THE SPECTRA OF ENONES AND CONJUGATED DIENES

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a thesis by

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## ABSTRACT

The ultra-violet absorption spectra of
α,β-unsaturated aldehydes, α,β-unsaturated ketones
and conjugated dienes are discussed with special
reference to the effect of steric interaction on
spectra. Assignments of s-cis or s-trans conform-
ations are made when possible. A modification of
the rules for determining wavelength of maximal
absorption in conjugated compounds is proposed.
Some effects in the spectral curves of conjugated
dienes are discussed. Evidence is presented that
in these series spectra may be determined by
inductive effects.

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Preface

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## INTRODUCTION

For about eighty years it has been known that many compounds, particularly those containing a system of conjugated double bonds, absorb ultra-violet and visible light selectively. That is to say, only light of certain wavelengths is absorbed, the wavelengths differing from compound to compound. The absorption has been shown to be due to the migration of a partial electronic charge from ground state to give an excited state with greater ionic character.[1] While it is possible to write limiting structures for both ground and excited states, the actual state will in each case be a resonance hybrid of several structures. In addition, each excited state and each ground state will have many sub-levels of vibrational and rotational energy, and in a polyatomic molecule there will also be torsional sub-levels.

The well-known rules governing quantisation of energy would lead one to expect an absorption spectrum to consist of a large number of closely spaced lines, as in the case of a diatomic molecule. This has been observed for absorption by vapours,[2] but perturbation by solvent molecules may make "forbidden" transitions allowed in solution and in addition the energy value of each level may be perturbed from

its value in the vapour phase. Further, commercial spectro-photometers are not able to resolve very closely spaced lines. This limitation and the necessity for using wide slit-widths (up to 2 mm.) at short wavelengths with consequent wide band-widths (up to 1 m$\mu$ at wide slit-widths) makes it difficult or impossible to observe fine structure. Therefore the spectrum determined is that of the band envelope (see Figure 1). Nevertheless, the information given by spectra in solution is of value, having been used for (1) quantitative analysis, as in the case of vitamin A[3] (2) determination of structure (as in the case of $\alpha$-cyperone[4]) (3) the study of reaction kinetics, (eg.[5]) (4) identification of compounds, (eg.[6]) (5) the study of hydrogen bonding (eg.[7]) and (6) as a sensitive indicator of steric interaction (eg.[8]) (vide infra). Many other applications have been described.

The nomenclature of absorption spectroscopy has been varied: the band at about 280 m$\mu$ in the spectrum of aromatic compounds has been called variously the "B"[9], "C"[10], and "secondary"[11] band. In the present thesis the nomenclature of Moser and Kohlenberg[12] is used in which bands are designated A,B,C and D in order of increasing wavelength from 200 m$\mu$. The present thesis concerns the B bands of the compounds discussed: this band is referred to by many authors as the K band. It is customary to specify the position of an absorption

band by the position of wavelength of maximal absorption, which in the case of B bands is usually 200-300 m$\mu$, with molecular extinction coefficient ($\varepsilon_{max}$) 5,000-30,000.

The B band of butadiene, and hence of all compounds with a pair of double bonds in conjugation, has been ascribed by Mulliken[1] to an N$\rightarrow$V transition, that is a transition in which a $\pi$ electron in a bonding orbital undergoes excitation to a $\pi$ antibonding orbital of higher dipole moment and energy. This does not result in fission of the molecule, since the atoms concerned are still united by a $\sigma$ bond.

## PART I

### The Nature of Spectral Effects

If the spectrum of a compound is compared with the spectrum of a derivative of that compound (e.g. acetophenone with o-methylacetophenone) there may be differences in $\lambda_{max}$ or $\varepsilon_{max}$ or both. For example, acetophenone in ethanol absorbs maximally at 240 m$\mu$, $\varepsilon_{max}$ 12,500 and o-methylacetophenone in ethanol at 242 m$\mu$, $\varepsilon_{max}$ 8,500.[13] The observed changes may be caused by steric, electrical (inductive, mesomeric or field), or mass effects, or by any combination of these.

### Steric Effects

Evidence has accumulated that steric effects are frequently of greater importance in determining electronic spectra than electrical effects. For instance, acetophenone and o-halogenoacetophenones absorb maximally at very similar

wavelengths, though with different intensities. In cyclohexane or ether acetophenone shows $\lambda_{max}$237-238 m$\mu$, $\varepsilon_{max}$12,500[10]; $\underline{o}$-fluoroacetophenone $\lambda_{max}$233 m$\mu$ $\varepsilon_{max}$9, 500[10]; $\underline{o}$-chloroacetophenone $\lambda_{max}$235 m$\mu$, $\varepsilon_{max}$5, 700[10]; and $\underline{o}$-bromoacetophenone $\lambda_{max}$234-236 m$\mu$, $\varepsilon_{max}$4,900[10]. Another example is provided by $\underline{o}$-nitroanisole in ethanol ($\lambda_{max}$249 m$\mu$, $\varepsilon_{max}$3,400)[14], $\underline{o}$-nitroacetophenone in ethanol ($\lambda_{max}$254 m$\mu$, $\varepsilon_{max}$6,000)[10], and nitrobenzene in ethanol ($\lambda_{max}$260 m$\mu$, $\varepsilon_{max}$8,000)[15]. In spite of the great differences in mesomeric and inductive effects of the methoxy-, acetyl-, and hydrogen radicals the absorption spectra differ by only comparatively small amounts. The figures therefore suggest that the effect of the substituent groups on the nitrobenzene spectrum is determined, at least to a large extent, by the steric effect of the group rather than its mesomeric or inductive effect. The theory of steric interaction does not, however, attribute all spectral effects to steric interaction: mesomeric effects are often of greater importance particularly when steric effects are impossible or very small.

## The Buttressing Effect

It has sometimes been found that, in the aromatic series, 2, 3-disubstitution gives more pronounced steric effects than 2-monosubstitution. This has been attributed to a "buttressing" effect of the 3-group on the 2-group[15]. If the hypothesis is correct that the 3-group makes the 2-group more

difficult to dislodge then the buttressing effect should be rather sensitive to the nature of the substituents: alternative theories would predict only slight differences between the effects of similar groups. Table I gives absorption data for a number of 2, 3- and 5, 6-tetrasubstituted paranitroanilines in which, as predicted, the magnitude of steric interaction decreases in the order dimethyl > cyclohexyl > cyclopentyl. (cf.[16, 17])* This order would be expected if the determining factor is the size of the substituent groups, but not if it is the electrical properties of the groups, since mesomeric and inductive effects differ little for the substituents examined. The rigidly held cyclohexyl group would be expected to interfere with the amino group less than two methyl groups, and the cyclopentyl group, in which the ortho-methylene group is bent away from the amino group, should interfere even less.

Evidence for the existence of the buttressing effect has also been provided by the rates of racemisation of biphenyls[18] where meta-substitution gives a slower rate of racemisation than para-substitution.

There is also evidence that a buttressing effect can be exerted through a hydrogen atom. For example, 3, 3'-dimethoxy-biphenyl absorbs with lower intensity than biphenyl[19] due to the meta methoxy group bending the ortho hydrogen atoms and so increasing their effective interference radii. Forbes and Mueller have tabulated a large number of examples of meta substituted

* See Ref. 155 for a different order.

compounds absorbing with lower intensity than the corresponding unsubstituted compounds[15] even though the wavelength of maximal absorption is practically unchanged.

Evidence of a different nature for the existence of the buttressing effect is provided by hydrogen bonding.[20] The compound 2, 5-dihydroxydiethylterephthalate is strongly hydrogen bonded, but 3, 6-dibromo-2, 5-dihydroxydiethyl terephthalate is not: this has been attributed to the bulky bromine atoms dislodging the hydroxyl groups from the plane of the benzene ring.

Additional evidence for the existence of a buttressing effect through hydrogen is provided by the observation that for meta-nitrobenzaldehyde in carbon tetrachloride the infrared carbonyl band occurs as a closely spaced doublet[14]. This has been attributed to the buttressing effect of the nitro group on the ortho hydrogen atom, causing the molecule to exist in s-cis and s-trans conformations.

## Conjugation and Steric Effects

The observations outlined above provide strong evidence for the existence and importance of steric effects, but underline an important point: that it is difficult to obtain molecules entirely free of steric hindrance.

Wepster[21] has pointed out that steric hindrance need not be interpreted only in the classical sense, the mere bulk of a substituent causing a molecule to assume a configuration different

from that preferred in the absence of hindrance. It is more probable that the effect of steric hindrance, so far as ultra-violet spectra are concerned, is to be attributed to its effect on the resonance energy of the molecule. Spectacular examples have been given by Cram and co-workers[22a] of the effect of twisting a benzene ring, and a very recent example[22b] shows that an olefinic linkage twisted at 90° to a benzene ring shows no evidence of conjugation with the ring.

## Classification of Steric Effects

Braude and co-workers[23] have divided steric effects in ultraviolet spectra into two types, I and II. The spectrum of a compound is compared with that of a similar but unhindered compound. The reference compound may be the unsubstituted compound, but sometimes a compound with the substituent in a different position is preferred, to allow for effects which are not steric in origin. In type I effects a change in intensity of maximal absorption is observed, but no change in wavelength of maximal absorption (changes of $\pm$ 5 m$\mu$ are not considered significant). In type II effects there is change in both wavelength of maximal absorption and intensity of absorption. A third type has been added: that in which the characteristic absorption of the chromophore is entirely absent, and the molecule absorbs as two distinct molecules. An example of this type of spectral effect is provided by bimesityl, which shows absorption characteristic of two molecules of mesitylene[24] with little evidence of biphenyl

absorption. This nomenclature should be distinguished from that proposed by Heilbronner and Gerdil[25]. Even among workers who agree on the importance of steric effects there has been little agreement on the underlying mechanism.

Type II effects may be attributed to changes in energy of both ground and excited states. A single bond between two double bonds is known to show some double bond character. For example, the single C-C bond in butadiene is 1.46 A long, compared with 1.54 A for a pure single C-C bond, and 1.33 A for a pure double C=C bond[26]. This percentage of double bond character, which has been estimated at 18% for butadiene[26] and acrolein[27] causes resistance to twisting about the conventional single bond, and may even give rise to the existence of distinct isomers, referred to as s-cis or cisoid, and s-trans or transoid.

In a molecule AB such as acetophenone, where A = $C_6H_5-$, and B = $-CO.CH_3$, resonance will cause the molecule to take up a conformation in which A and B are coplanar in both ground and excited states. In a hindered compound, such as 2,6-dimethylacetophenone, the coplanar conformation will not be possible. In the ground state strain can be reduced by twisting of the acetyl group about the single bond until it is no longer coplanar with the benzene ring: this will be accompanied by loss of resonance energy. Therefore the energy of the ground state will be raised relative to that of the unhindered compound. On electronic excitation the spatial configuration of the atoms will not alter ( Frank-Condon principle )

but the increased double bond character of the acetyl- to phenyl- bond will cause even greater resistance to twisting and hence even greater loss of resonance energy. Hence the energy of the excited state will be raised even more than that of the ground state (cf.[28]). Hence excitation will require more energy than in the case of the unhindered compound, and light of shorter wavelength will be absorbed. That is equivalent to saying that 2,6-dimethylacetophenone should show a type II effect relative to acetophenone. In ethanol, acetophenone shows $\lambda_{max}$ 240 m$\mu$, $\varepsilon_{max}$12,500 and 2,6-dimethylacetophenone $\lambda_{infl}$241 m$\mu$,$\varepsilon_{infl}$2,100.[29] The bathochromic wavelength displacement may be attributed to a compensating effect of the two methyl groups since relative to 2,4-dimethylacetophenone ($\lambda_{max}$ 251 m$\mu$, $\varepsilon_{max}$ 13,000 [29])2,6-dimethyl-acetophenone does show the expected hypsochromic wavelength displacement.

The mechanism described above readily explains hypsochromic wavelength displacements. Bathochromic effects caused by steric hindrance can be accounted for on the same mechanism by supposing that excitation leads to a decrease in the bond order of the bond linking the chromophore to the nucleus, giving rise to less loss of resonance in the excited state than ground state (Refs. 17,30,31). Hypsochromic wavelength displacements are usually observed in the benzaldehyde, acetophenone, biphenyl and NN-dimethylaniline series, but not, apparently, in the ketoazulene series.[25] The above remarks apply only to wavelength displacements which can be attributed to steric hindrance, and the example

quoted of 2,6-dimethylacetophenone shows the difficulty of distinguishing steric effects from others.

## The Nature of Type I Effects.

The above mechanism for type II effects has been generally accepted, but there has been less agreement on the mechanism underlying type I steric effects.

Braude et al.[32] suggested that in compounds exhibiting a type I steric effect the excited state is planar or nearly so. The ground state is non-planar (see figure 2). According to the Franck-Condon principle the position of the atoms will not alter appreciably during electronic transition. Hence transitions will not take place from most ground states, since very large amounts of energy would have to be absorbed to reach the excited state. With each state will be associated a number of sub-levels of energy shown in figure 2 as horizontal lines. Braude and his collaborators[32,33] suggested that in the ground state a few molecules would exist in higher sub-levels from which transitions to the electronically excited state would be possible. Since only a few molecules could exist in such states the transition would take place with low intensity. In figure 2, possible transitions are represented by full lines and forbidden transitions by broken lines. This will be referred to as Braude's type I mechanism.

Forbes and Mueller[8] have modified this mechanism by supposing that compounds showing a type I effect exist in both s-cis and s-trans conformations. One of these (occasionally both) will be sterically hindered, and the ground state potential energy

curve will be displaced to a position in which its minimum is far removed from 0°. Some transitions may take place from this conformer by the mechanism suggested by Braude et al. The other conformer will be unhindered or less hindered, and the minima of its potential energy curves in ground and excited states will be close to 180°. Consequently transitions from the latter conformer will take place with high intensity. Figure 3 shows how energy varies with interplanar angle. This theory has been applied to explain the drop in intensity between p-methylacetophenone and o-methylacetophenone, and the absence of any comparable decrease in intensity between o-tolualdehyde and p-tolualdehyde[8]. Figure 4 shows that in o-methylacetophenone steric hindrance occurs between the acetyl methyl group and the ortho methyl group, in one conformational isomer but not the other. Very little, if any hindrance is predicted by the scale drawing of o-tolualdehyde.(Fig.5)

Forbes[34] has discussed steric effects in terms of a (hypothetical) planar molecule A-B-C. While this cannot be attained in practice a suitable approximation may be achieved by using AB, or ABC where the relative positions of A,B, and C are different. For example, o-methylacetophenone may be compared with acetophenone or p-methylacetophenone. When B and C are coplanar but the chromophore A is not, a type I effect will be observed since the energy of the ground state will be only slightly different from the ground state energy of the unhindered compound. Thus a type I effect is associated with weak steric interaction. When no two of A, B and C are coplanar the energies of both ground and excited states will be raised relative to the

*The diagrams of Figures 4 and 5 are drawn using covalent radii, even though these are known to be smaller than interference radii: van der Waals radii are larger than interference radii. (Ref.33)

unhindered compound, and a type II effect will be shown. (See Figure 6). Thus a type II steric effect is associated with large steric hindrance.[34]

The mechanisms described above have been disputed in special cases[35], but more recently the fundamental difference between type I and type II effects has been called in question by Heilbronner and Gerdil.[25] These authors have observed that certain hindered l-acetyl derivatives of azulene showed a bathochromic wavelength displacement, whereas they interpret the Braude mechanism to predict a hypsochromic wavelength displacement. They discuss steric effects in terms of a molecule X-Y. The change in bond order ($\Delta p_{xy}$) for the X-Y bond on going from ground state to excited state is calculated by molecular orbital theory. Assuming no steric hindrance of resonance, the change in wavelength between XY and a reference compound will be given by $\Delta\lambda = k(\Delta p_{xy})$ where k is a constant. Steric hindrance will raise the energy of both ground and excited states, but the excited state usually more than the ground state, by a factor $M_\Theta$ related to the angle of twist $\Theta$. Therefore, to a first approximation $\Delta\lambda = K\Delta p_{xy} \cdot M_\Theta$. Thus the sign of the wavelength displacement will depend on $\Delta p_{xy}$. Heilbronner and Gerdil give figures showing that for acetophenones, bond order difference in going from ground state to excited state is positive, for $\alpha,\beta$-unsaturated ketones $\Delta p$ is approximately equal to zero, and for azulenic ketones the bond order decreases on transition from ground to excited state. The above figures are related by

Heilbronner and Gerdil to the frequent occurrence of hypsochromic
wavelength displacements in acetophenones, the non-occurrence of
wavelength displacements (other than 'additive' displacements)
in $\alpha,\beta$-unsaturated ketones, and bathochromic wavelength displace-
ments in azulenic ketones. Type I effects are considered to arise
whenever ground and excited states are fortuitously raised by
equal amounts.

