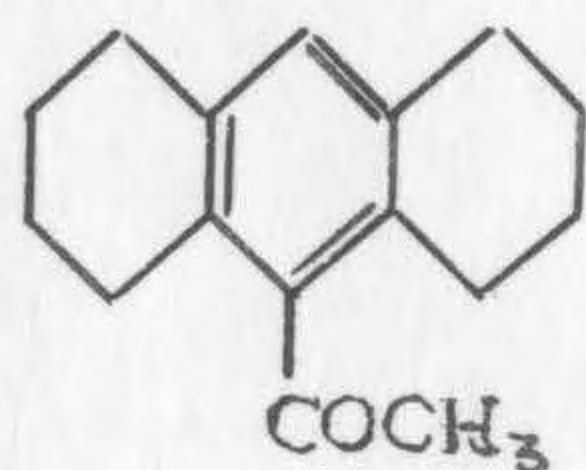The introduction of a methyl group in the <u>para</u>- position of acetophenone causes a bathochromic shift of 12 mμ, with an increase in ϵ of 2500. Assuming the absence of any steric effect, we may justifiably assume an entirely similar spectrum for <u>ortho</u>-methylacetophenone, since the mesomeric effect is approximately the same for the <u>ortho</u>- and <u>para</u>- positions, and the difference in inductive effect between the two positions is small by

comparison. Observing the actual spectrum of 2-methylacetophenone, it becomes apparent that the steric effect causes a hypsochromic shift of about 10 mμ, with an attendant decrease in ϵ of 6500. Propiophenone has a corresponding shift of 9 mμ, and the loss in intensity is 6000. To fully appreciate the effect of steric interference, the hindered ortho- compound should be compared with the para- analogue, rather than with the parent compound. This effect becomes apparent in o-methylbenzaldehyde, where steric influences are small, and in 4-acetylhydrindacene (II), where the introduction of a second methylene group causes a bathochromic shift of about 10 mμ.

The sensitivity of the band to para- substituents has led to the assumption of electronic transitions associated with para- resonance forms of type IC (3).

IC
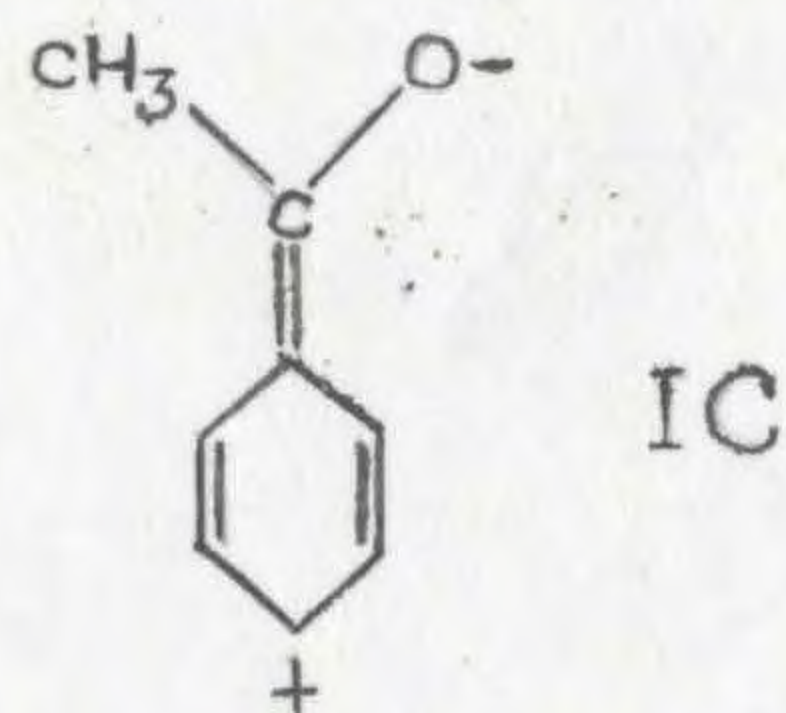
It can be seen from Figure 2 that a decrease

3. Cram, D. J., and Cranz, F. W., J.A.C.S., 71, 1362, (1949).

FIGURE I
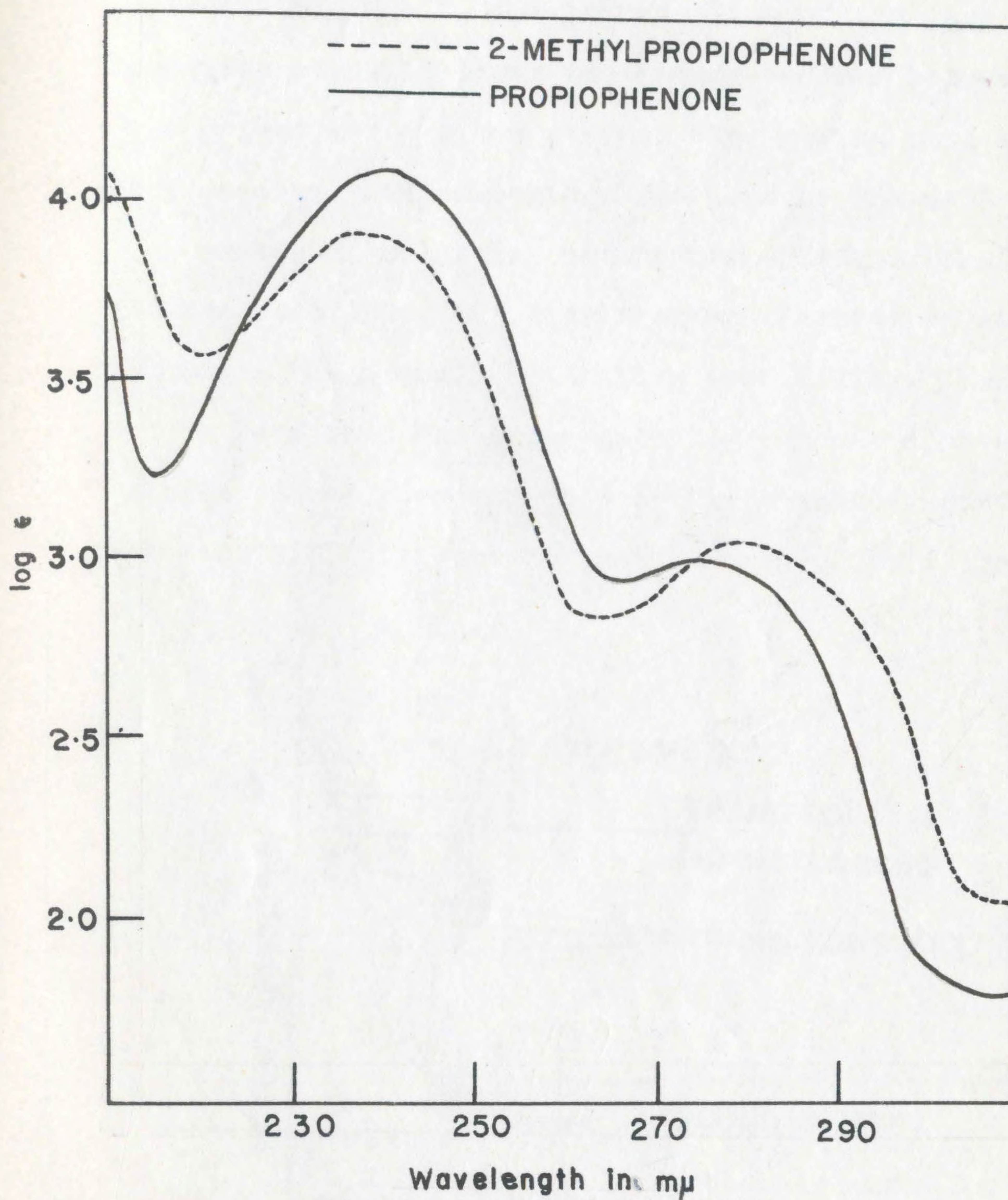
ABSORPTION SPECTRA OF PROPIOPHENONE AND
2-METHYLPROPIOPHENONE IN ETHANOL