Forbes[36] has pointed out that if the interpretation
given above is correct a type I effect should be uncommon:
examination of many sets of examples from aliphatic, aromatic,
and heterocyclic compounds shows the effect to occur more
frequently than one could expect on the basis of chance.[34]

It appears to the present author that the above
mechanisms are by no means incompatible. For a given change of
bond order, $\Delta\lambda$ is proportional to $M_\theta$. When $\theta$ is small, $\Delta\lambda$ will
be small, that is, a type I effect will be shown, but it is
precisely in these circumstances that Braude's mechanism, as
modified by Forbes and Mueller, also predicts a type I effect.
Heilbronner and Gerdil[25] compute interplanar angles by using van
der Waals radii, but it is known that the latter are greater
than the effective interference radii of atoms in solution. The
mechanism of Forbes and Mueller[8] suggests that usually one conformer
exists in a planar or near planar conformation and therefore $\theta$
is small, leading to a small value of $\Delta\lambda$. In type II effects $\Delta p$
and $\theta$ are large. Calculations[25] show that for ketoazulenes the

X-Y bond has less double bond character in the excited state than in the ground state. Therefore there will be less hindrance of resonance in the excited state than in the ground state, and the energy level of the excited state will be lowered relative to the ground state. This follows from either mechanism. The effect is shown in Figure 6(b).

Heilbronner and Gerdil consider that in compounds showing type I effect both ground and excited states are raised by equal amounts, Forbes considers that both are unchanged. This apparent disagreement may be reconciled by considering that Forbes refers changes of energy of a hindered molecule to the _same_ molecule in an unhindered state, whereas Heilbronner and Gerdil appear to use energies as would be determined, for example, by thermochemical methods. Thus Forbes would consider all unhindered compounds of similar constitution to have similar ground state energies.

Wepster[21] has also criticised Braude's mechanism on the ground that in certain polynuclear compounds where a nitrogen atom is in three rings it cannot assume a planar conformation. However, calculation[21] shows that the difference in bond order between ground and excited states of NN-dimethylaniline is only 0.09. Hence it may be assumed that potential energy curves are very similar in both ground and excited states. One would expect similar changes in ground and excited states of the compounds discussed by Wepster and hence similar excitation energies.

Many attempts have been made to calculate wavelengths of maximal absorption on the basis of wave-mechanical calculations

of ground and excited states. Murrell and Longuet-Higgins[37],[38] have discussed spectra in terms of two possible excited states. In one, the $\pi$ electrons of the ground state conjugated system are spread over the whole molecule in the excited state. This is called an electron-transfer (E.T.) state. Another possible excited state is that in which the $\pi$ electrons originally associated with each double bond remain associated with that bond in the excited state. This is called locally-excited (L.E.) state. Murrell[37] has shown that in an E.T. transition steric hindrance leads to decreased intensity but no wavelength change, or possibly a small bathochromic wavelength displacement: an L.E. transition gives rise to a hypsochromic wavelength displacement.

Erskine and Waight[39] have recently criticised the mechanism of Braude and his collaborators on the ground that decreasing temperature should lead to a lower proportion of molecules in an excited level and therefore either a decreased intensity or hypsochromic wavelength displacement. Investigation of the spectra of a number of $\alpha,\beta$-unsaturated ketones at room temperature and at -198° showed no significant change in either intensity or wavelength of maximal absorption.[39] From these observations Erskine and Waight have concluded that Braude's type I mechanism is improbable, and have ascribed the B band of $\alpha,\beta$-unsaturated ketones to transition to an E.T. state.

Against this view may be urged the point that diagrams relating energy to interplanar angle contain a very large margin of error in the ground state, and are almost completely hypo-thetical for the excited state. It is therefore not possible

to draw quantitative conclusions with any degree of certainty
from the potential energy diagrams published by Braude et al.[33,32]
Figure 7 shows that it is possible to draw potential energy
diagrams in such a way that lowering temperature may lead either
to a lower population of excited states and therefore a reduction
in intensity of absorption, or to an increased population of
another conformational isomer and hence to an increase of intensity.
The subject of potential energy curves is referred to again below.

## Further Remarks on Steric Effects

If the hypothesis of steric interaction is correct, a
gradual increase in the size of the interfering group should give
rise to progressively more marked steric effects. This would be
expected to make itself evident by, initially, a progressive
decrease in absorption intensity with little change in wavelength
of maximal absorption. This has been observed for acetophenone,
propiophenone and pivalophenone[33,40] and also for 2-methylnitro-
benzene, ($\epsilon_{max}$ 6,070), 2-ethylnitrobenzene ($\epsilon_{max}$ 5,300), 2-iso-
propylnitrobenzene ($\epsilon_{max}$ 4,150) and 2-t-butylnitrobenzene
($\epsilon_{max}$ 1,540)[41] In the latter case the largest decrease is observed
between the isopropyl and tert-butyl compounds: this is attributed
to the fact that rotation about the Ar-N bond can produce a
conformation in which the nitro- group fits between the methyl
groups of the isopropyl group[41]

Yet another good example of a series of compounds
showing marked type I effect is the NN-dimethylaniline series

(See Table II). Increasing the size of the <u>ortho</u> substituent gives a decreased extinction coefficient with only a slight change in wavelength. Again there is a great decrease in intensity between the <u>isopropyl</u> and <u>tert</u>-butyl compounds. In the NN-dimethylaniline series resonance favours the formation of structures with the two methyl groups symmetrically placed with respect to a plane through the Ar-N bond and perpendicular to the plane of the benzene ring. Hence the strain cannot be reduced significantly by taking up a new position of rotation.[21,41]

Further examples of type II effects are provided by the biphenyl series (see Table III). Increased steric hindrance gives rise to a more marked type II effect, and in the highly substituted compounds the characteristic biphenyl absorption is destroyed entirely and the compound behaves spectroscopically as a mixture of unconjugated compounds. For example, bimesityl absorbs as two molecules of mesitylene. This may be called an example of a type III steric effect.

## Rotational Isomerism

Braude has shown by comparison of the spectra of benzene, biphenyl, diphenylmethane, and 1,2-diphenylethane that slight conjugation can be transmitted through one, or to a very slight extent through two, carbon atoms.[42] Nevertheless, conjugation is appreciable only for adjacent unsaturated groups. Figures given above show that this can lead to considerable double bond character for the central bond formally written as a single bond. This in turn leads to the possibility of existence of <u>s-cis</u> and <u>s-trans</u> isomers with only a low barrier

opposing conversion of one to the other. Even in ethane the
height of the energy barrier to rotation about the single bond
is estimated at 2.9 kcals per mole[43] and in ethylene the barrier
to rotation about the double bond is approximately 25 kcals per
mole[44] The energy barrier hindering rotation about the central
C-C bond has been estimated at 5 kcals per mole in both butadiene
and acrolein, and the energy difference between the rotational
isomers has been estimated to be about 2.5 kcals per mole[44]
Because of the low energy barrier it will often not be possible
to isolate the separate isomers, but they will nevertheless
exist long enough compared with the time for electronic excitation
($10^{-15}$ secs.) to be considered distinct entities spectroscopic-
ally. In this connection the rates of racemisation of optically
active biphenyls are of interest.[18]

Jones, Forbes and Mueller[46] found the ratio of the
rotational isomers of o-bromoacetophenone to be 2.8:1 at room
temperature (not stated, assumed 295°K), 5.1:1 at 385°K, and
3.2:1 after cooling to room temperature again. These figures
assume the apparent molecular extinction coefficients of s-cis
and s-trans isomer to be equal.

The conversion of an s-cis to an s-trans isomer may
be regarded as a unimolecular reaction A ⇌ B, the equilibrium
constant being the ratio of one form to the other. Denoting
the equilibrium constant at T° by $K_t$ and at T'° by $K_{t'}$ and the
free energy change in the reaction by $\Delta F$,

$$\log_e K = \frac{-\Delta F}{RT} + \text{constant}$$

whence $\log_e K_t - \log_e K_{t'} = \frac{-\Delta F}{R}\left(\frac{1}{T} + \frac{1}{T'}\right)$

In the case of Jones, Forbes and Mueller's figures this gives, using K = 2.8 and 5.1, $\Delta F$ = 1.5 kcals per mole. Using K = 5.1 and 3.2, $\Delta F$ = 1.2 kcals per mole.

The figures of the same authors for o-nitroacetophenone (K = 2.8 and 3.0 at room temperature, 7.9 at 106°C) leads to values of 2.75 and 2.6 kcals per mole for $\Delta F$. In each case the value of $\Delta F$ is in reasonable agreement with the values of $\Delta E$ determined (for different compounds) by different methods. It should be noted that the above values of free energy difference are not incompatible with moderately large differences of internal energy ($\Delta E$), since $\Delta F = \Delta E - T\Delta S$, where $\Delta S$ is the change in entropy. Figures for the entropy difference between rotational isomers are not available, but for such closely related substances as rhombic and monoclinic sulphur the entropy difference is 0.2 units, making it probable that the entropy difference between rotational isomers is not vanishingly small, perhaps owing to different vibrational possibilities.

Additional support for the existence of rotational isomers has been provided by micro-wave spectra[44] and ultrasonic relaxation analysis.[47]

## The Nature of Sub-Levels of Energy in Hindered Molecules

It is known that a double bond has considerable resistance to twisting, and consequently it has been the practice to draw potential energy curves for molecules capable of rotation about a formal single bond, as parabolas. Some

investigators have preferred, by analogy with the well-known
potential energy curve of a diatomic molecule, to draw Morse
curves. It seems evident that resistance to rotation will be
very great in the direction requiring interfering groups to
occupy the same position in space, but less great in the
opposite direction. Therefore it seems preferable to the present
author to draw potential energy curves as shown in Figure 8.

Braude and Timmons[48] have pointed out that repulsion
energy falls off with increasing interplanar angle more rapidly
than resonance energy (see Figure 9) and consequently resonance
energy will still be appreciable at quite large interplanar
angles: indeed the authors cited calculate that resonance energy
does not become negligible until an interplanar angle of 67° is
attained. Wepster[21] has pointed out that a combination of van
der Waals repulsion energy curves and resonance energy curves
may give a curve for total energy related to interplanar angle
very different from the usual Morse curve: there may be a very
flat minimum or even a double minimum. (See Figure 10). It
would seem then that views based on a false analogy with a
diatomic molecule must be treated with reserve. The sub-levels
are probably not pure vibrational nor pure torsional sub-levels,
but combinations of both. It is of interest to note that most
published diagrams of transitions show transition taking place
from the ends of the lowest level: analogy with a diatomic
molecule would predict that the brightest transition should be
from the centre of the lowest level.

Braude[32] estimated the spacing of the sub-levels to be
less than 3 kcals per mole, and gave a probable value of 1 kcal

per mole. The present author believes the spacing to be much smaller. The vapour phase spectrum of benzene[2] shows 110 lines between 283 and 262 mμ, and it is known that in the ground electronic state of benzene there are 20 fundamental frequencies[50] The vapour phase spectrum of benzene as given by Gillam and Stern[51] consists of a large number of lines, approximately 100 between 1200 fresnels and 1300 fresnels. 1200 fresnels corresponds to 250 mμ, and 1300 fresnels to 231 mμ. Assuming the spacing to be one fresnel, the energy difference between each line is given by $E = h\nu$, whence $E = 0.094$ kcals per mole. It is therefore reasonable to assume that to a first approximation the energy sub-levels in benzene are 0.1 kcals per mole apart. In biphenyl the energy levels of each phenyl nucleus must be about as closely spaced, and in addition there will exist sub-levels of torsional energy. It therefore seems probable that sub-levels are separated by very small amounts of energy.

It is of interest to compute the fraction of molecules occupying excited states. Assuming energy differences of 0.1 kcal per mole, by the Boltzman distribution law, if $n_i$ is the number of molecules in the ith excited state, and n the number in the ground state, $n_i = ne^{-\frac{E}{RT}}$, whence the number in the first excited state at 300° is 0.19, and the fraction in the second excited state is 0.036. There would thus seem to be no reason why a decreased proportion of molecules in excited states should give rise to any significant change in wavelength of maximal absorption, and thus no serious objection to Braude's mechanism as modified by Forbes and Mueller.

## Interference Radii

It is known that steric interaction is shown when scale diagrams using covalent radii would predict none, and that interaction does not occur when diagrams using van der Waals radii would predict it.[23] It seems then that the effective interference radius of an atom or radical in solution lies between its covalent and van der Waals radii. Investigations of interference radii have been made using ultra-violet spectra[15,5] and rates of racemisation of biphenyls.[53,54] The latter method can give only minimum values of interference radii, since considerable energy difference between stereoisomers is necessary for resolution to be possible. The former method gives a sensitive indication of steric effects but is open to the objection that it may not distinguish steric effects from others.

Assuming biphenyl to be just hindered, the _ortho_ hydrogen atoms must just touch, and hence must have an effective interference radius of 0.90A.[54] However, there is evidence that biphenyl is non-planar in the vapour phase[55] and it has been argued that it is non-planar in solution.[52] If the latter suggestion is correct, the interference radius of a hydrogen atom in solution should be greater than 0.90A, and a value of 0.95 $\pm$ 0.1 A has been suggested.[52] By assuming that acetophenone is just hindered with respect to benzaldehyde, Forbes and Mueller[52] have suggested a value of 1.7 A as the interference radius of a methyl group, and 1.0 $\pm$ 0.15 A as the interference radius of an oxygen atom in C=O.

Attention should be drawn to an empirical rule proposed by Adams (cf.[56]) that in substituted biphenyls of the type 2,2'a-6,6'-b-biphenyl, if the sum of the covalent bond lengths C-a and C-b is 2.90 A or greater, it will be possible to resolve the biphenyl.

## On The Relation Between Ultra-Violet And Infra-Red Spectra

Ultra-violet spectra are produced by transitions between ground state and electronic excited state. Steric effects, for reasons set out above, will usually be more marked in excited state than ground state. Therefore ultra-violet spectra are a sensitive indicator of steric effects.[8,13] In contrast, assignments of the transitions responsible for each band are often not made or not agreed, and even the influence of minor changes in environment can be given widely varying interpretations. As an example, 2,4,6-trimethylstyrene is considered by Forbes[36] to show no wavelength displacement relative to styrene and therefore no significant difference in energy, whereas Heilbronner[57] considers the compound to show a hypsochromic wavelength displacement of 18 mµ relative to what would be expected for a trimethyl substituted styrene, and hence a considerable change in energy.

Infra-red spectra are associated with much smaller changes of energy and are produced by changes from low-lying levels of the ground state to somewhat higher levels of the ground state. Therefore steric effects are of lesser importance in infra-red spectra.[13]

The bands found most useful for the compounds considered in this thesis are the carbonyl stretching band (referred to subsequently as the carbonyl band) and the olefinic stretching frequency (referred to subsequently as the olefinic frequency).

In saturated ketones the carbonyl frequency is 1725 cm.$^{-1}$ to 1706 cm.$^{-1}$ (in solution) but conjugation of this group with an olefinic bond lowers the frequency to between 1685 cm.$^{-1}$ and 1620 cm.$^{-1}$ (Ref.[58]). Barrow[45] has shown that the apparent molecular extinction coefficient is related to the resonance energy of the system. The olefinic frequency occurs at 1680 cm$^{-1}$ to 1620 cm.$^{-1}$ in a mono-olefine, but in a conjugated diene at about 1650 cm.$^{-1}$ and splits into two bands.[58]

If a type I effect is caused by the displacement of one group only from the plane of the molecule[34] its frequency should be little changed from that of the unhindered molecule. In illustration, the carbonyl frequencies in acetophenone, o-methylacetophenone, o-fluoroacetophenone, benzaldehyde, and o-tolualdehyde vary little (from 1690 cm.$^{-1}$ to 1709 cm.$^{-1}$) though the apparent intensities vary greatly.[13] In contrast, the carbonyl frequency in o-nitroacetophenone is 21 cm.$^{-1}$ different from that in acetophenone at higher frequencies.[13] The ultra-violet absorption spectrum is typical of the nitrobenzene moiety, in excellent agreement with the suggestion that the bulky nitro-group dislodges the acetyl group from the plane of the benzene ring with consequent loss of resonance energy.

One useful feature of infra-red spectra is the presence of fine structure which can be resolved more easily than in ultra-

violet spectra. If a compound exists as two conformational
isomers the resonance energy of the s-trans form should be greater
than that of the s-cis form, since linearity facilitates
delocalisation of electrons. Consequently the frequency of the
carbonyl groups and their apparent extinction coefficients
should differ. Similarly, in one conformer, field effects such
as attraction by a positive charged group of the negative end of
the carbonyl group should cause an alteration of the carbonyl
frequency. Therefore the carbonyl band should occur as a closely
spaced doublet. This has been observed[14] and examples will be
referred to below.

### The Role of Solvent

The effect of solvent on spectra has been found to
depend on the polarity of the solute. Hydrocarbons show only
slight if any displacement of the wavelength of maximal absorption
with changed polarity of solvent (see below), whereas the wave-
length of maximal absorption of a polar solute is dependent on
the polarity of the solvent. For $\alpha,\beta$-unsaturated carbonyl
compounds empirical relations have been drawn up. (See Table IV).
In general, a solute which becomes markedly more polar in the
excited state absorbs at longer wavelengths in solvents of
higher dielectric constant than in solvents of low dielectric
constant[27]; solutes whose polarity in the excited state is little
different from that in the ground state show little change of $\lambda_{max}$
with changing dielectric constant. It would be expected that
compounds in which the excited state has less polar character
than the ground state should absorb at shorter wavelengths in

solvents of high dielectric constant, and this has been observed for certain merocyanine dyes[27]

Jacobs and Platt have concluded that, at least in the case of piperylene[59], integrated absorption intensities do not differ in the vapour phase and solution. The same is true of isoprene. Mathematical correlations between wavelength displacements and solvent properties have been attempted[60,61,62]

TABLE I

STERIC HINDRANCE IN DERIVATIVES OF PARANITROANILINE
(After Arnold and Craig)[148]

| Compound | $\lambda_{max}(m\mu)$ | $\varepsilon_{max} \times 10^{-3}$ |
|---|---|---|
|  | 395 | 1.57 |
|  | 393 | 1.97 |
|  | 397 | 2.24 |
|  | 385 | 7.3 |
|  | 372 | 12.8 |

<u>TABLE II</u>

ULTRA-VIOLET ABSORPTION SPECTRA OF NN-DIMETHYLANILINES

| Substituent | Solvent | $\lambda_{max}(m\mu)$ | $\varepsilon_{max}$ | Reference |
|---|---|---|---|---|
| None | <u>n</u>-heptane | 250 | 13,750 | a |
| <u>o</u>-Methyl | " | 247.5 | 6,300 | a |
| <u>oo</u>'-Dimethyl | " | 259 | 2,200 | a |
| <u>p</u>-Methyl | " | 254 | 15,100 | a |
| <u>o</u>-Fluoro | " | 250 | 11,600 | a |
| <u>o</u>-Chloro | " | 256 | 7,600 | a |
| <u>o</u>-Bromo | " | 254 | 5,900 | a |
| 2,4,6-Trimethyl | <u>iso</u>octane | 257 | 2,500 | b |
| 2-<u>t</u>-Butyl | " | 250* | 630 | b |

\* Inflection

a) Refs.[150,151]   Wavelengths recalculated in $m\mu$
                    by the present author.
b) Ref. 152
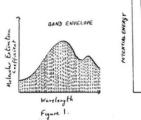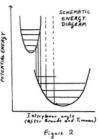
TABLE III

ULTRA-VIOLET ABSORPTION SPECTRA OF SUBSTITUTED BIPHENYLS

| Substituent | Solvent | $\lambda_{max}(m\mu)$ | $\epsilon_{max}$ | Ref. |
|---|---|---|---|---|
| None | Ethanol | 249 | 17,000 | a |
| 2-Methyl | " | 235 | 10,500 | a |
| 2-Ethyl | " | 233 | 10,500 | a |
| 2-n-Propyl | " | 233 | 10,000 | a |
| 2-Isopropyl | " | 233 | 11,000 | a |
| 2-n-Butyl | " | 233 | 10,500 | a |
| 2,2'-Dimethyl | " | 227 | 6,800 | b |
| 3,3'-Dimethyl | " | 255 | 16,500 | c |
| 4,4'-Dimethyl | " | 260 | 20,000 | c |
| 2,2'-Dihydroxy | " | 242 | 10,000 | c |
| 3,3'-Dihydroxy | " | 255 | 12,000 | c |
| 4,4'-Dihydroxy | " | 265 | 22,400 | c |
| 2,2'-Dimethoxy | Hexane | 230 | – | c |
| 3,3'-Dimethoxy | " | 250 | 12,000 | c |
| 4,4'-Dimethoxy | " | 263 | 21,700 | c |
| 2,6-Dimethyl | Light petroleum | 231* | 5,600 | d |
| 2,6,2'-Trimethyl | " | 230* | 4,000 | d |
| 2,6,2',6'-Tetramethyl | " | none | – | d |

* Inflection
a) Reference 19
b) Reference 153
c) Reference 154
d) Reference 120

Figure 1.



SCHEMATIC ENERGY DIAGRAM

Interplanar angle
(After Braude and Timmons)

Figure 2.



Figure 3
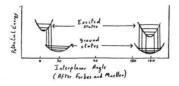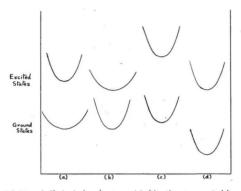
*o*-methylacetophenone

Figure 4



*o*-toluuldehyde

Figure 5

Excited
States

Ground
States

(a)   (b)   (c)   (d)
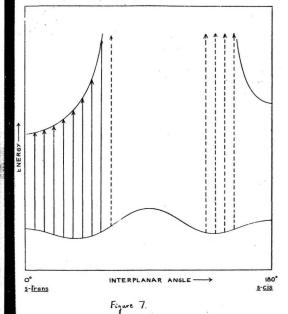
(a) More double bond character in excited state than in ground state
(b) Less double bond character in excited state than in ground state
(c) Energy of both states raised, excited state more than ground state
(d) Energy of both states lowered, ground state more than excited state

Figure 6

ENERGY

INTERPLANAR ANGLE ⟶

0°
s-trans

180°
s-cis

Figure 7.

SCHEMATIC ENERGY DIAGRAM

Energy

Interplanar angle

0°   90°   180°

Figure 8

Figure 9.
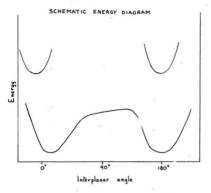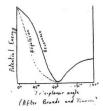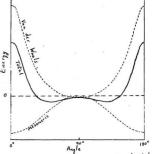


Dependence of total energy on van der Waals
& mesomeric energy (after Wepster)

Figure 10

PART II

## α,β-Unsaturated Carbonyl Compounds
## Empirical and Theoretical Considerations.

α,β-Unsaturated carbonyl compounds exhibit intense
absorption in the region 200-250 mμ and some[63] were amongst the
first compounds whose absorption spectra were determined.  Early
work showed that absorption occurred at longer wavelength and
with greater intensity than in the corresponding unconjugated
isomers and that further conjugation to give a dienone or trienone
gave absorption at even longer wavelengths.

In 1941 R.B. Woodward[4] examined ultra-violet absorption
data for a large number of compounds containing an olefinic
bond conjugated with a carbonyl group.  These had been determined
by many investigators in several solvents, but could be corrected
to one solvent (ethanol) by means of the empirical table of
solvent corrections given in Table IV.  These corrections, and
the unreliability of data obtained by some early methods, gave
rise to an element of uncertainty in the figures used.  Neverthe-
less Woodward was able to conclude that each alkyl group added
to the basic methylvinyl ketone skeleton gave a bathochromic
wavelength displacement.  While the value varied from compound
to compound the average value was 10 mμ per alkyl group, this
value being rather insensitive to the nature of the alkyl group.
Woodward therefore suggested[4] as an empirical generalisation,
that a monosubstituted α,β-unsaturated ketone absorbs maximally
at $225 \pm 5$ mμ, a disubstituted α,β-unsaturated ketone at $239 \pm 5$
mμ, and a trisubstituted α,β-unsaturated ketone at $254 \pm 5$ mμ.

A later amendment[64] showed that each exocyclic double bond gives a further bathochromic displacement of 5 m$\mu$.

The value of the rules was shown immediately by their application to show that $\alpha$-cyperone must be a trisubstituted compound, not disubstituted as previously formulated: this conclusion was supported by chemical evidence. The rules were again used[65] to show that Heilbron's formula for 3-acetoxy-$\Delta^5$ (6)-norcholestene-7-carboxylic acid must be incorrect, since the compound did not show the absorption characteristic of an $\alpha,\beta$-unsaturated ketone. This conclusion was again in accordance with strictly chemical evidence.

Later, Gillam and Evans[66] carried out a more comprehensive investigation on the spectra of $\alpha,\beta$-unsaturated compounds including some simple non-cyclic compounds not available to Woodward. They found Woodward's rules to be well substantiated, even in the case of the simplest trisubstituted compound, 3,4-dimethyl-pent-3-en-2-one. They also found that although the displacement per alkyl group varied from 5 m$\mu$ to 19 m$\mu$ the displacement was greater for a $\beta$ group than an $\alpha$ group. Fieser[67] has quoted values of, on average, 10 m$\mu$ for an alkyl group in the $\alpha$ position, and 12 m$\mu$ for an alkyl group in the $\beta$ position. In a conjugated dienone each alkyl group in the $\gamma$ or $\delta$ position gives a displacement of 18 m$\mu$.[67]

Gillam and Evans extended[68] their studies to $\alpha,\beta$-unsaturated aldehydes, and found a similar rule, though with different

figures, to be obeyed. They proposed that a monosubstituted
α,β-unsaturated aldehyde absorbs maximally at $220 \pm 5$ mμ, a
disubstituted compound at $230 \pm 5$ mμ, and a trisubstituted
compound at $242 \pm$ mμ. Both Gillam and Evans, and Woodward found
that the presence of a six-membered ring had little effect on
spectra, other than that attributable to its effect as two alkyl
substituents, but differences were shown when the olefinic
linkage occurred in a five-membered ring. For example, cyclopenten-
3-one in ethanol absorbs maximally at 218 mμ, $\varepsilon_{max}$9,500, whereas
cyclohexen-3-one under the same conditions has $\lambda_{max}$ 224.5 mμ,
$\varepsilon_{max}$10,300.[69] This difference is usually attributed to strain,
since the double bond formed in the excited state will be more
strained when in a five-membered ring than when in a six-membered
ring. Schubert and Sweeney have suggested[69] that if, in a cyclic
α,β-unsaturated ketone, excitation leads to a displacement of
electronic charge towards the site of strain, a hypsochromic
wavelength displacement will be observed: displacement of
electronic charge away from the site of the strain will give rise
to a bathochromic wavelength displacement. This is strikingly
confirmed by the spectra of some 1-acetylcycloalkenes.[69] 1-
Acetylcyclopentene absorbs with $\lambda_{max}$239 mμ, $\varepsilon_{max}$13,000, 1-acetyl-
cyclohexene with $\lambda_{max}$232-3 mμ, $\varepsilon_{max}$13,000, 1-acetylcycloheptene
with $\lambda_{max}$236 mμ $\varepsilon_{max}$10,000. In this series there is a bathochromic
displacement in passing from the six- to the five-membered ring,
in contrast to the hypsochromic displacement observed when the
carbonyl group is exocyclic to the ring. (See above). In 1-
acetylcyclopentene there will be a certain amount of ring strain

which will be partially relieved on excitation to the less highly
strained cyclopentylidene state. Hence the energy of the ground
state is raised relative to that of the excited state. In 1-
acetylcyclohexene there is little strain difference between the
ground cyclohexenyl state and the excited cyclohexylidene state
so the compound absorbs, as expected, at shorter wavelengths than
the corresponding cyclopentenyl compound, and in fact at much
the same wavelength as the acyclic compound 3-methylpent-3-$\underset{\text{en}}{\cancel{yl}}$-2-
one (see Table VII). A similar example from the same authors is
equally surprising: 2-cyclopentylidenecyclopentanone absorbs
with $\lambda_{max}$259 mμ, and 2-_iso_propylidenecyclopentanone at 252 mμ.
Again the effect of relief of strain is well marked. It is,
however, possible that steric effects also play a part in
determining the wavelength of maximal absorption for the compounds
considered.

The electronic transitions involved in the absorption
spectra of α,β-unsaturated carbonyl compounds have been discussed
by Walsh[70]. An isolated double bond shows absorption below the
wavelength range of most spectrophotometers, that is below 200 mμ,
with $\varepsilon_{max}$ about 10,000. A saturated ketone shows a high intensity
band below 200 mμ and an additional weak band at 270-290 mμ,
$\varepsilon_{max}$about 20. In saturated aldehydes the latter band occurs at
somewhat longer wavelengths. In an α,β-unsaturated carbonyl
compound both these bands are displaced. A B band appears at
200-250 mμ, $\varepsilon_{max}$ approx. 10,000: this is often called the K band.[71]
A weak band also appears at about 320 mμ, with $\varepsilon_{max}$about 50: this

is called the R band.[71] The position of each band is dependent
on the solvent, and as solvent polarity increases the two bands
move together. The K band is thought to be due to the conjugated
system (hence K for konjugiert) and the R band is thought to arise
from transitions involving the carbonyl group (hence R for radikal).
Support for this assignment is provided by the observation that
the R band disappears when the radical is no longer present. For
example, mesityl oxide in concentrated sulphuric acid exhibits no
R band since the C=O group becomes C=OH+.[51]

McMurry and Mulliken have shown that the K (or B) band
arises from an N--> V transition, while the R band arises from a
transition involving the lone pair non-bonding electrons on the
oxygen atom.[72] One of these electrons undergoes transition to a
$\pi$ antibonding orbital (N--> A transition): the transition is
forbidden, hence the absorption band is weak. A transition is also
possible (N --> B) in which one of the lone pair electrons on the
oxygen atom is promoted to a $\sigma$ antibonding orbital, but the
wavelength of the transition is shorter than that of the N--> V
transition, and the position of the band is independent of solvent.