in the interplanar angle, caused by an increase in amount of double bond character between the phenyl-carbon link, due to the introduction of the para-substituent, will lower the energy barrier between the ground and excited states, thus giving rise to the observed bathochromic shift, and by increasing the number of molecules having near-planar vibrational states permitting of transition to the excited state, increase the overall transition probability. Hence it is seen that the ortho-methyl group has a greater steric effect than apparent at first glance, since it must also overcome resonance forms of this type.
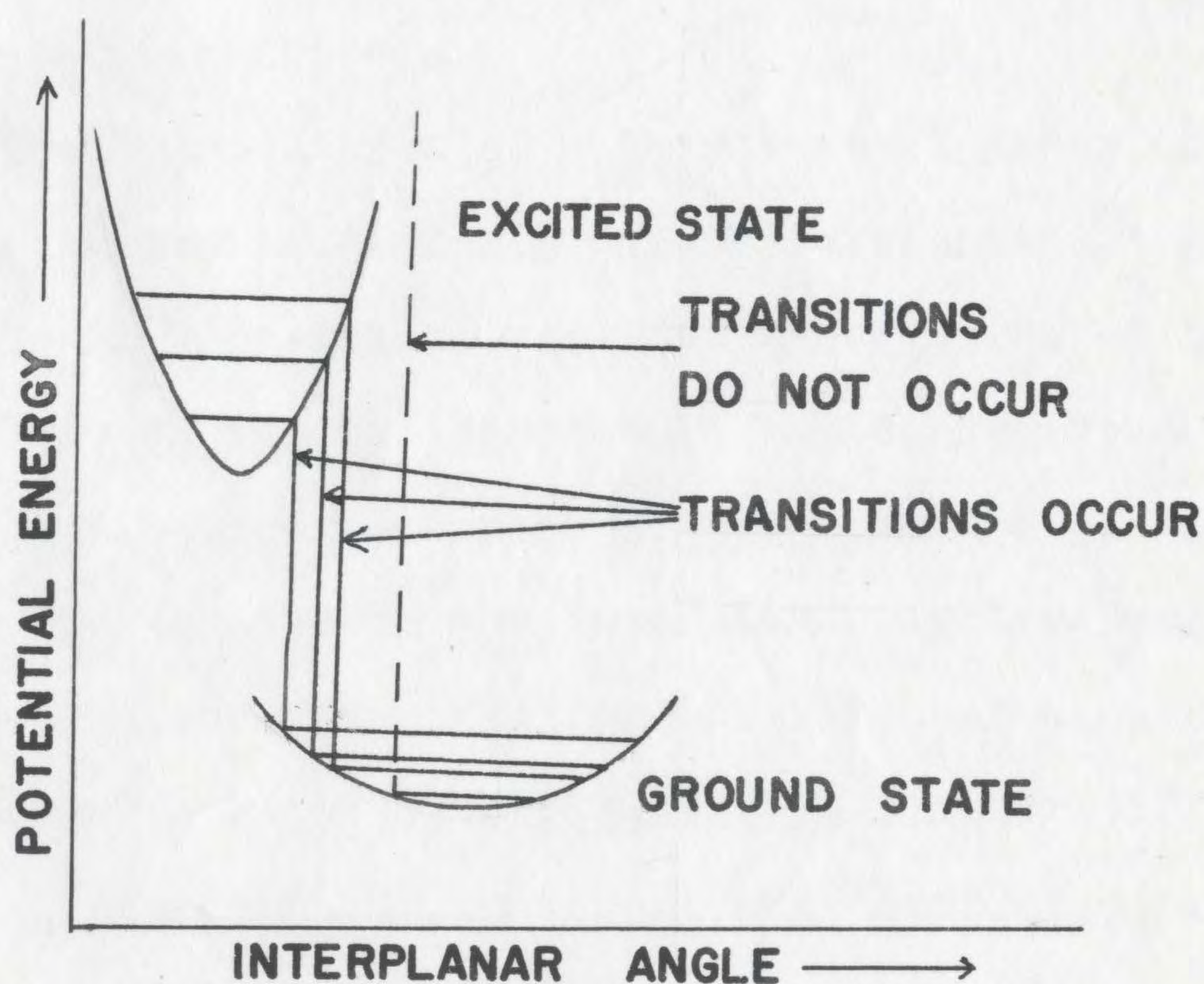
FIGURE 2

Spatial Orientation of Hindered Ketones.