While the above empirical rules for the position of
wavelength of maximal absorption in conjugated ethylenic aldehydes
and ketones have been well substantiated, less attention has been
given to intensities of absorption. No doubt this has been due,
in part, to the unstable nature of the compounds and the difficulty
of preparing compounds uncontaminated by the unconjugated isomer.
(Cf.[23,73])

Rotational Isomerism

Most theories of the spectra of α,β-unsaturated ketones have been discussed with reference to 1-acetylcyclohexene ($\lambda_{max}$232 mμ, $\varepsilon_{max}$13,000) and 1-acetyl-2-methylcyclohexene ($\lambda_{max}$249 mμ, $\varepsilon_{max}$6,890) in ethanol in both cases.[74] Even for these compounds very variable values of $\varepsilon_{max}$ have been reported.

Braude and Timmons[48] have suggested that the s-trans form of an α,β-unsaturated ketone will be more stabilised by resonance than the s-cis form, since linearity facilitates electron delocalisation. They assumed that small steric interactions would cause displacements from the planar position, though the conformation would remain distorted s-trans. This follows from the fact that resonance energy falls off with increasing inter-planar angle less rapidly than repulsion energy. (See Fig.9) Only when steric interaction became very large would an s-cis conformation be more favourable energetically than an s-trans conformation. In support of their distorted s-trans assignment, Braude and Timmons quoted the lower carbonyl frequency of 1-acetyl-2-methylcyclohexene as compared with 1-acetylcyclohexene. The ethylenic stretching frequency in 1-acetyl-2-methylcyclohexene is 60 cm$^{-1}$ less than for an isolated double bond, but close to that of compounds with a fixed s-trans configuration. The decreased absorption intensity shown by 1-acetyl-2-methylcyclohexene was accounted for by the Braude mechanism described in Part I.

Braude and Sondheimer[33] have suggested that ultra-violet absorption spectra may be used to calculate interplanar angles. Let the molecular extinction coefficient of an unhindered compound

be $\varepsilon_o$ and its interplanar angle be $\Theta_1$. Let the corresponding
values for a similar but hindered compound be $\varepsilon$ and $\Theta_2$. Then
there should be a relation between $\varepsilon/\varepsilon_o$ and $\Theta_2 - \Theta_1$. Since $\varepsilon/\varepsilon_o$
$= 1$ when $\Theta_2 - \Theta_1 = 0°$ and $180°$, and $\varepsilon/\varepsilon_o = 0$ when $\Theta_2 - \Theta_1 = 90°$,
the simplest relation is $\varepsilon/\varepsilon_o = \cos^2 (\Theta - \Theta_1)$.

Assuming $\Theta_1 = 0°$ in the unhindered compound this
simplifies to $\varepsilon/\varepsilon_o = \cos^2\Theta_2$. Some support for this expression
is provided by Dewar's[75,76,17] calculation that resonance energy is
proportional to $\cos^2$(angle of twist). Using the formula derived
above Braude, Sondheimer and collaborators calculated interplanar
angles for several compounds and found values in rough agreement
with those deduced from electron diffraction and dipole moment data.
In the case of 1-acetyl-2-methylcyclohexene their value[48] of the
interplanar angle was 44°.

Turner and Voitle have argued[74] that coplanarity will be
favoured even at the expense of conversion of an s-trans conformer
to an s-cis conformation. The energy barrier between s-cis and
s-trans conformations is known to be small, hence Turner and
Voitle considered that small steric interactions might cause a
preference for one conformation rather than the other. They have
suggested[74] that the intensity of absorption of a molecule is
proportional to the square of its dipole moment (cf.[1,77]) and
hence, in the case of molecules of similar constitution, to the
square of the distance between the ends of the dipole. Since the
ends of the dipole will be closer in s-cis 1-acetyl-2-methylcyclo-
hexene than in the corresponding s-trans conformation they argued
that the low absorption intensity suggested an s-cis conformation.

It is more probable that absorption intensity is proportional to the square of the change of dipole moment, (see below) but the argument is not effected.

If the hypothesis of Turner and Voitle is correct, every compound with an s-cis conformation should have a lower absorption than the corresponding s-trans conformation. This is hard to reconcile with the rather high absorption intensity of mesityl oxide (see Table VII) which both dipole moment studies[78] and ultrasonic relaxation data[47] show to exist entirely in the s-cis conformation. (Cf. Ref. 39).

According to Braude and Sondheimer[33] the factors influencing absorption intensity are (1) change in dipole moment on going from ground state to excited state (2) area of the chromophore and (3) selection rules. Several interpretations may be given to the expression 'area of the chromophore'. It may mean the area of each molecule of the absorbing species measured along the chain of atoms, or it may be a hypothetical figure referring to the distance between the ends of the dipole. In the case of a conjugated carbonyl compound the migration of charge on excitation may be assumed to take place along the $\pi$ orbitals, hence the length of the chromophore may be expected to mean the length measured along the chain of atoms. This would not vary for s-cis and s-trans isomers. The present author suggests that when comparing dipole moments care should be taken to ensure that the lengths of the dipolar forms are comparable (see Parts III and IV).

Forbes and Mueller[8] have modified both the hypotheses outlined above by supposing that even an unhindered compound exists in both s-cis and s-trans conformations, though not necessarily or even probably to equal extents. Introduction of steric hindrance would be expected to hinder the coplanarity of one conformer more than the other: in the case under consideration the s-trans isomer will be more hindered than the s-cis on account of the large size of the methyl group compared with the carbonyl oxygen atom. The absorption intensity of the hindered isomer will be reduced (Braude's type I mechanism) while that of the other will not be affected, or will be affected less. The authors cited have proposed to modify the equation of Braude et al. to $\varepsilon/\varepsilon_0 = \frac{1}{2}[\cos^2(\Theta_2 - \Theta_1) + \cos^2(\Theta_4 - \Theta_3)]$ where $\Theta_1$ is the interplanar angle in one unhindered conformation, $\Theta_2$ the angle in the same hindered conformation, $\Theta_4$ and $\Theta_3$ the angles in the other conformation, hindered and unhindered respectively. Assuming $\Theta_1$ and $\Theta_3$ to be approximately zero this reduces to $\varepsilon/\varepsilon_0 = \frac{1}{2}[\cos^2\Theta_2 + \cos^2\Theta_4]$ In the case of a symmetrically substituted compound their equation reduces to $\varepsilon/\varepsilon_0 = \cos^2\Theta$, identical with that of Braude and his collaborators. They claim that the infra-red spectrum will have contributions from hindered and unhindered forms.

It has been pointed out by Wepster[21] that on account of the flat shape of the potential energy curve, only average values of interplanar angles can be calculated.

Braude and Timmons[48] have claimed that the difference between the carbonyl and ethylenic frequencies ($\nu_{C=O} - \nu_{C=C} = \Delta\nu$)

is greater ($\Delta\nu > 75$ cm$^{-1}$) for s-cis compounds than for s-trans compounds ($\Delta\nu < 75$ cm$^{-1}$). Waight and Erskine[39] have examined some other $\alpha,\beta$-unsaturated carbonyl compounds, including some of fixed conformation and found that for compounds known or thought to be s-trans $\Delta\nu < 50$ cm$^{-1}$ and for those known or thought to be s-cis $\Delta\nu > 65$ cm$^{-1}$. The same authors have drawn attention to a correlation found in polycyclic systems: in an s-cis compound the peak heights of the C=O and C=C bands are nearly equal, but in an s-trans compound the C=C band is much weaker. Waight and Erskine have found that while there is no correlation between relative peak heights in acyclic and monocyclic compounds the apparent molecular extinction coefficient of the C=O band is much higher in s-trans compounds ($\varepsilon^a > 300$) than in s-cis compounds ($\varepsilon^a < 300$). Also the half-band width is much greater for s-cis compounds than s-trans. For 1-acetyl-2-methylcyclohexene $\nu_{C=O} - \nu_{C=C} = 71$ cm$^{-1}$ and the half-band width is 47 cm$^{-1}$ (compared with < 20 cm$^{-1}$ for compounds of known s-trans conformation). The apparent molecular extinction coefficient of the C=O band is 276, and the apparent molecular extinction coefficient of the C=C band is 66. While each of the latter figures is a little higher than corresponding figures for compounds known to be wholly s-cis, they are much closer to the figures for s-cis compounds than to those for s-trans compounds. Hence Waight and Erskine have concluded that 1-acetyl-2-methylcyclohexene exists in the s-cis conformation.

TABLE IV

EFFECT OF SOLVENT ON SPECTRA OF α,β-UNSATURATED KETONES

| SOLVENT | CORRECTION TO ETHANOL (mμ) |
|---------|---------------------------|
| Ethanol | 0 |
| Methanol | −1 |
| Chloroform | ±0 |
| Diethyl ether | +6 |
| n-Hexane | +7 |

(After Woodward,[4] cf. Scheibe, Rösaler and Backenköler[149])

PART III

## α,β-Unsaturated Aldehydes

The work of Evans and Gillam[68] leading to empirical relationships between the wavelengths of maximal absorption of α,β-unsaturated aldehydes has been summarised in Part II. The latter authors were, however, unable to examine a simple tri-substituted α,β-unsaturated aldehyde.

In the present investigation all possible methyl substituted acroleins have been examined except the unknown <u>cis</u>-crotonaldehyde and angelaldehyde. Values of $\lambda_{max}$ and $\varepsilon_{max}$ are given in Table V. Many of the values of $\varepsilon_{max}$ are not in good agreement with those recorded by previous authors (see experimental). Since all measurements were made under identical conditions the figures may be intercompared with some confidence.

Figure 11 shows the band shapes of all the compounds in cyclohexane to be similar, and similar shapes are shown in ethanol. To avoid the labour of graphical integration it is customary to take integrated absorption intensities to be proportional to maximal absorption intensity. The present author suggests that a better approximation, in the case of compounds with similar band shapes, is to be obtained by multiplying the ratio of maximal absorption coefficients by the ratio of half-band widths.* Table VIa shows that there is a certain amount of band widening in the compounds examined but Table VIb shows that this does not affect

*Half-band widths should be in wave-numbers for this purpose, but for small ranges of wavelength the differences are qualitatively similar.

the order of intensities of the methyl- substituted acroleins.

Microwave absorption spectroscopy[44] has shown acrolein to possess a predominantly s-trans structure, in agreement with dipole moment studies[78] which indicated a contribution of only about 2% of the s-cis conformation at room temperature. Dipole moment data indicated the difference in energy between the two conformations to be only 2.5 kcals per mole, and the energy barrier hindering rotation to be only 5 kcals per mole. The low value of the energy barrier has also been confirmed by ultrasonic relaxation data.[47] This would indicate relatively easy conversion of one conformer to the other. In the vapour phase the infra-red carbonyl frequency of acrolein is reported to occur as a doublet[79] at 1733 and 1714 $cm^{-1}$, the two bands being of nearly equal intensity. This is consistent with the previous indications that acrolein exists in both s-cis and s-trans conformations. In carbon tetrachloride solution (concentration about 0.01 M) the band occurs[79] at 1704 $cm^{-1}$.

Crotonaldehyde is known to have a trans configuration of methyl and formyl groups, and is known[44] to be largely s-trans. The β-methyl group gives additional resonance stabilisation shown by dipole moment studies[80], ultra-sonic relaxation data[47], and infra-red spectra. The displacement of the wavelength of maximal absorption in the ultra-violet to longer wavelengths than in acrolein may also be taken as evidence for additional resonance stabilisation. It is probable that hyperconjugated resonance structures such as $H+CH_2.CH:CH.CHO^-$ participate in both ground and excited states.[81]

In β-methylcrotonaldehyde [$(CH_3)_2C:CH.CHO$] the introduction of a second β-methyl group relative to crotonaldehyde might lead to steric interaction between the methyl group and the formyl hydrogen atom, but diagrams drawn using the proposed interference radii of Forbes and Mueller[52] show very little difference in steric hindrance between the s-cis and s-trans conformations. (See Figure 12). Resonance stabilisation will therefore tend to maintain the molecule in a planar s-trans conformation. The infra-red spectrum shows the carbonyl frequency to be 1683 cm$^{-1}$, ε$^a$260 and the olefinic frequency (in carbon tetrachloride) to occur as a doublet at 1636 cm.$^{-1}$, ε$^a$ 62 and 1618 cm.$^{-1}$, ε$^a$ 46. The two figures may be evidence for s-cis, s-trans isomerism, since the differences between the figures and that of the carbonyl frequency are those expected for such isomers (see Part II) but the assignment is only tentative. The apparent intensity figures appear to be somewhat closer to those for an s-cis compound than s-trans. For crotonaldehyde in carbon tetrachloride the carbonyl frequency occurs at 1685 cm$^{-1}$, ε$^a$ 234. [58] The distinct decrease in absorption intensity relative to crotonaldehyde might be taken as evidence for slight steric hindrance to coplanarity: the interplanar angle calculated by Braude's method is 37°. On the other hand the half-band width for β-methylcrotonaldehyde is considerably greater than for crotonaldehyde (see Table VIa) and the approximate integrated absorption intensity (Table VIb) is much closer to that of crotonaldehyde. Using approximate integrated absorption intensities the calculated interplanar angle is 16°.

α-Methacrolein compared with acrolein shows a bathochromic wavelength displacement of 10 mμ in cyclohexane and 9 mμ in ethanol,

in agreement with the rules formulated by Evans and Gillam. It is clear that resonance stabilisation of the type postulated for crotonaldehyde cannot be operative in α-methacrolein: it might therefore be expected that α-methacrolein would exhibit at least as much tendency as acrolein to exist in s-cis conformations to some extent. Also there might be slight steric interaction between the bulky α methyl group and the formyl group. Ultrasonic absorption data have shown[47] that an appreciable, but unspecified, proportion of α-methacrolein exists in the conformation of higher energy. The dipole moment of α-methacrolein is 2.72 Debye, compared with 2.90 Debye for acrolein[78,82] The reduction may be caused by a combination of several factors. The chief ionic structure contributing to the resonance hybrid will be $+CH_2-C(CH3): CH-O-$ and the dipole moment of this will depend upon whether it exists in an s-cis or s-trans conformation. Contributions from

$$- CH_2-C\begin{smallmatrix}CH_2\ +H\\ \\CHO\end{smallmatrix}$$

will also be opposed to the resonance form described previously and will lead to reduction in dipole moment. There will probably also be a contribution from

$$+H_2C-C\begin{smallmatrix}CH_2\ +H\\ \\ \\H\end{smallmatrix}C-O-$$

It is difficult to account for the bathochromic wavelength displacement on introduction of an α alkyl group: one might expect that reduction of dipole moment would lead to easier separation of charge and hence to absorption at longer wavelengths but a

similar affect cannot be invoked in alkyl substituted butadienes (see Part V). Walsh[70] has shown that increasing the polarity of the carbonyl group leads to increasing repulsion between the electrons of the double bond and the lone pair electrons on the oxygen atom. Hence both lone pair and $\pi$ bonding electrons become more weakly bound, and all transitions move to longer wavelength. Resonance structures of the type $-CH_2-C\overset{CH_2+H}{\underset{H-C:O}{}}$ will increase the polarity of the carbonyl group relative to the ethylenic bond and might be invoked to account for the wavelength displacement. Another hypothesis is that only the inductive effect of the group is important: that addition of electrons to the $\pi$ electron system facilitates excitation. The latter hypothesis permits the greater displacement shown by a $\beta$-methyl group to be attributed to its hyperconjugative effect in addition to its inductive effect. Against the proposed hypothesis must be quoted evidence from aromatic compounds that inductive effects are of little importance in determining spectra[15] The present author suggests that on account of the very different nature of the $\pi$ electron systems in aromatic and aliphatic compounds conclusions drawn from the former may be applied to the latter only with considerable reserve: this is indeed suggested by the very small wavelength displacement (2 m$\mu$) on introducing an _ortho_ methyl group into acetophenone[10] compared with the figure for aliphatic compounds. A displacement of 12 m$\mu$ is observed[10] on introducing a _para_ methyl group, whereas comparison with $\delta$ substituents in aliphatic dienones would lead one to expect a displacement of 18 m$\mu$.