The spectra of 2-methylacetophenone and 2-methylpropiophenone have been discussed previously (cf. page 5), and it has been shown that the preferred configuration is one in which the carbonyl oxygen atom is adjacent to the ortho-methyl group.

In the case of 2,6-dimethylacetophenone, the molecule can no longer take up a favorable steric configuration, i.e., two methyl groups must now be adjacent. Hence, the interplanar angle is increased considerably, and conjugation is almost completely inhibited.

The introduction of a third methyl group in the para- position of 2,6-dimethylacetophenone gives rise to an increase of para-resonance forms of type IC. This causes an increase in the double bond character between the phenyl group and the carbonyl group, which lessens the interplanar angle, thus increasing the transition probability and causing the observed bathochromic shift. A similar difference occurs between 2,3,5,6-tetramethyl- and 2,3,4,5,6-pentamethylacetophenone.

4-Acetylhydrindacene (II)

In the case of 4-acetylhydrindacene, there is

no preferred spatial orientation, and we may compare
its spectrum to that of 2,6-dimethylbenzaldehyde
and 2,6-dimethylacetophenone. The absorption max-
imum at 252 mμ is similar to that of 2,6-dimethyl-
benzaldehyde. The intensity of absorption indicates
a slight amount of steric strain corresponding to
the usual decrease in the number of planar ground
states. There is a decrease of intensity with re-
spect to acetophenone, and an increase relative to
2,6-dimethylacetophenone. This indicates that the
ortho-methylene group of the cyclopentyl ring offers
steric resistance intermediate between an ortho-
hydrogen atom and an ortho-methyl group. This is
to be expected, and is reinforced by an examination
of scale models.

9-Acetyloctahydroanthracene (IV)

In this molecule, the ortho-methylene group
is held in a position where steric interference in
considerably enhanced. This agrees with the findings
of Arnold and Craig[4] who found from reactivity dif-
ferences and in part from an interpretation of car-
bonyl Raman frequencies, that the steric hindrance
decreases around the carbonyl group in the order
V > IV > III > II. The methylene group causes a con-

4. Arnold, R. T., and Craig, P. N., J.A.C.S. 70,
2791, (1948).

siderable increase in the interplanar angle, thus
increasing the transition energy and giving rise
to the hypsochromic shift. Comparing with the
spectra of 2,3,5,6-tetramethylacetophenone, it may
be deduced that the ortho-methylene group in the
cyclohexyl ring offers slightly less steric resis-
tance than the ortho-methyl group in the tetra-
substituted acetophenone, the latter methyl group
offering in turn considerably more resistance than
the ortho-methyl group in 2,6-dimethylacetophenone.
This difference may be explained by the so-called
"buttressing effect" of the meta-positioned methyl
group in the tetramethylacetophenone, i.e., the
meta-positioned methyl groups prevent the "bending
away" of the ortho-methyl group, thus causing the
latter to interfere to a greater degree with the
keto-group, and preventing the attainment of a
sterically favorable position.

4-Acetyl-5,6-dimethylindane (III)

For this compound, two structures (IIIA and
IIIB, cf. page 8) are possible. It is possible
that the ortho-methylene group in this molecule,
by taking up the sterically most favorable position,
i.e., one in which the two ortho-hydrogen atoms
would form a saddle, could contribute to the co-

FIGURE 3
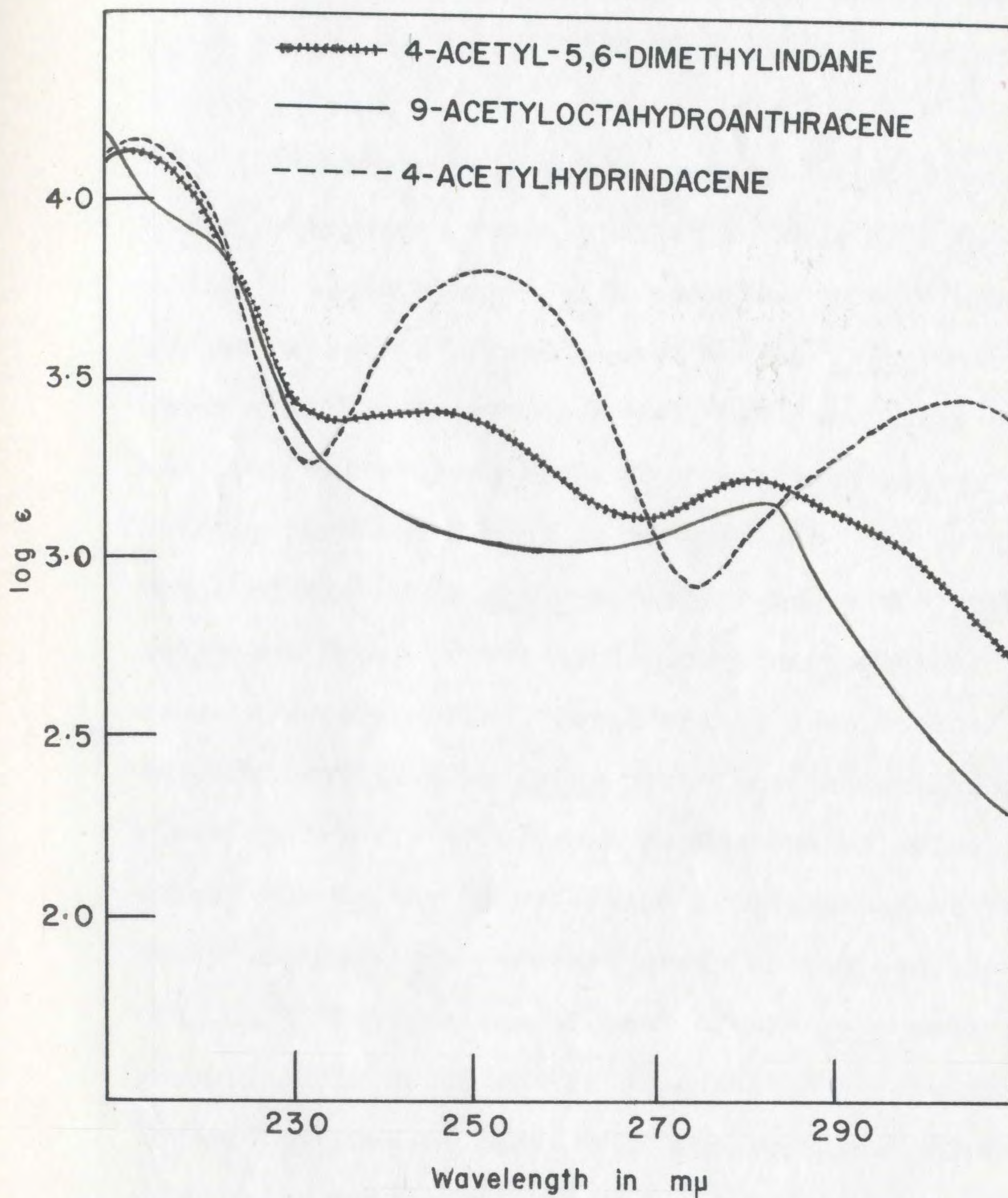
ABSORPTION SPECTRA OF 4-ACETYLHYDRINDACENE, 9-ACETYLOCTAHYDROANTHRACENE, AND 4-ACETYL-5-6-DIMETHYLINDANE IN ABSOLUTE ETHANOL

planarity of the molecule. This effect, together
with the tendency toward uniplanarity due to the
para- resonance forms, will be opposed by the usual
steric effect.

If structure IIIA predominates, the spectrum
would be expected to be similar to that of 2,6-
dimethyl acetophenone, with modifications. Thus the
amount of steric effect caused by the ortho-methyl
group would be increased due to the previously de-
scribed "buttressing effect" of the meta-methyl group .
This in turn would tend to be offset by the substit-
ution of the other ortho-methyl group by the ortho-
methylene group of the cyclopentyl ring, which,
as seen before, offers considerably less steric
interference than an ortho-positioned methyl group.
Since the steric effect has been shown to arise
mainly due to the interference of the keto-methyl
group with the ortho-methyl group of the benzene
ring, the "buttressing effect" of the meta-methyl
group in IIIA would not be expected to have a pro-
nounced influence, because of the smallness of the
carbonyl oxygen atom. Therefore, in structure IIIA
one would predict that the total steric effect should
be less than in the case of 2,6-dimethylacetophenone.

Concerning structure IIIB, the "buttressing effect" *(Cf. page 8)*

of the <u>ortho</u>-methyl group should have a consider-

able effect, as previously discussed in the compar-

ison of 2,6-dimethylacetophenone with the tetra-

methyl acetophenone, and therefore the spectrum

should resemble that of the tetra-methylacetophen-

one. From the data, it will be seen that only

structure IIIA is reasonable from the above con-

clusions. This is indeed what would be expected

from overall steric considerations, and is also

borne out by the consideration of scale models.

<u>5-Acetyl-6,7-dimethyltetralin</u> (V)

In this example, two structures, VA and VB

(see page 8) are possible. If structure VB were

correct, the spectrum would resemble that of tetra-

methylacetophenone, since the buttressed <u>ortho</u>-

methyl group in the tetra-substituted acetophenone

presumably would offer only slightly more steric

resistance to the small keto-oxygen molecule than

would the <u>ortho</u>-methylene group of the cyclohexyl

ring. If VA were the correct structure, then the

spectrum should resemble that of 9-acetyloctahydro-

anthracene, with allowance for the fact that the

buttressed methyl group might interfere slightly

FIGURE 4
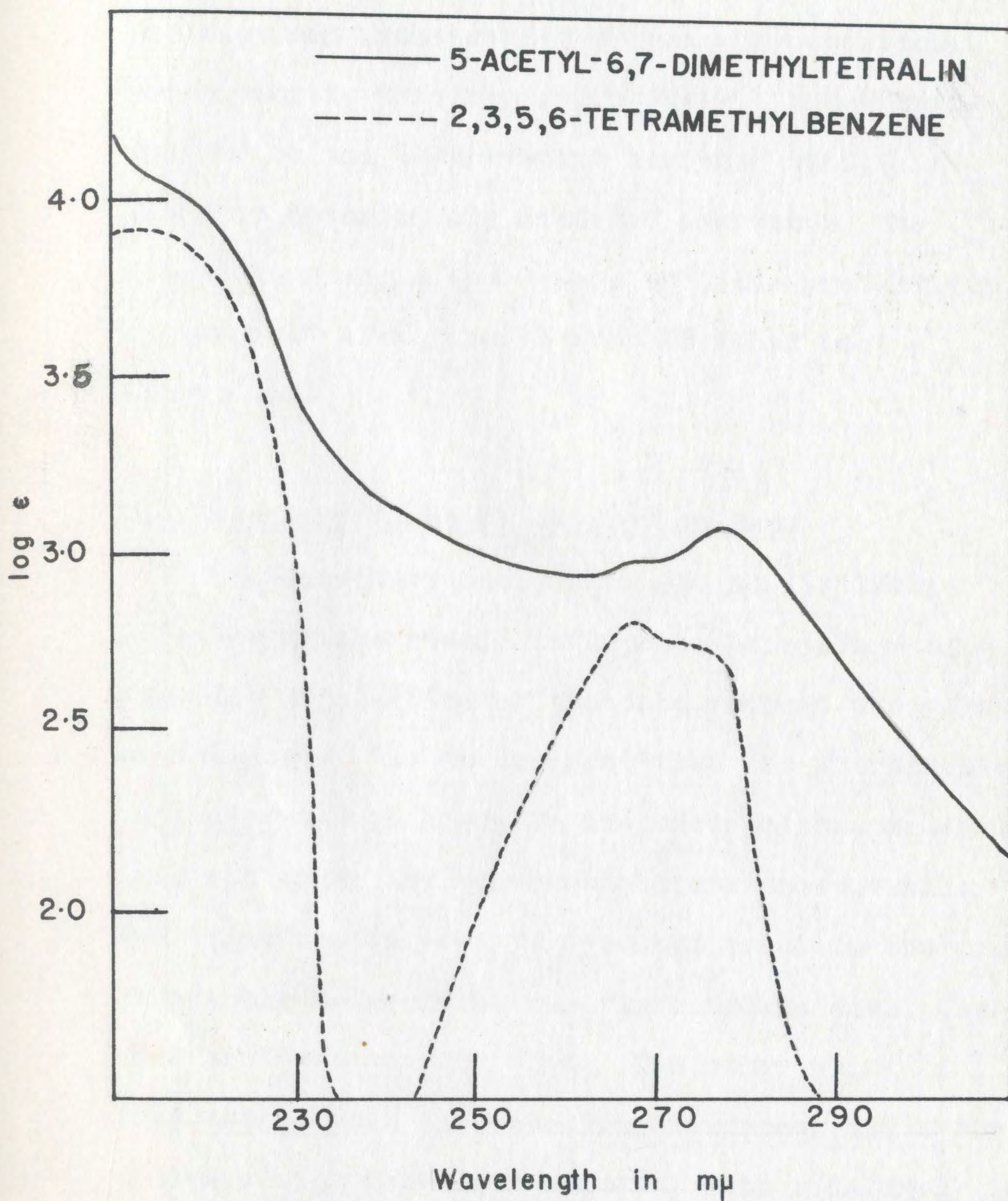
ABSORPTION SPECTRA OF 5-ACETYL-6,7-DIMETHYL-
TETRALIN AND 2,3,5,6-TETRAMETHYLBENZENE
IN ABSOLUTE ETHANOL