Returning to the question of the conformation of α-methacrolein, the carbonyl frequency in carbon tetrachloride is 1702 cm.$^{-1}$ ($\varepsilon^a$ 240) and the olefinic frequency 1637 cm.$^{-1}$ ($\varepsilon^a$ 16). $\Delta\nu$ = 65 cm.$^{-1}$ and $\varepsilon^a_{C=O} \approx 250$. These figures are close to those for s-cis compounds (see Part II), confirming the hypothesis that α-methacrolein exists to an appreciable extent in s-cis and non-planar s-trans conformations.

In tiglaldehyde the wavelength displacement relative to α-methacrolein is 10 mμ in ethanol, 9.5 mμ in cyclohexane, similar to those (11 and 10 mμ respectively) between crotonaldehyde and acrolein. This is consistent with the view that the β-methyl group in tiglaldehyde functions in a similar manner to that in crotonaldehyde, that is, hyperconjugation increases the length of the conjugated chain. Tiglaldehyde is known to have the two methyl groups disposed in the cis configuration[83] and the predominant conformation is



Nevertheless, the dipole moment of tiglaldehyde is less than that of croton- aldehyde (3.39 Debye compared with 3.54 Debye[78]) and $\varepsilon_{max}$ for tiglaldehyde compared with that for α-methacrolein is less than $\varepsilon_{max}$ for crotonaldehyde compared with $\varepsilon_{max}$ for acrolein. Some of the reduction of dipole moment can be ascribed to the participation of resonance forms similar to those given for α-methacrolein, but it appears probable that tiglaldehyde also exists in the s-cis conformation to an appreciable extent. Scale diagrams indicate slight overlap between the methyl groups, hence it would be expected

that a buttressing effect would increase the C=C-C angle and the $CH_3$ -C-H angle. This in turn would cause loss of planarity and account for the slightly lower value of $\varepsilon_{max}$ than that found for crotonaldehyde.

2,3-dimethylbut-2-enal shows a considerably larger bathochromic wavelength displacement on introducing the second methyl group than that obtained on introducing the first (19 and 17.5 mμ in ethanol and cyclohexane respectively, compared with 10 and 9.5 mμ for the first methyl group). A similar large displacement (17.5 and 15 mμ) is observed on introducing the second β-methyl group into crotonaldehyde (compare displacements of 11 and 10 mμ between crotonaldehyde and acrolein). This phenomenon appears to be general, since similar large displacements on introducing a second β-methyl group are observed in the α,β-unsaturated ketones and dienes (see Parts IV and V). This phenomenon does not appear to have been reported previously (but see Part V). This point is further discussed later in this Part.

The intensity decrease between tiglaldehyde and 2,3-dimethylbut-2-enal may also be ascribed to steric interference in 2,3-dimethylbut-2-enal between the β-methyl group <u>cis</u> to the formyl group and the hydrogen atom of the formyl group, causing the molecule to take up non-planar <u>s-cis</u> and <u>s-trans</u> conformations. Support for this is provided by the rather low[39] ($\varepsilon_{C=O}/\varepsilon_{C=C} = 374/122$) ratio of apparent intensities of the carbonyl and olefinic bands. Hence, 2,3-dimethylbut-2-enal is assigned a partial <u>s-cis</u> conformation.

Table IV shows that (in this and similar series) a hypsochromic wavelength displacement of 6 mμ is observed on changing solvent from ethanol to cyclohexane. The present work shows this to be true to a first approximation, but the actual displacement varies between 3 and 7.5 mμ, and the range for α, β-unsaturated ketones is 3 to 7 mμ (see Table VII). Only for crotonaldehyde and β-methylcrotonaldehyde is a higher extinction coefficient found in ethanol than in cyclohexane (see Table V). This may be correlated with the tendency of these compounds to exist in planar s-trans conformations. It is suggested that ethanol molecules will tend to attach themselves to the carbonyl group thus lengthening the conjugated chain and increasing steric interaction with the β-methyl groups (cf.[84]). The mechanism proposed may also account for the relatively small wavelength displacements between ethanol and cyclohexane for α-methacrolein and tiglaldehyde.

Several investigators (cf. [1, 77]) have suggested that the intensity of absorption of a dipolar chromophore is proportional to the square of the distance between the ends of the dipole. Assuming the partial charges at the ends of the dipole to be the same in crotonaldehyde as in acrolein, the ratio of $\varepsilon_{max}$ for crotonaldehyde to $\varepsilon_{max}$ for acrolein should be 1.48. The observed ratio in cyclohexane is 17,300: 12,000, i.e. 1.44. The observed ratio in ethanol is 17,900: 11,200, i.e. 1.58. These results are consistent with the hypothesis that crotonaldehyde in ethanol contains a greater proportion of s-trans conformations than acrolein

as suggested above. Similar comparisons are set out in Table IX. In spite of the scanty and somewhat conflicting data on dipole moments, the agreement for α,β-unsaturated aldehydes in cyclohexane is good but less good in ethanol. There is no agreement in the case of α,β-unsaturated ketones.

The spectral effects in α-methacrolein and tiglaldehyde are only tentatively ascribed to steric effects, but the effects in β-methylcrotonaldehyde and 2, 3-dimethylbut-2-enal are ascribed with some confidence to steric effects, since they are similar to those observed between benzaldehyde and o-tolualdehyde[14] and between acetophenone and o-methylacetophenone[13].

Since it appears general in this series for an alkyl group to give a bathochromic wavelength displacement, the displacements between acrolein and crotonaldehyde on the one hand, and between β-methylcrotonaldehyde and 2,3-dimethylbut-2-enal on the other are not ascribed to steric effects. The above consideration, and the low extinction coefficient of β-methylcrotonaldehyde relative to crotonaldehyde leads the author to classify the spectral effect between these two compounds as a type I steric effect. The wavelength displacement is attributed to the participation of resonance forms similar to those described for α-methacrolein. Steric interaction will cause hindrance to coplanarity of the methyl and formyl groups, and this will be reduced by twisting about the C-C bond formally written as a single bond between the formyl group and olefinic moiety. Considerations set out previously show that loss of planarity will cause more loss of

resonance energy in the excited state than in the ground state, hence β-methylcrotonaldehyde will show a hypsochromic wavelength displacement relative to a similar unhindered reference compound. Such a reference compound is provided by cyclohexylideneacetaldehyde since a cyclohexylidene group is known[17] to cause less steric hindrance than a methyl group or a methyl group buttressed by another methyl group. As expected, β-methylcrotonaldehyde absorbs at shorter wavelengths and with lower intensity than cyclohexyl-ideneacetaldehyde (see Table V). It should be pointed out that some assumptions are implicit in this treatment, since the inter-fering system in β-methylcrotonaldehyde is a _gem_ dimethyl group, and not two buttressed methyl groups.

Table VIa shows that in compounds thought to be sterically hindered there is slight but distinct band widening. This may be compared with the similar effect in infra-red spectra of _s-cis_ compounds (see Part II) and may prove to be general (see Parts IV and V).

If the assignment of spectral effects to steric inter-action is correct there must be some interaction between a _cis_ methyl group and the formyl hydrogen atom in the _s-trans_ conform-ation. Scale diagrams indicate the distance between the centres of the methyl group and the formyl hydrogen atom to be 2.48A in the _s-trans_ conformation, and the distance between the centres of the methyl group and carbonyl oxygen atom in the _s-cis_ conform-ation to be 2.50A. Forbes and Mueller[52] have suggested from examples in the aromatic series that the effective interference radii in solution of the atoms and groups concerned are:

hydrogen 0.95±0.1 A, O(inC=O) 1.0±0.15 A, and $CH_3$ 1.7±0.2A. Using these values it is seen that slight overlapping to the extent of 0.22 A would be expected in β-methylcrotonaldehyde. The present author suggests that the effective interference radius of a *gem* dimethyl group is somewhat larger than would be expected from scale diagrams. Repulsion between like partial charges on the terminal methyl groups will cause an increase in the C-C-C angle, and hence a decreased distance between the terminal methyl group and the formyl hydrogen atom. On the other hand very recent studies have shown the H-C-H angle in ethylene[85] to be 116°, whereas an older value for the $CH_3$-C-$CH_3$ angle in isobutylene or tetramethylethylene[86] was 111°30'. However the latter authors favoured 110±5° for the H-C-H angle in ethylene. The evidence for increase of angle in the *gem* dimethyl group is therefore inconclusive.

The reason for the larger displacement of $\lambda_{max}$ on introducing a second β-methyl substituent may be related to the above suggestion. Increased possibilities of resonance among forms of the type given in Figure 13 would be expected to lead to rather large bathochromic displacements. It is of interest to note that a rather similar phenomenon is shown by the infra-red carbonyl bands. Acrolein in carbon tetrachloride shows a carbonyl band at 1704 cm.[-1][79] crotonaldehyde in carbon tetrachloride at 1696 cm.[-1][79] and β-methylcrotonaldehyde in carbon tetrachloride at 1683 cm.[-1]

A second mechanism may be suggested. The partial positive charge on the methyl group *cis* to the formyl group may exert a field effect on the partial negative charge of the oxygen atom in

the s-cis conformation, thus stabilising it in a planar state. This would lead to stabilisation in both ground and excited states and absorption at longer wavelengths than an unstabilised compound. The same argument would account for the large wavelength displacements between pent-3-en-2-one and mesityl oxide (see Table VII). This mechanism would require the large displacement to be due to the presence of a methyl group cis to the carbonyl rather than to its being the second group. Some support is afforded by the absorption spectra in ethanol of angelic acid ($\lambda_{max}$215.5 m$\mu$, $\epsilon_{max}$9,400) and tiglic acid ($\lambda_{max}$212.5 m$\mu$, $\epsilon_{max}$12,500)[87]. Unfortunately there appear to be no data for other pairs of geometrical isomers in this series. Cis-crotonaldehyde has never been prepared, and angelaldehyde has never been prepared in a pure state. The only comparable pair of isomers examined appears to be cis and trans piperylene, for which Jacobs and Platt[59] found $\lambda_{max}$226 and 223 m$\mu$, respectively, and $\epsilon_{max}$22,000 and 26,000 respectively, but the explanation is less simple in that case owing to the absence of large dipole moments. It should be noted that in 1,2-disubstituted ethylenes where each group is itself a chromophore the trans isomer usually absorbs at longer wavelength than the cis isomer, as would be expected for a longer conjugated system. Examples are cis and trans stilbene, 1,2-dibenzoylethylene, 1-phenylbuta-1,3-diene, and cinnamic acid.[88] These cases should be distinguished sharply from those considered in the present thesis, where one of the groups concerned in cis-trans isomerism is not a chromophore.

An apparent exception to the rule that a second β substituent causes a larger displacement than the first is compound

 ($\lambda_{max}$ 240 mμ) compared with  ($\lambda_{max}$ 235 mμ)

It seems probable that the proposed formulae are erroneous, and the original authors quoted them only as probable formulae.

TABLE V

ULTRA-VIOLET ABSORPTION SPECTRA OF α,β-UNSATURATED ALDEHYDES

| | Solvent: | ETHANOL | | CYCLOHEXANE | |
|---|---|---|---|---|---|
| Compound | | $\lambda_{max}(m\mu)$ | $\varepsilon_{max}$ | $\lambda_{max}(m\mu)$ | $\varepsilon_{max}$ |
| Acrolein $CH_2{:}CH.CHO$ | | 207 | 11,200 | 203 | 12,000 |
| α-Methacrolein $CH_2{:}C(CH_3).CHO$ | | 216 | 11,000 | 213 | 11,100 |
| Crotonaldehyde $CH_3.CH{:}CH.CHO$ | | 218 | 17,900 | 213 | 17,300 |
| Tiglaldehyde $CH_3.CH{:}C(CH_3).CHO$ | | 226 | 16,100 | 222.5 | 16,700 |
| β-Methylcrotonaldehyde $(CH_3)_2C{:}CH.CHO$ | | 235.5 | 11,900 | 228 | 11,400 |
| 2,3-Dimethylbut-2-enal $(CH_3)_2C{:}C(CH_3).CHO$ | | 245 | 13,000* | 240 | 13,500* |
| Cyclohexylideneacetaldehyde $C_5H_{10}C{:}CH.CHO$ | | 238 | 16,000* | 231.5 | 16,000* |

*Estimated. See experimental part.

<div align="center">

TABLE VI a

</div>

HALF-BAND WIDTHS OF α,β-UNSATURATED ALDEHYDES

| Compound | Half-Band Width (mμ) |
|---|---|
| Acrolein | 10 |
| Crotonaldehyde | 10 |
| α-Methacrolein | 10 |
| β-Methylcrotonaldehyde | 14 |
| Tiglaldehyde | 10 |
| 2,3-Dimethylbut-2-enal | 17, 12 (asymmetrical) |
| Cyclohexylideneacetaldehyde | 12 |

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All measurements are in cyclohexane.

Half-band widths are measured to the nearest mμ, and are half-widths at half maximum intensity.

<div align="center">

TABLE VI b

</div>

APPROXIMATE INTEGRATED ABSORPTION INTENSITIES IN CYCLOHEXANE

| Compound | Intensity |
|---|---|
| Acrolein | 12,000 |
| Crotonaldehyde | 17,300 |
| α-Methacrolein | 11,100 |
| Tiglaldehyde | 16,700 |
| β-Methylcrotonaldehyde | 16,000 |
| 2,3-Dimethylbut-2-enal | 16,200, 23,000 |
| Cyclohexylideneacetaldehyde | 19,200 |

Intensity units are arbitrary, taking acrolein as 12,000.

B-BANDS OF α,β-UNSATURATED
ALDEHYDES IN CYCLOHEXANE

Crotonaldehyde : --- Acrolein : ......... β-Methylcrotonaldehyde:
-·-·- α-Methacrolein: ---·--- Tiglaldehyde: -·-·-· 2,3-Dimethylbut-2-enal.
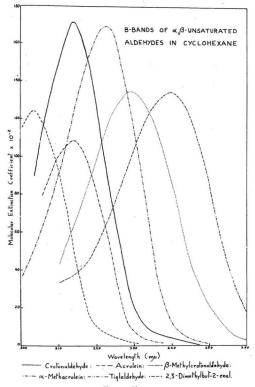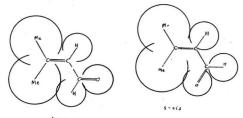
Figure 11

s-trans                    s-cis

β-methylcrotonaldehyde

Figure 12



Resonance forms of β-methylcrotonaldehyde

Figure 13

PART IV.