with the keto-oxygen atom. The data seem to point
to structure VA rather than VB, which is what one
might expect from overall steric considerations.
Absorption in this region, however, is due prin-
cipally to the "tetramethyl benzene" band, and
since in these highly hindered compounds, the
interplanar angle approaches 90°, the probability
in favor of structure VA over VB is at best a
slight one.

The Secondary Carbonyl Absorption Band

The secondary band, near 280 mμ, is little
affected by the steric influences heretofore dis-
cussed. Examination of the data present two points
of interest. One is the fact that the introduction
of a para-methyl group in the acetophenone molecule
does not cause any remarkable occurrences, while
the introduction of a para-methyl group in the pro-
piophenone molecule causes the complete disappear-
ance of the secondary band. The other point of
interest is that in 4-acetylhydrindacene (II), there
exists a high degree of symmetry with relatively
little steric hindrance. The secondary band of this
molecule has undergone a bathochromic shift of about
28 mμ. It would be presumptuous to draw any

conclusions on such nebulous data, and any explanation

must await further experimental work, which is in progress.

This work indicates that the band may concern itself with

the angle of incidence of the photon.

2,4-dinitrophenylhydrazones

The absorption spectra of the 2,4-dinitrophenyl-

hydrazones of some of the ketones, together with reference

compounds, are listed in Table II.

Unsubstituted Compounds

Cyclohexanone 2,4-dinitrophenylhydrazone absorbs

maximally at 362 mu. Since in this case there is no cross-

conjugation possible, this maximum must be attributed to

the $\diagdown$C=N-NH-R group, (R = 2,4-dinitrophenylhydrazone

chromophore). The spectrum of benzaldehyde, acetophenone,

and propiophenone 2,4-dinitrophenylhydrazones indicate cross

conjugation, as evidenced by a bathochromic shift and an

increase of absorption intensity. The spectrum of iso-

butyrophenone 2,4-dinitrophenylhydrazone shows that the re-

placement of a hydrogen atom in propiophenone 2,4-dinitro-

phenylhydrazone by a methyl group causes a transition from

a planar to a non-planar molecule. Para-resonance forms

make their usual contribution by lowering the energy of

the excited state more than that of the ground state,

as is evidenced by the spectrum of 4-methylpropiophenone

2,4-dinitrophenylhydrazone. In 2-methylpropiophenone

2,4-dinitrophenylhydrazone, the introduction of the ortho-

methyl group causes a complete loss of conjugation, and the spectrum is similar to that of cyclohexanone 2,4-dinitrophenylhydrazone.

TABLE II

Absorption Spectra of 2,4-Dinitrophenylhydrazones of Acetophenones and Related Compounds in Chloroform.

Wave-lengths and intensities of the main maxima.

Carbonyl compound	λmax mμ	ϵ max	Color
Benzaldehyde	372	29,000	Red
Acetophenone	372	25,000	Red
Propiophenone	374	25,000	Red
4-Methylpropiophenone	380	25,500	Red
2-Methylpropiophenone	362	23,500	Red
Isobutyrophenone	362	23,500	Yellow
Cyclohexanone	362	23,500	Yellow
4-Acetylhydrindacene	366	24,000	Orange
4-Acetyl-5,6-dimethylindane	362	22,000	Orange

The spectrum of 4-acetylhydrindacene 2,4-dinitrophenylhydrazone indicates an intermediate amount of steric hindrance, and that of 4-acetyl-5,6-dimethylindane 2,4-dinitrophenylhydrazone

shows a complete lack of coplanarity. 9-Acetyl-
octahydroanthracene (IV), 5-acetyl-6,7-dimethyl-
tetralin (V), tetramethyl-, pentamethyl-, and
pentaethylacetophenones do not form 2,4-dinitro-
phenylhydrazones, oximes, or semicarbazones under
the usual conditions. The amount of steric hin-
drance may sometimes be estimated from the color
of the 2,4-dinitrophenylhydrazones. (See Table II).

Substituted Benzoic Acids

An interesting example of the relation of spec-
tra to electronic and steric effects is provided
by a recent paper[5] on the spectra of various tri-
substituted benzenes. In this work, the authors
attempt to correlate the spectra of the tri-sub-
stituted compounds with those of the corresponding
di-substituted compounds. They choose β-resorcylic
acid as a representative example of a tri-substitu-
ted benzene, and report the data listed in Table III.