## The Spectra of α,β-Unsaturated Ketones

Saturated ketones and unsaturated ketones in which the olefinic bond and carbonyl group are not in conjugation show very weak absorption ($\varepsilon_{max}$ about 100, $\lambda_{max}$ about 260 mμ). On the other hand, when the olefinic link and the carbonyl group are in conjugation, two bands appear (see Part II), one at 200-250 mμ of high intensity (about 10,000) and the other at longer wavelength and lower intensity (about 100). The former is often referred to as the K band[71] (k for konjugiert) and has been regarded as having its origin in transitions involving the entire conjugated system, and the other is often called the R band (r for radikal) and has been regarded as arising from transitions in the carbonyl group. That is, as pointed out in Part III, the K band is due to an N-->V transition, and the R band to an N-->A transition. In the present work only the K band is considered, and is called, in accordance with the system described in the introduction, the B band. The empirical correlations of Woodward, Evans and Gillam, and Fieser, have been described in Part II.

Acrolein and methylvinyl ketone absorb at the same wavelength and with similar intensities: it is therefore probable that their conformations are similar. This conclusion is reinforced by the observation[78] that the dipole moments of acrolein and methylvinyl ketone are very similar, 2.90[78] and 2.98[89] Debye respectively in solution. It might be anticipated that the

functional differences between a ketonic group and an aldehydic
group would arise from a difference in partial charge on the
carbonyl oxygen atoms, hence the agreement of dipole moments
would be fortuitous. This conclusion is vitiated by the similarity
of dipole moments of p-tolualdehyde (3.24 Debye) and p-methyl-
acetophenone (3.20 Debye)[80] in which s-cis s-trans isomerism
cannot occur. Hence it is probable that both acrolein and methyl-
vinyl ketone exist largely in the s-trans conformation. This
conclusion is supported by ultra-sonic relaxation data[47] which
indicate that methylvinyl ketone exists largely in the s-trans
conformation, but with an appreciable (unstated) proportion of
the higher energy form.

Replacement of a β-hydrogen atom by a methyl group
would be expected to give the trans isomer and it is difficult
to see why this should affect the s-cis, s-trans ratio. Hyper-
conjugation should encourage the formation of planar s-trans
conformations though slight increase of the C-C=C angle might
give rise to slight steric hindrance of the s-trans form. Taking
Estok and Dehn's (quoted) value[80] for the dipole moment of pent-3-
en-2-one (3.26 Debye in dioxan) and Estok and Sikes' value[89] for
the dipole moment of methylvinyl ketone in dioxan (2.98 Debye)
the ratio of $\varepsilon_{max}$ for pent-3-en-2-one to that for methylvinyl
ketone should be 1.19, precisely that observed. The carbonyl
frequency occurs at 1677 cm$^{-1}$ ($\varepsilon^a$ 320), and the olefinic frequency
at 1631 cm$^{-1}$ ($\varepsilon^a$ 140). Since $\Delta\nu = 46$ cm$^{-1}$ these figures also
support the assignment of an s-trans conformation.

Estok and Dehn[80] have ascribed equal proportions of s-cis and s-trans conformations to pent-3-en-2-one, since, although acrolein and methylvinyl ketone have almost identical dipole moments, the moment of pent-3-en-2-one is less than that of crotonaldehyde (3.58 Debye in dioxan, as measured by the authors named). On the other hand, the similarity of wavelength displacement between pent-3-en-2-one and methylvinyl ketone (11.5 mμ in ethanol, 10 mμ in cyclohexane) and between crotonaldehyde and acrolein (11 mμ in ethanol, 10 mμ in cyclohexane) and concordance of the square of the dipole moment rule would indicate that crotonaldehyde and pent-3-en-2-one have similar conformations. A Mechanism is available for the difference of assignments. Microwave spectroscopic measurements[44] have indicated that in acrolein the dipole moment lies $14° \pm 2°$ from the C=O axis. This may be caused by slight steric interaction between a β-hydrogen atom and the formyl group. In crotonaldehyde the $CH_3.C:C$ angle will be slightly increased, causing a little more steric hindrance, but hyperconjugation will favour the formation of planar forms. In view of the slight nature of steric interaction in crotonaldehyde the factors favouring planarity may outweigh those opposing it. In methylvinyl ketone the larger methyl group will give rise to more steric hindrance and therefore less planarity than in acrolein. When steric hindrance is increased by replacement of a β-hydrogen atom by a methyl group the opposition to planarity will be comparable with the factors favouring it. Therefore the acetyl group will take up a distorted s-trans position, and the dipole moment will lie at some angle to the C=O axis. Some support

for this suggestion is afforded by infra-red spectroscopic
evidence. The carbonyl and olefinic frequencies of methylvinyl
ketone are 1687 and 1619 cm$^{-1}$ respectively. The value of $\Delta\nu$,
68 cm$^{-1}$ is close to that for an s-cis compound. In pent-3-en-2-
one, $\nu_{C=O}$ = 1677 cm$^{-1}$, $\varepsilon^a$ 320; $\nu_{C=C}$ = 1631 cm$^{-1}$ $\varepsilon^a$ 140. These
figures support an s-trans conformation.

As in the case of crotonaldehyde, the wavelength displace-
ment may be attributed to the participation of resonance forms
such as
$$H + CH_2 : CH - CH \diagdown \atop CH_3 C - O -$$

In methylisopropenyl ketone [$CH_2 : C(CH_3) . CO . CH_3$] the
wavelength displacement, relative to methylvinyl ketone, is 9 m$\mu$
in ethanol and 9.5 m$\mu$ in cyclohexane. The difference between
these figures and those for pent-3-en-2-one (11.5 and 10 m$\mu$
respectively) is significant. The low value of $\varepsilon_{max}$ relative to
methylvinyl ketone would suggest that the molecule has, to some
extent, assumed a non-planar conformation. This would be expected
by analogy with $\alpha$-methacrolein and would not be inconsistent with
the low dipole moment of methylisopropenyl ketone (2.74 Debye in
benzene, 2.80 Debye in dioxan[89]). These figures are close to the
dipole moments of the saturated ketones methylisopropyl ketone
(2.76 Debye)[89] and methylethyl ketone (2.76 Debye)[89] both in
benzene. The reduced dipole moment could also be ascribed to the
participation of resonance forms such as
$$CH_2 + H \atop -CH_2 - C . CO . CH_3 .$$
Lamb and de Groot[47] have also shown from ultra-sonic absorption data
that a proportion of methylisopropenyl ketone exists in the
higher energy form.

The low dipole moment, compared with that of methylvinyl ketone, would lead one to expect methyl$\underline{iso}$propenyl ketone to have a lower extinction coefficient than methylvinyl ketone. Since $\varepsilon_{max}$ is actually a little more intense (see Table VII) it must be concluded that the rule relating ratio of absorption intensities with square of the dipole moment[77] applies only to molecules of one and the same conformation, or to compounds in which the dipole moment is directed along the chromophore. The carbonyl frequency of methyl$\underline{iso}$propenyl ketone occurs at 1681 cm$^{-1}$ ($\varepsilon^a$ 400) and the olefinic frequency at 1631 cm$^{-1}$ ($\varepsilon^a$ 36). These figures favour an s-$\underline{trans}$ conformation.

In mesityl oxide the wavelength displacement relative to pent-3-en-2-one is 16 m$\mu$ in both ethanol and cyclohexane. As in the analogous aldehydes, the second methyl group gives a much larger wavelength displacement than the first. Scale diagrams (see Figure 14) show considerable steric hindrance between the terminal methyl groups and the acetyl methyl group in the s-$\underline{trans}$ conformation. The s-$\underline{cis}$ conformer would therefore be expected to be the stable conformation, and this conclusion is supported by the low dipole moment of mesityl oxide (2.84 Debye in benzene[78]) and ultra-sonic relaxation data[47]: the latter indicate the s-$\underline{cis}$ isomer to be the only stable isomer at room temperature. The carbonyl frequency is 1690 cm$^{-1}$, $\varepsilon^a$ 270 and the olefinic frequency 1620 cm$^{-1}$, $\varepsilon^a$ 220. These figures are consistent with an s-$\underline{cis}$ conformation, though $\Delta\nu$ is not as large as in compounds with a fixed s-$\underline{cis}$ conformation.

In 3-methylpent-3-en-2-one $[CH_3.CH:C(CH_3).CO.CH_3]$ the wavelength displacement relative to pent-3-en-2-one is 8 m$\mu$ in both ethanol and cyclohexane. Relative to methyl_iso_propenyl ketone the displacements are 10.5 m$\mu$ in ethanol, and 8.5 m$\mu$ in cyclohexane. The displacements are significantly smaller than between pent-3-en-2-one and methylvinyl ketone. This is consistent with an increased proportion of s-cis conformations in 3-methylpent-3-en-2-one. The carbonyl frequency is 1672 cm.$^{-1}$, $\varepsilon^a$ 410, and the olefinic frequency 1644 cm.$^{-1}$, $\varepsilon^a$ 85, whence $\Delta\nu = 28$ cm.$^{-1}$, favouring an s-trans conformation. On the other hand, Estok and Dehn[80] conclude from the identity of dipole moments of 3-methylpent-3-en-2-one and pent-3-en-2-one that the former exists as a mixture of s-cis and s-trans conformers in approximately equal amounts. A buttressing effect similar to that postulated for tiglaldehyde would be expected to give an increased proportion of s-cis conformations. The present author favours a mixture of s-cis and s-trans conformations, with the latter predominating.

The molecular extinction coefficient in both ethanol and cyclohexane is lower than calculated from the ratio of dipole moment of 3-methylpent-3-en-2-one to that of methylvinyl ketone (see Table IX), as would be expected from the interpretation given above for methyl_iso_propenyl ketone. As postulated for aldehydes, solvation of the carbonyl group should increase steric hindrance in ethanol relative to cyclohexane; this is consistent with the extinction coefficients in those solvents.

Scale diagrams of 3,4-dimethylpent-3-en-2-one
$(CH_3)_2C:C(CH_3).CO.CH_3$ indicate that both s-cis and s-trans
conformations are hindered, the latter less than the former
(see Figure 15). Gillam and Evans[66] found for this compound in
ethanol $\lambda_{max}$ 249 m$\mu$, $\varepsilon_{max}$4,000, and concluded that the compound
was impure. The present figures ($\lambda_{max}$245.5 m$\mu$, $\varepsilon_{max}$5,800 in
ethanol, and $\lambda_{max}$238.5 m$\mu$, $\varepsilon_{max}$6,400 in cyclohexane) are in
agreement with those given by Erskine and Waight[39] ($\lambda_{max}$ 245.5 m$\mu$,
$\varepsilon_{max}$6,000 [ in ethanol or cyclohexane]) and may be regarded as
established. The very low value of $\varepsilon_{max}$ would be expected for a
compound with no stable planar conformations. The infra-red
spectrum (in carbon tetrachloride) shows $\nu_{c=o}$1687 cm$^{-1}$, $\varepsilon^a$200;
$\nu_{c=c}$1622 cm$^{-1}$, $\varepsilon^a$ 62. The difference in frequency is not such as
to enable one to judge whether the compound is s-cis or s-trans,
but the low values of apparent extinction coefficients suggest
that the compound has less resonance energy than the other $\alpha,\beta$-
unsaturated ketones considered, as would be expected of a non-
planar compound. Consequently 3, 4-dimethylpent-3-en-2-one is
assigned a non-planar s-cis conformation. This is also indicated
by the low extinction coefficient relative to 2,3-dimethylbut-2-
enal. The dipole moment is 2.88 Debye in benzene, and 2.91 Debye
in dioxan[89]. These values are slightly higher than those for
mesityl oxide (2.79 and 2.83 Debye in benzene and dioxan respect-
ively).[89] In an s-cis compound addition of an $\alpha$-methyl group
would be expected to increase the dipole moment.[89] Thus relative
to mesityl oxide, 3, 4-dimethylpent-3-en-2-one shows a type I
steric effect.

Assuming mesityl oxide to be planar, the interplanar angle in 3,4-dimethylpent-3-en-2-one is 45°. Calculation (for which the author is indebted to Mr. J.C. Deardin) shows the distance between the centres of the terminal and acetyl methyl groups to be 3.2 A, whence the effective interference radius of a methyl group is 1.6 A. This is in good agreement with the value proposed by Forbes and Mueller.[52]

In 3,4-dimethylpent-3-en-2-one the wavelength displacements are, relative to mesityl oxide, 9.5 mμ in ethanol and 7.5 mμ in cyclohexane. Relative to 3-methylpent-3-en-2-one they are 17.5 mμ in ethanol, 15.5 mμ in cyclohexane. Precisely as in the case of aldehydes, a second β-methyl group gives a much larger bathochromic wavelength displacement than the first. The proposed explanation is the same as that for the aldehydes: more possibilities of resonance among the hyperconjugated forms. It would seem that part of the bathochromic displacement of 5 mμ attributed to an exocyclic double bond may be due to the occurrence of such a bond as a terminal dialkyl group. Figures given by Schubert and Sweeney[69] for 1-acetylcyclopentene ($\lambda_{max}$239 mμ), and 2-methyl-1-acetylcyclopentene ($\lambda_{max}$ 253 mμ) also 1-acetylcyclohexene ($\lambda_{max}$232-3 mμ) and 2-methyl-1-acetylcyclohexene ($\lambda_{max}$249 mμ) also show a large displacement on introducing the second methyl group: hence the phenomenon appears to be general. However, as pointed out in Part III, the evidence is not sufficient to indicate whether this is due to the gem dimethyl group or to the second group's taking up a cis position.

2-methylhex-2-en-4-one $[(CH_3)_2 \; C{:}CH.CO.CH(CH_3)_2]$ absorbs at the same wavelength as mesityl oxide (see Table VII) and with somewhat lower intensity. It is assigned an s-cis conformation. 2,3,5-trimethylhex-2-en-4-one $[(CH_3)_2 \; C{:}C(CH_3).CO.CH(CH_3)_2]$ absorbs at rather shorter wavelengths and with much lower intensity than 3, 4-dimethylpent-3-en-2-one, and hence shows a type II effect relative to that compound.

Table VIIIa lists the half-band widths of α,β-unsaturated ketones (Cf Figure 16). As in the case of the aldehydes, those thought to exist appreciably in s-cis conformations show wider half-band widths than those believed to be largely s-trans. A surprising example is pent-3-en-2-one. Table VIIIb shows that approximate integrated absorption intensities calculated as described in Part III, do not differ in order to any great extent, but the absorption intensity of mesityl oxide becomes even greater than would be estimated from $\varepsilon_{max}$ .

It has been claimed[74] that an s-cis compound should show a lower absorption intensity than an s-trans compound of similar constitution. There seems to be abundant evidence that mesityl oxide exists in the s-cis conformation, yet its absorption intensity is rather high. On the other hand, there is also evidence that mesityl oxide is anomalous in other respects. Cook[79] has recently found that in its donor properties the carbonyl group of mesityl oxide resembles a saturated compound rather than an α,β-unsaturated ketone. The present author suggests that field attraction between the partial positive charges on the β-methyl

groups and the negative charge on the carbonyl oxygen atom
stabilises the compound in a planar state. In that case, excitation
should require, besides energy to separate charge, energy to
increase potential energy due to attraction of unlike charges.
This may account for the fact that wavelength displacements
between mesityl oxide and pent-3-en-2-one are rather smaller than
those between 3, 4-dimethylpent-3-en-2-one and 3-methylpent-3-en-
2-one, since the bathochromic displacement due to addition of a
methyl group will be partially offset by a hypsochromic displace-
ment. On the other hand, a compound stabilised as suggested
should show absorption with little dependence on solvent.