The authors state that the primary band of
salicylic acid has no analogue in the spectrum of
β-resorcylic acid, and further that the first pri-

5. Doub, L., and Vandenbelt, J. M., J.A.C.S. 77,
4535, (1955).

mary band of the tri-substituted compound may be related to the most displaced band of the component di-substituted compounds. They point out that the first primary bands of the di-substituted compounds frequently do not occur in the tri-substituted compound, and in concluding add that steric effects are usually small in absorption spectra.

TABLE III

ABSORPTION SPECTRA OF β-RESORCYLIC ACID

AND RELATED COMPOUNDS IN ETHANOL

Wave-lengths and intensities of the main maxima

Compound	λmax mμ	ϵmax
β-Resorcylic Acid	256	13,600
Salicylic Acid	237	9000
Resorcinol	–	–
p-Hydroxybenzoic Acid	255	14,000

Application of steric and electrical effects as outlined above should prove of interest in this case.

Benzoic Acid

Benzoic acid absorbs maximally with smaller

intensity of absorption than acetophenone. As has been pointed out[6], this may be ascribed to the fact that <u>in the excited state</u> the concentration of electrons in the carboxyl group is greater than that in the acetyl group. The two structures may be represented as follows:

It is seen that in the case of benzoic acid, there will be less double bond character in the excited state relative to acetophenone. Hence benzoic acid will be more sensitive to steric effects, since the carboxyl group may be twisted out of the plane of the benzene ring more easily than the acetyl group. The hindrance is presumed to occur mainly in the excited state, which accounts for the fact that the steric effect is manifested by a decrease in absorption intensity rather than by a pronounced hypsochromic shift of the band (compare acetophenone).

6. Forbes, W. F., and Sheratte, M. B., Light Absorption Studies, part II, Can. J. Chem., <u>33</u>, in the press, (1955).

However, due to replacement of the methyl group
in acetophenone by the hydroxy group in benzoic acid,
the negative inductive effect of the hydroxy group
will stabilize ground state resonance forms to a
greater extent than in acetophenone. Also, in
benzoic acid the excited state has a somewhat high-
er energy than acetophenone due to a larger charge
separation. Hence the energy of transition in
benzoic acid is greater than that of acetophenone,
causing benzoic acid to absorb maximally at
shorter wavelength with decreased intensity, (λmax
227 mμ: ϵ max 11,000).[5]

p-Hydroxybenzoic Acid

The introduction of a hydroxy group in the
para- position, due to the usual resonance stabi-
lization, lowers the energy level of the excited
state more than that of the ground state, thus caus-
ing the observed bathochromic shift and increased
intensity of absorption, as in the acetophenones.

Salicylic Acid

In the case of salicylic acid, the purely
electronic effect of the hydroxy group will be off-
set to some degree by steric interference of the
carboxyl group with the ortho-hydroxy group. The
resonance effect of the ortho-hydroxy group may

may be considered to be equal to that of the para-
hydroxy group, but the inductive effect will be
greater in the ortho- position. This will tend
to stabilize polar excited states of type IE, thus
giving a further bathochromic shift.

IE
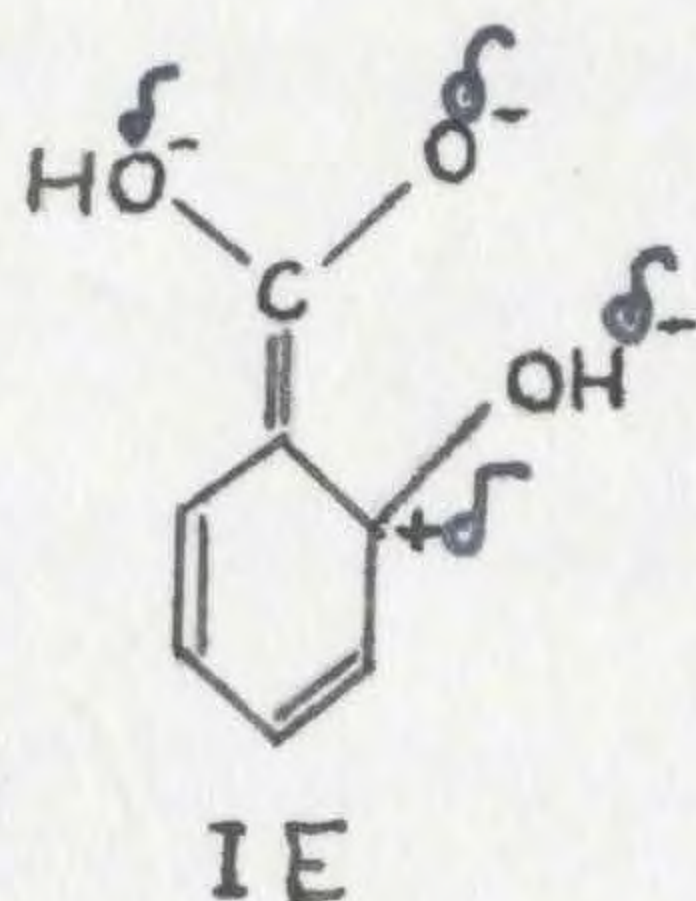
Hence the steric effect of the ortho-hydroxy group
is somewhat larger than appears at first glance,
since it must overcome this difference in inductive
effect. Thus it can be seen that the steric effect
causes a hypsochromic shift of 19 mμ, and a decrease
in intensity corresponding to a ratio of extinction
coefficients of 0.64 (9000/14,000), comparing with
the para- compound.

β -Resorcylic Acid

If, now, another hydroxy group is introduced
in the para- position of salicylic acid, the increas-
ed stabilization of the excited state relative to
the ground state due to the resonance contributions
will cause a further bathochromic shift and a

corresponding increase in absorption. In this case, and also in the case of 2-methyl- and 2,4-dimethyl-acetophenone, the increase in stabilization due to para- resonance forms is very closely equal to the decrease in stabilization due to steric inter-ference. Thus λmax and ϵmax of the para- compound closely correspond to those of the 2,4-disubstitut-ed compounds. The possibilities of dimer formation and hydrogen-bonding at the low concentrations used in spectral work are being investigated at this time, and present data do not permit a detailed discussion of these topics.

From the above discussion, it can be seen that an interpretation of the operative electronic and steric effects leads to a more precise correlation of the spectra in this particular example than is possible with empirical terms. An examination of spectral data available in the literature shows steric effects to be widely prevalent, and in any critical discussion of spectroscopic evidence, the importance of steric hindrance cannot be overlooked.

EXPERIMENTAL PART

The ultraviolet spectra were determined by
standard methods using a Unicam SP 500 spectro-
photometer. ϵ represents the molecular extinction
coefficient defined by $\epsilon = \log_{10}(I_o/I)cl$, where I_o
and I equal the intensity of incident and trans-
mitted light, respectively, c equals the concentra-
tion in moles/liter, and l equals the cell thickness
in centimeters.

Melting points are uncorrected, and the analyses
were carried out in the micro-analytical laboratory
(Mr. F. H. Oliver) of the Department of Organic
Chemistry, Imperial College, London, England.
Benzaldehyde, Acetophenone, Propiophenone, Iso-
butyrophenone.

The commercially available compounds were re-
distilled to constant refractive index and intensity
of absorption. Light absorption in ethanol: see
Table I. The 2,4-dinitrophenylhydrazones of these
as well as of the other carbonyl compounds described
below, were chromatographed over alumina from
chloroform-benzene and crystallized, unless other-
wise stated, from ethanol-ethyl acetate mixtures.
Benzaldehyde 2,4-dinitrophenylhydrazone crystallized
from glacial acetic acid as red needles, m.p. 241-

242°, (Johnson[7] (6) gives m.p. $239\text{-}240^{\circ}$); acetophen-
one 2,4-dinitrophenylhydrazone crystallized from
glacial acetic acid as red needles, m.p. 250°,
(Johnson[7] (6) gives m.p. $247\text{-}248^{\circ}$); propiophenone
2,4-dinitrophenylhydrazone crystallized as red
plates, m.p. $196\text{-}197^{\circ}$ (decomp.) (Johnson[7] (6) gives
m.p. $193\text{-}194^{\circ}$); isobutyrophenone 2,4-dinitrophenyl-
hydrazone crystallized as yellow monoclinic prisms,
m.p. $165\text{-}166^{\circ}$ (Johnson[7] (6) gives m.p. $161\text{-}162^{\circ}$).
Light absorption in chloroform: see Table II.

4-Methylpropiophenone

Anhydrous aluminum chloride (9.1 gm.) was added
to toluene (100ml.) and propionyl chloride (6.3 gm.)
was added dropwise with stirring at $0^{\circ}C$. After
stirring for one hour, the mixture was hydrolyzed
and isolated in the usual manner. The product
distilled at $110^{\circ}/12$ mm., yield 5,5 gm. (55%),
$n_D^{22.5}$ 1.5264. (Birch, et al.[8] (7) give boiling point
$135^{\circ}/30$ mm.; n_D^{20} 1.5278). Light absorption in
ethanol: see Table I. The 2,4-dinitrophenyl-
hydrazone crystallized from ethyl acetate as red
monoclinic prisms, m.p. 209° (decomp.).

7. Johnson, G. D., J.A.C.S. 75, 2720, (1953).

8. Birch, S. F., Dean, R. A., Fidler, F. A., and
Lowry, R. A., J.A.C.S., 71, 1362, (1949).

(Cullinane et al.[9] (8) give m.p. 201°). Light
absorption in chloroform: see Table II.

<u>2-Methylpropiophenone</u>

2-Methylpropiophenone was prepared according
to the method of Birch et al.[8] (7), and was obtained
as a colorless liquid, b.p. 100°/8 mm., n_D^{22} 1.5243
(Birch et al.[8] (7) give n_D^{20} 1.5250), yield 9.2 gm.,
(62%). Light absorption in ethanol: see Table I.
The 2,4-dinitrophenylhydrazone crystallized from
ethanol as red plates, m.p. 115°. Anal.: Calc for
$C_{15}H_{14}O_4N_4$: C, 57.3; H, 4.5; N, 17.8. Found: C,
57.3; H, 4.5; N, 17.7%. Light absorption in
chloroform: See Table II.

<u>2,3,5,6-Tetramethylacetophenone</u>

Durene (4 gm.), prepared from xylene by the
method of Smith[10] (9), was dissolved in carbon di-
sulfide (40 ml.) at 0°. Aluminum chloride (4 gm.)
was added to the stirred mixture in small portions
followed by the dropwise addition of acetyl chloride
(2.4 gm.) over a period of ten minutes. Stirring
was continued for three hours at 0°, and the mix-
ture was then allowed to stand overnight at room

9. Cullinane, N. M., Chard, S. J., and Leyshon,
D. M., J. Chem. Soc., 376, (1952).

10. Smith, L. I., Organic Syntheses, Collective
Vol. II, John Wiley & Sons, Inc., New York, 1943,
p. 248.

temperature. It was then poured onto an ice-hydro-
chloric acid mixture and extracted with ether.
After drying, removal of the ether afforded the
acetophenone in 55% yield, which crystallized from
petroleum ether (40-60°) as colorless plates, m.p.
75°. (Meyer[10] gives m.p. 73°). No oxime, semi-
carbazone, or 2,4-dinitrophenylhydrazone could be
obtained under the usual conditions. Light ab-
sorption in ethanol: see Table I.

2,3,4,5,6-Pentamethylacetophenone

Pentamethylbenzene (2 gm.), prepared by the
method of Smith[10] (9), was dissolved in carbon di-
sulfide (50 ml.) and treated with aluminum chloride
(1.8 gm.) and acetyl chloride (1.1 gm.) as described
above. The product, which crystallized from methanol
as colorless needles, m.p. 87°, was obtained in 90%
yield. Anal.: Calc. for $C_{13}H_{18}O$: C, 82.1; H, 9.5%.
Found: C, 82.1; H, 9.7%. No oxime, semicarbazone,
or 2,4-dinitrophenylhydrazone could be obtained
under the usual conditions. Light absorption in
ethanol: see Table I.