## TABLE VII

ULTRA-VIOLET ABSORPTION SPECTRA OF α,β-UNSATURATED KETONES

| Compound | solvent: ETHANOL | | CYCLOHEXANE | |
|---|---|---|---|---|
| | $\lambda_{max}$ (mμ) | $\epsilon_{max}$ | $\lambda_{max}$ (mμ) | $\epsilon_{max}$ |
| Methylvinyl ketone $CH_2{:}CH.CO.CH_3$ | 208.5 | 9,800 | 205 | 9,500 |
| Methylisopropenyl ketone $CH_2{:}C(CH_3).CO.CH_3$ | 217.5 | 10,400 | 214.5 | 10,700 |
| Pent-3-en-2-one $CH_3.CH{:}CH.CO.CH_3$ | 220 | 11,900 | 215 | 11,400 |
| 3-Methylpent-3-en-2-one $CH_3.CH{:}C(CH_3).CO.CH_3$ | 228 | 13,300 | 223 | 13,600 |
| Mesityl oxide $(CH_3)_2C{:}CH.CO.CH_3$ | 236 | 11,800* | 231 | 11,000* |
| 3,4-Dimethylpent-3-en-2-one $(CH_3)_2C{:}C(CH_3).CO.CH_3$ | 245.5 | 5,800 | 238.5 | 6,400 |
| 2-Methylhex-2-en-4-one $(CH_3)_2C{:}CH.CO.CH_2CH_3$ | 235 | 9,600 | 231 | 9,800 |
| 2,3,5-Trimethylhex-2-en-4-one $(CH_3)_2 C{:}C(CH_3). CO.CH(CH_3)_2$ | 242-243 | 3,020 | 236-237 | 3,470 |

* Estimated.   See experimental part.

## TABLE VIII.

### HALF-BAND WIDTHS OF α,β-UNSATURATED KETONES

| Compound | Half-band width (mμ) |
|---|---|
| Methylvinyl ketone | 10 |
| Methylisopropenyl ketone | 10 |
| Pent-3-en-2-one | 12 |
| Mesityl oxide | 14 |
| 3-Methylpent-3-en-2-one | 11 |
| 3,4-Dimethylpent-3-en-2-one | 15 |
| 2-Methylhex-2-en-4-one | 13 |
| 2,3,5-Trimethylhex-2-en-4-one | 15 |

All half-band widths are measured to the nearest mμ.
All measurements are made in cyclohexane and are
half-widths at half maximum intensity.

### TABLE VIII b

APPROXIMATE INTEGRATED ABSORPTION INTENSITIES IN CYCLOHEXANE
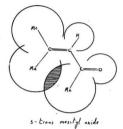
| Compound | Intensity |
|---|---|
| Methylvinyl ketone | 9,500 |
| Methylisopropenyl ketone | 10,700 |
| Pent-3-en-2-one | 13,700 |
| 3-Methylpent-3-en-2-one | 15,000 |
| Mesityl oxide | 15,400 |
| 3,4-Dimethylpent-3-en-2-one | 9,600 |
| 2-Methylhex-2-en-4-one | 12,700 |
| 2,3,5-Trimethylhex-2-en-4-one | 5,600 |
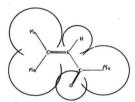
Intensity units are arbitrary, taking methylvinyl ketone as 9,500

TABLE IX

RELATIONSHIPS BETWEEN ABSORPTION INTENSITY AND DIPOLE MOMENT
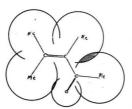
| Compound | μ (in benzene) | $\varepsilon/\varepsilon_0$ in EtOH | $\varepsilon/\varepsilon_0$ in cyclohex. | $(\mu/\mu_0)^2$ |
|---|---|---|---|---|
| **Aldehydes** | | | | |
| Acrolein | 2.88 | | | |
| α-Methacrolein | 2.72 | 0.98 | 0.93 | 0.89 |
| Crotonaldehyde | 3.50 | 1.58 | 1.44 | 1.48 |
| Tigaldehyde | 3.39 | 1.43 | 1.39 | 1.39 |
| **Ketones** | | | | |
| Methylvinyl ketone | 2.98 | | | |
| Methylisopropenyl ketone | 2.74 | 1.06 | 1.13 | 0.85 |
| Pent-3-en-2-one | 3.20 | 1.21 | 1.20 | 1.15 |
| Mesityl oxide | 2.79 | 1.20 | 1.16 | 0.88 |
| 3-Methylpent-3-en-2-one | 3.20 | 1.36 | 1.43 | 1.55 |
| 3,4-dimethylpent-3-en-2-one | 2.56 | 0.58 | 0.67 | 0.93 |

Aldehydes are compared with acrolein, ketones with methylvinyl ketone. Dipole moment data are from refs. 80 and 89. $\mu_0$ is the dipole moment of the reference compound, $\mu$ that of the compound considered. $\varepsilon_0$ is the molecular extinction coefficient of the reference compound, $\varepsilon$ that of the compound considered.

s-trans mesityl oxide
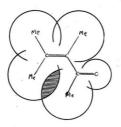


s-cis mesityl oxide

Figure 14

s-cis 3,4-dimethylpent-3-en-2-one



s-trans 3,4-dimethylpent-3-en-2-one

Figure 15

B-BANDS OF α,β-UNSATURATED KETONES IN CYCLOHEXANE

Molecular Extinction Coefficient × 10⁻²

Wavelength (mμ)

——Methylvinyl ketone; ----Pent-3-en-2-one; ······Mesityl oxide
—·—·Methylisopropenyl ketone; ------3-Methylpent-3-en-2-one; —··—··3,4-Dimethylpent-3-en-2-one

Figure 16

PART V.

The Spectra of Conjugated Dienes
Relationships Between Structure and Spectra.

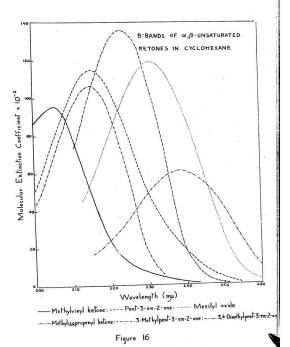A single olefinic linkage, unless highly substituted,[90] absorbs at wavelengths outside the range of most spectrophotometers that is below 200 m$\mu$, but a compound containing two conjugated olefinic linkages exhibits intense absorption in the region 215-270 m$\mu$.

The ultra-violet spectrum of butadiene has been discussed by Mulliken[1] who identified the band at 217 m$\mu$ with an N$\rightarrow$V transition. Molecular orbital calculations showed that four transitions were possible, N$\rightarrow$V$_1$, V$_2$, V$_3$ and V$_4$. The spectra of s-cis and s-trans butadiene should differ little, but for the s-trans conformer the N$\rightarrow$V$_2$ and V$_3$ transitions should be forbidden by symmetry considerations, whereas for the s-cis conformation they should be allowed. Mulliken concluded that butadiene must exist almost entirely in the s-trans conformation. Careful study of the spectrum of butadiene has revealed the existence of a weak series[91] corresponding to that expected for s-cis butadiene. Rasmussen, Tunnicliff and Brattain[92] have argued that infra-red and Raman spectroscopy indicate butadiene to be mostly s-trans but with a large proportion of s-cis at room temperature, but this conclusion seems to be at variance with thermodynamic data[93]( which indicate the presence of only about 4% of the s-cis form at room temperature), electron impact data[70]

and high resolution spectroscopy.[91] Ultra-sonic relaxation data indicate less than 2% of butadiene to be s-cis at room temperature.[47] Further, but weaker evidence for the s-trans conformation of butadiene is provided by the observation[94] that the dipole moment of butadiene is zero, whereas the s-cis conformer would be expected to have a small but appreciable moment. However, the energy barrier between the two conformations is small, estimated at 5 kcals per mole, and the energy difference between the two conform-ations is estimated at 2.5 kcals per mole.[44]

Electron diffraction studies indicate the central C-C bond in butadiene to be only 1.46 A long, compared with 1.54 A for a single bond in ethane and 1.33 A for a double bond in ethylene; this indicates a small amount of double bond character in the central bond, and this is supported by the existence of a small but appreciable resonance energy in butadiene and its derivatives. In butadiene the resonance energy as measured by heat of hydrogenation is 3.5 kcals per mole.[27] One would therefore expect resonance energy to maintain the molecule in a planar s-trans conformation.

The excited state is assumed to be $+CH_2-CH=CH-CH_2-$, though this will be only a limiting form, the transition being perhaps from one containing 45% of the ionic form to one contain-ing 55%. Thus steric hindrance to planarity should be little different in ground and excited states.

Woodward[65] drew up empirical rules relating structure and wavelength of maximal absorption. He quoted a figure of 217 mμ for the wavelength of maximal absorption of butadiene in ethanol, with a bathochromic displacement of 5 mμ per alkyl group. The presence of a ring was found to have no effect other than its normal substitutive effect, except that each exocyclic double bond gave a further bathochromic displacement of 5 mμ. In the case of an unsymmetrically substituted diene the wavelength of maximal absorption could be calculated by averaging that of two symmetrically substituted dienes.

In polycyclic compounds[95] the wavelength of maximal absorption is dependent on whether the double bonds in conjugation are in one ring or two. With one exocyclic double bond, as in allylidenecyclohexane[95], the absorption intensity is low, but with two exocyclic double bonds $\varepsilon_{max}$ again rises. The reason for this phenomenon is obscure.

It is noteworthy that the wavelength displacement per methyl group in the diene series is half that found for α,β-unsaturated carbonyl compounds. Woodward explained this as being due to the presence of two C:C bands in the former and only one in the latter. This explanation appears to presuppose that the B-band in α,β-unsaturated carbonyl compounds is a displaced ethylene band. This conclusion is hard to reconcile with the present ascription of a B band to a transition involving the entire conjugated system, an ascription supported by the insensitivity to substitution of the same band in semicarbazones and 2,4-dinitrophenylhydrazones[96], and its displacement to longer wavelengths in dienones[17]. The

The present author postulates that the difference can be rationalised by considering the presence of a large permanent dipole moment in $\alpha,\beta$-unsaturated carbonyl compounds. The negative end of the dipole is on the carbonyl oxygen atom, and the positive end on the terminal carbon atom. In the excited state, each partial charge will be increased. A methyl group may share these charges by an inductive, hyperconjugative, or field mechanism, and hence separation of charge will be relatively easy. In dienes there is only a small permanent dipole moment, and therefore excitation may take place to give the positive charge at either end of the molecule (cf [69]). The charge-sharing mechanism postulated above will be operative in only half the excited states, and hence only half the wavelength displacement would be expected. In piperylene, for example, the excited state would have contributions from $+CH_3.CH:CH:CH.CH_2-$ and $CH_3.\overset{-}{C}H.CH:CH.CH_2+$. Some evidence in support of this mechanism is provided by the large wavelength displacement on introducing a second methyl group on the $\gamma$-carbon atom of piperylene. (See Table X). 4-methyl-1,3-pentadiene will have a larger dipole moment than other simple alkyl-substituted dienes, and hence absorption of light may take place to give the positive end of the dipole on the gem dimethyl group. Thus the absorption of 4-methyl-1,3-pentadiene should simulate that of an $\alpha,\beta$-unsaturated aldehyde or ketone. This conclusion is supported by the rather poorly defined fine structure of the spectral curve of 4-methyl-1,3-pentadiene.

The general accuracy of Woodward's rules is substantiated

by the present work (see Table X for absorption spectra of dienes)
with one important exception. Precisely as observed for aldehydes
and ketones (Parts III and IV) a second terminal methyl group
gives a much larger bathochromic wavelength displacement than the
first. Butadiene absorbs in ethanol at 217.5 m$\mu$, piperylene in
ethanol at 223 m$\mu$, and 4-methyl-1,3-pentadiene in ethanol at
232.5 m$\mu$. The very large wavelength displacement between piperylene
and 4-methyl-1,3-pentadiene does not appear to have been observed
previously, though in a semi-empirical relation between $\lambda_{max}$ and
substitution, Hirayama used[97] a factor of 0.13 for R and 0.17 for

R' in $\begin{matrix} R \\ R' \end{matrix} C=$

Similar large displacements are observed in the vapour phase.
Data published by Shell[98] show that trans-piperylene in the vapour
phase has $\lambda_{max}$ 213 m$\mu$, cis-piperylene 216 m$\mu$, and 4-methyl-1,3-
pentadiene $\lambda_{max}$ about 222 m$\mu$. A partial explanation has been given
above, and one may add that equivalent resonance forms involving
both terminal methyl groups, as in the case of aldehydes and ketones
(see Parts III and IV) will lower the energy of the excited state.
It is interesting to note that the extinction coefficient of 4-
methyl-1,3-pentadiene is somewhat lower than that of piperylene,
and this may be due to the approximation to an unsaturated aldehyde
suggested above, or it may be due to slight steric interaction of
the type postulated for $\beta$-methylcrotonaldehyde (Part III).

If the interpretation given above in terms of dipole
moments is correct there should be only a small wavelength displace-
ment between 2-methyl-2,4-hexadiene and 2,5-dimethyl-2,4-hexadiene,

since the former should have a dipole moment little different from that of piperylene, and the latter should have zero dipole moment. Unfortunately, attempts to prepare 2-methyl-2,4-hexadiene gave inconclusive results (see experimental portion, Part VI).*

It is noteworthy that no wavelength displacement is observed between 4-methyl-1,3-pentadiene and 2,4-dimethyl-1,3-pentadiene (see Table X). The very low absorption intensity of the latter compound should be noted. Scale diagrams, using the inter-ference radii proposed by Forbes and Mueller, indicate the s-trans conformation of 2, 4-dimethyl-1,3-pentadiene to be greatly hindered, and the s-cis conformation only slightly less so. (see Figure 20). Hence it is probable that 2,4-dimethyl-1,3-pentadiene [$(CH_3)_2C$; $CH.C(CH_3):CH_2$ ] exists in a non-planar s-cis conformation, and that the steric effect is type II. (It seems reasonable to treat displacements of less than 5 mμ as significant in this series). Relative to 2-methyl-1,3-pentadiene [ $CH_3.CH:C(CH_3):CH$ ] for which $\lambda_{max}$ in isooctane[98] is 227 mμ, $\epsilon_{max}$24,500, the wavelength displacement is the usual 5 mμ. Confirmation of the assignment of a type II effect is provided by the absorption of 1,1-dimethyl-3-t-butyl-1,3-butadiene (see Table X) at even shorter wavelengths (225 mμ in both ethanol and cyclohexane) and with even lower intensity. In the latter compound, increased steric hindrance causes a type II steric effect relative to 2,4-dimethyl-1,3-penta-diene. Assuming 4-methyl-1,3-pentadiene to be essentially planar,

* Zingiberene, usually formulated    might be thought to provide an acceptable approxi-mation but this is vitiated by the demonstration (Refs.99,100) that its formula is actually

Braude's relation $\varepsilon/\varepsilon_o = \cos^2 \theta$ indicates the interplanar angle in 1, 1-dimethyl-3-$t$-butyl-1,3-butadiene to be 58°, not far from the 67° at which resonance energy is calculated to become negligible

Scale diagrams of isoprene show the methyl group and remote hydrogen atom to be just touching. The dipole moment of isoprene is reported[94] to be 0.38 Debye, very close to that of propylene. This is attributed[94] to the contribution of resonance forms of the type $-CH_2-C-CH=CH_2$.

$$CH_2 + H$$

This might impose a slight tendency to an s-cis conformation, but it will probably be less than the tendency of a diene system to assume an s-trans conformation.