2,3,4,5,6-Pentaethylacetophenone

Pentaethylbenzene (5.1 gm., n_D^{25} 1.5130),

10. Meyer, V., Ber., 29, 847, (1896).

prepared by the method of Smith and Guss,[12] (11),

was treated with aluminum chloride (3.2 gm.) and

acetyl chloride (2.7 gm.) as described above. The

product which crystallized from 95% ethanol as

colorless needles, m.p. 143.5-144°, was obtained

in 80% yield. Anal.: Calc. for $C_{18}H_{28}O$: C, 83.0;

H, 10.9%. Found C, 83.0; H, 11.0%. No oxime, semi-

carbazone, or 2,4-dinitrophenylhydrazone could be

obtained under the usual conditions. Light absorption

in ethanol: see Table I.

4-Acetyl-5,6-dimethylindane (III)

5,6-Dimethylindane (1.9 gm., $n_D^{26.5}$ 1.5318),

prepared by the method of Arnold and Craig[4] (4),

in carbon disulfide (30 ml.) was treated with

aluminum chloride (1.7 gm.) and acetyl chloride

(1 gm.) as described above. Fractionation at 3

mm. afforded the indane as a pale yellow oil, which

solidified on standing and crystallized from pet-

roleum ether (40-60°) as monoclinic prisms, m.p.

42.5°. Arnold and Craig[4] (4) report m.p. 43° for

this compound. Light absorption in ethanol: see

Table I. The 2,4-dinitrophenylhydrazone crystallized

12. Smith, L. I. and Guss, C. O., J.A.C.S. 62,
2625, (1940).

from benzene as yellow plates, m.p. 196-197°. Anal.:

Calc. for $C_{19}H_{20}O_4N_4$: C, 61.9; H, 5.5; N, 15.2%. Found:

C, 61.9; H, 5.5; N, 15.1%. Light absorption in chloro-

form: see Table II.

4-Acetylhydrindacene (II), 9-Acetyloctahydroanthracene

(IV), and 5-Acetyl-6,7-dimethyltetralin (V).

These compounds were crystallized to constant melting

point. Their preparation has been described (4, 13), and

Professor Arnold kindly provided the required specimens.

The last two compounds form no oximes, semicarbazones, or

2-4 dinitrophenylhydrazones. The 2,4-dinitrophenylhydrazone

of 4-acetylhydrindacene crystallized from ethanol as orange

needles, m.p. 185°. Anal.: Calc. for $C_{20}H_{20}O_4N_4$: C, 63.15;

H, 5.3; N, 14.7%. Found: C, 63.2; H, 5.3; N,14.6%. Light

absorption in chloroform: see Table II.

The following experiments were performed in an attempt

to synthesize 4-acetyltetrahydrobenz(f)indane and 2,3,5,6-

tetraethylacetophenone.

Reaction of β-Chloropropionyl Chloride with Tetralin.

Aluminum chloride (25 gm.) was placed in a flask

with carbon disulfide (100 ml.). β-Chloropropionyl

chloride (25 gm.) was added in portions

13. Arnold, R. T., and Rondestvedt, E. J., J.A.C.S.,
68, 2176. (1946).

through the condenser. The solution turned red, and was refluxed for 45 min., giving a liquid layer and a reddish-brown solid. The liquid and solid were added in portions to tetralin (14.5 gm.), which was cooled in an ice bath. After the addition was complete, the mixture was stirred for one hour, and poured onto ice. Extraction with ether, evaporation, and recrystallization from petroleum ether (40-60°) yielded 20.5 gm. of product (I) (49% based on tetralin), m.p. 65°. The 2,4-dinitrophenylhydrazone crystallized from glacial acetic acid as red needles, m.p. 207.5-208.5 (decomp.). Anal.: Calc. for $C_{19}H_{19}N_4O_4Cl$: N, 13,94%. Found: N, 13,79%.

Cyclization of (I).

Phosphoric acid (5 gm., sp. gr. 1.7), phosphorous pentoxide (5 gm.) and formic acid (5 gm., 91%) were mixed in a beaker, and the resulting cloudy suspension (10 gm.) was poured in a 50 ml. round-bottomed flask. (I) (1 gm.) was added in one lot, and the mixture (two layers) was heated (80-90°) on a water bath for two hours. It was allowed to cool, decomposed with ice, and extracted with ether. The residue (1 gm.) was dissolved in ethanol and 2,4-dinitrophenylhydrazine (equiv. amount) was

added, together with hydrochloric acid (2 ml.,

conc.). After heating, the precipitate was diss-

olved in chloroform, and chromatographed over

alumina, using benzene as an eluent. The band was

redissolved and chromatographed again. Only one

band was obtained. Recrystallization from glacial

acetic acid gave yellow needles, m.p. 247.5-248.5°

(decomp.). Anal.: Calc. for $C_{16}H_{16}O_4N_4$: C, 58.53;

H, 4.91; N, 17.07%. Found: C, 62.54; H, 5.10;

N, 15.32%.

Ethylation of 1,3,5- and 1,2,4-triethylbenzenes.

To a mixture (16.2 gm., n_D^{21} 1.4950) of triethyl

benzenes obtained from a Friedel-Crafts alkylation

was added aluminum chloride (1 gm.). Ethyl bromide

(8 gm.) was then added dropwise over a period of

one hour, the mixture was stirred at room temperature

for three hours, and allowed to stand overnight.

Recovery and distillation at reduced pressure gave

only starting material, (n_D^{21} 1.4950).

The above procedure was repeated, except the

mixture was heated on a water bath for six hours.

Recovery in the usual manner gave tetraethylbenzenes,

(10.9 gm., n_D^{22} 1.5048), starting material (2.9 gm.),

and approximately one gram of undistillable

residue, which showed a blue fluorescence.

The results of Smith and Guss[12] (11) in separating the tetraethylbenzene fraction into its respective isomers by sulfonation with chlorosulfonic acid, separation by fractional crystallization, and de-sulfonation by steam distillation from sulfuric acid could not be reproduced. No limiting value for the sulfuric acid concentration necessary for the Jacobsen rearrangement to take place could be found in the literature.