In 2,3-dimethyl-1,3-butadiene, $[CH_2:C(CH_3).C(CH_3):CH_2]$ on the other hand, the effect of steric hindrance at both ends of the molecule will lead to moderately large van der Waals repulsive forces, and hence to a considerable tendency to assume an s-cis conformation. Since there is no terminal methyl group to stabilise a planar conformation, the diene would be expected to show a somewhat lower absorption intensity than a diene of fixed s-cis or s-trans conformation, and as Table X shows, 2,3-dimethyl-1, 3-butadiene does exhibit a somewhat lower molecular extinction coefficient than other dienes, apart from those exhibiting considerable steric hindrance. The resonance energy of 2, 3-dimethyl-1, 3-butadiene, as measured by heat of hydrogenation[27] is 2.9 kcals per mole, lower than that of either butadiene or piperylene. This is consistent with a conformation which is to some extent non-planar s-trans. Dipole moment data are also of interest. The dipole moment of isoprene is 0.38 Debye, that of 2,3-dimethyl-1,3-butadiene

is 0.52 Debye.[94]  If 2,3-dimethyl-1,3-butadiene were s-trans it
should have zero dipole moment: if it were s-cis it should have a
moment twice that of isoprene.  Dipole moment data therefore
favour a conformation predominantly, but not exclusively, s-cis.

In 3,4-dimethyl-1,3-pentadiene $[(CH_3)_2 C:C(CH_3).CH:CH_2]$
the high value of $\varepsilon_{max}$ would suggest that the compound exists
predominantly in the s-trans conformation.  It is surprising that
$\lambda_{max}$ for this compound is the same as that for 4-methyl-1,3-penta-
diene.  A possible explanation is that crowding of methyl groups
round the ethylenic bond (cf.[101]) causes an increase of the $CH_3.C.CH_3$
angle, with consequent steric hindrance of the hydrogen atom on
carbon 2.  This in turn would cause a type II steric effect.  An
alternative explanation would be that resonance forms involve
either the terminal methyl groups or the methyl group on carbon 3,
but the same effect would be expected to be operative in tri-
substituted $\alpha,\beta$-unsaturated aldehydes and ketones.

The author prefers to assign the effects to an inductive
mechanism.  The inductive effect of the terminal methyl groups
will give a high density of electrons in the 3,4 olefinic bond
which may repel electrons into the 3-methyl group, which will
therefore be unable to exert its usual inductive and hyperconjugative
effects.  Some support is afforded by the observation that 1-t-butyl
1,3-butadiene in ethanol has $\lambda_{max}$ 224 m$\mu$, $\varepsilon_{max}$ 25,000[102] only 1 m$\mu$
different from piperylene.  This could not be explained readily in
terms of hyperconjugative effects.  If additional methyl groups
were added to the other end of the conjugated chain in 4-methyl-1,
3-pentadiene they would be in a region of lower electron density

and would exert inductive and hyperconjugative effects as usual.
An interesting parallel to the hypothesis that inductive effects
are important in determining the spectra of these compounds is
provided by spectroscopic ionisation potential data.[103] s-trans
Butadiene has an ionisation potential of 9.022 v, isoprene of
8.805 v, and 2,3-dimethyl-1,3-butadiene of 8.668 v. The lowering
between isoprene and 2,3-dimethyl-1,3-butadiene is less than that
between butadiene and isoprene, attributed[103] to transfer of
negative charge from the methyl group to the double bond. Although
not strictly analogous, Price and Tutte have found[104] that the
small change in heat of hydrogenation between tri- and tetra-
methylethylene may be attributed to transfer of negative charge
to the double bond with, presumably, less transfer as the electron
density in the double bond increases.

The high absorption intensity of piperylene and the
"normal" value of the wavelength displacement relative to butadiene
suggests that piperylene exists in the s-trans conformation, as
would be expected. This is supported by the high dipole moment
of piperylene,[94] 0.68 Debye. Further evidence for the large
contribution of hyperconjugation to the resonance energy is
provided by the resonance energy as determined by heat of hydrogen-
ation,[27] namely 4.2 kcals per mole as compared with 3.5 kcals per
mole for 1,3-butadiene. On the other hand, evidence has been
presented above that inductive effects are also of importance in
determining ultra-violet spectra.

The piperylene used in the present work was probably a
mixture containing 13% cis isomer.[59] The infra-red spectrum

showed bands at 1600 cm.$^{-1}$ $\varepsilon^a$ 48; and 1652 cm.$^{-1}$ $\varepsilon^a$ 47. The low value of the olefinic frequencies, and their comparatively high intensities, support the allocation of considerable resonance energy to piperylene. In this connection it may be mentioned that 2,4-dimethyl-1,3-pentadiene, shown to be sterically hindered (vide supra) shows three olefinic bands, at 1600 cm.$^{-1}$, $\varepsilon^a$ 12; 1628 cm.$^{-1}$ $\varepsilon^a$ 31; and 1653 cm.$^{-1}$, $\varepsilon^a$ 18. There appears to be no ready explanation for the presence of three frequencies, but the low values of $\varepsilon^a$ are consistent with steric hindrance of resonance.

Hexa-2,4-diene showed a band in the infra-red at 1653 cm.$^{-1}$ $\varepsilon^a$9. The all-trans isomer should have no band in this region so it is probable that the compound contained a little cis-trans or less probably, cis-cis, isomer. It would be expected to exist as the s-trans conformer, and this is borne out by the high absorption intensity. Similarly one would expect 2,5-dimethyl-2, 4-hexadiene to exist in the s-trans conformation and the ultra-violet spectrum provides no reason to doubt this. The wavelength displacement between hexadiene and piperylene is rather small, 3 mμ in ethanol and 2.5 mμ in cyclohexane. On the other hand, the displacement between 2,5-dimethyl-2,4-hexadiene and 4-methyl-1, 3-pentadiene is, as expected, an average of 5 mμ per methyl group. On the other hand the displacement between 2,5-dimethyl-2,4-hexadiene and 2,4-hexadiene is high at an average of 8 mμ per methyl group. It is unfortunate that figures for 2-methyl-2,4-hexadiene are not available (see experimental). The available figures suggest that wavelength displacement is a function of

saturation of the $\pi$ electron system by electrons, but no more
quantitative conclusions can be drawn at present.

Precisely as in the case of $\alpha,\beta$-unsaturated aldehydes
(Part III) there are indications that an alkyl group cis to the
bond joining the vinyl moieties produces a greater bathochromic
wavelength than one trans. Jacobs and Platt,[59] also Shell[98] workers
have determined the spectra of the individual geometrical isomers
of piperylene. Unfortunately Jacobs and Platt were not able to
use pure geometrical isomers for all measurements, but they found
cis piperylene to absorb (in n-heptane) at $\lambda_{max}$ 226 m$\mu$, $\varepsilon_{max}$ 22,000,
and trans piperylene (in n-heptane) with $\lambda_{max}$ 223 m$\mu$, $\varepsilon_{max}$ 26,000.
These figures, together with Breiding and Pratt's data[87] on angelic
and tiglic acids (see Part III) support the view that a cis
methyl group gives a larger bathochromic wavelength displacement
than a trans group. Jacobs and Platt claimed only a slight
difference in intensity of absorption between the two isomers,
but $\varepsilon_{max}$ for the cis compound appears to be somewhat lower than
for the trans isomer. This may be attributed to slight steric
hindrance between the methyl group and hydrogen atom on carbon 2.
Against the hypothesis that a cis methyl group gives a larger
displacement than a trans group may be cited 1-vinylcyclohexene
($\lambda_{max}$ 230 m$\mu$) and 2-methyl-1-vinylcyclohexene ($\lambda_{max}$ 233 m$\mu$),[95] where
the methyl group is cis to the vinyl group and the wavelength
displacement is only 3 m$\mu$. The present author believes a re-exam-
ination of these figures would be valuable. Attention has been
drawn (vide supra) to Hirayama's empirical relation.

The cyclic dienes appear to be very different from acyclic compounds. When there is only one exocyclic double bond the absorption intensity is low (e.g. allylidenecyclohexane in ethanol has $\lambda_{max}$236.5 m$\mu$, $\epsilon_{max}$7,700 [95]). However, with two cyclic substituents absorption intensities rise to figures comparable with those of acyclic dienes.[95] This is difficult to reconcile with the high absorption intensity of 4-methyl-1,3-pentadiene.

The absorption spectra of cyclic dienes are of interest. Cyclopenta-1,3-diene in hexane absorbs at the surprisingly long wavelength of 238.5 m$\mu$, and with the surprisingly low intensity of 3,400.[51,104] Cyclohexa-1,3-diene in hexane has $\lambda_{max}$ 256 m$\mu$ (in hexane) $\epsilon_{max}$ 7,950.[105] These figures appear to support the hypothesis[74] that an s-cis compound will have a lower absorption intensity than an s-trans compound, but the present author prefers another explanation. Barton models show that cyclopentadiene exists in a highly strained planar configuration, which will be relieved somewhat on excitation, leading to a bathochromic wavelength displacement relative to 2,4-hexadiene. Models show 1,3-cyclohexadiene to exist in a non-planar conformation with interplanar angle about 20°. The non-planarity will account for the low intensity of absorption. The resonance energy of cyclopenta-1,3-diene is estimated[27] at 2.9 kcals per mole, and that of 1,3-cyclohexadiene at 1.8 kcals per mole. These figures support the view that there is less resonance energy in the cyclic compounds considered than in acyclic dienes, and the author ascribes to them a high proportion of ionic forms even in the ground state.

It is interesting to note that cyclopentadiene and cyclohexadiene do not show optical exaltation.[106] The ionisation potentials of cyclopentadiene (8.62 v) and 1, 3-cyclohexadiene (8.4 v) are lower than that of s-cis butadiene[70] (8.75 v) since the $\pi$ electrons are less firmly bound in the cyclic compounds than butadiene. As the ring size of a cyclic conjugated diene increases from six members to nine, $\lambda_{max}$ moves to shorter wavelength and $\varepsilon_{max}$ decreases: as the ring size then increases $\lambda_{max}$ moves to longer wavelengths and $\varepsilon_{max}$ increases.[96] This may also be correlated with the angle between the olefinic bonds. Barton models show that as ring size increases from cyclohexadiene to cyclononadiene the most favourable conformation is one in which the angle between the olefinic bonds is large, increasing to nearly 90° in cyclonona-1,3-diene. In larger rings the angle decreases. The effect of strain is also evident in 1,2-dimethylenecycloalkanes. In 1,2-dimethylenecyclobutane $\lambda_{max}$ (in hexane) is 237 m$\mu$, $\varepsilon_{max}$ 9,750, in 1,2-dimethylenecyclopentane (in hexane) $\lambda_{max}$ < 220 m$\mu$, and in 1,2-dimethylenecyclohexane (in hexane) $\lambda_{max}$ = 220 m$\mu$, $\varepsilon_{max}$ = 10,000.[107] These figures are related to the strain, since 1,2-dimethylenecyclobutane is highly strained, and the others only slightly strained[107] (Cf.[69]).

Table X shows that there is very little difference in the wavelength of maximal absorption in ethanol and cyclohexane (Cf.[95]). However, when there is a displacement, it is to longer wavelength in cyclohexane relative to ethanol, except in the case

of 2,4-dimethyl-1,3-pentadiene. This is the reverse of the order observed for α,β-unsaturated aldehyde and ketones. Attempts to explain the effect of solvent on absorption spectra have predicted that a non-polar molecule should absorb at the same wavelength in both polar and non-polar solvents (e.g.[108,109]) although a more recent theory has attempted to explain shifts in terms of polarizability of solvent and solute.[62] Since some of the dienes have a small but appreciable dipole moment one would expect either no change in wavelength with solvent or a displacement in the same direction as found for aldehydes and ketones.

The following hypothesis is tentatively proposed to account for the changes observed. In a polar molecule in a polar solvent, molecules of solvent will tend to attach themselves to molecules of solute (Cf.[109]) and so encourage separation of charge in both ground and excited states. Excitation will take place only in the direction of increasing the pre-existing formal charges at each end. In a non-polar solute, such as a conjugated diene, excitation may take place in either direction (Cf.[69]). In half the possible excited states excitation will lead to juxtaposition of like charges on solute and solvent molecule - this may even be the preferred conformation - requiring greater energy than would be required in the absence of such an effect. This would give rise to a slight hypsochromic displacement in a polar solvent. This suggestion has also been made by McConnell,[108] though with reference to different solutes. In some recent papers Kosower[110,111] has pointed out the importance for spectral effects of the propertie

of the "cybotactic" region of solvent molecules around each solute molecule, rather than bulk properties of solvent, such as dielectric constant. The same author has also pointed out that solvent-solute interaction may differ greatly in ground and excited states, since solvent molecules will not have time to rearrange to the most favourable configuration for the excited state.

## Fine Structure in the Spectra of Dienes and Polyenes

The most striking feature of the spectra of most dienes is the presence of a triple peak (see Figures 17, 18 and 19). The central one is usually sharp and always of highest intensity, the peak to the short wavelength side is well-marked but of somewhat lower intensity, and the peak to the long wavelength side is poorly marked and of still lower intensity. This triple peak has been noted for chlorobutadienes[112], polyenes containing one or more cis linkages (but not those which are all-trans),[113] trans-trans 1,4-diphenylbuta-1,3-diene,[114,115] certain biphenyls[116] and moderately strained cyclophanes.[22] In each of the latter two and the polyenes, the bands occur at longer wavelengths than in the dienes.

In the case of the dienes this fine structure has been attributed to vibrational sub-levels of energy,[103, 117] but no assignments of the vibrations have been made. The present author proposes to refer to the peaks in order of increasing wavelength as $B^-$, $B$, and $B^+$. In the vapour phase the fine structure is well-resolved (cf. spectra of trans piperylene and isoprene)[98] but for the present solution spectra, resolution into distinct peaks

could not be obtained, B⁻ being present as an inflection and B⁺ as a shoulder or inflection. The author believes the presence of this type of curve to be diagnostic of a conjugated diene, though care would be needed to distinguish the curve from the similar one given by a conjugated enyne.[51] On the other hand, the absence of this type curve does not prove the absence of conjugated olefinic linkages. (Vide infra).

Table XI shows that the spacings of the peaks are remarkably constant, the wavelength of B minus wavelength of B⁻, being 4.5 mμ to 5 mμ in ethanol, and wavelength of B+ minus wavelength of B being 6 mμ in ethanol. In cyclohexane the corresponding figures are 5 and 7 mμ. Table XI also shows that the ratio of intensities of the bands for compounds listed there is quite constant, at intensity of B⁻ / intensity of B = 0.90± 0.02 in ethanol, and intensity of B⁺ / intensity of B = 0.74± 0.09. In cyclohexane the agreement is even better, the corresponding figures being 0.91± 0.02, and 0.73± 0.03. Part of the wider tolerance for the ratio of B⁺ to B may be accounted for by the difficulty of picking out this weak inflection, and the sensitivity of the curve in this region to a slight error. The spacing is the same for cyclic dienes[117] so the fine structure cannot be attributed to s-cis, s-trans isomerism. Table X and Figures 17, 18 and 19 show that in some compounds, particularly where considerable steric hindrance has been deduced such as 2, 4-dimethyl-1,3-penta-diene; 1,1-dimethyl-3-t-butyl-1,3-butadiene; and 2,3-dimethylbuta-1,3-diene, the fine structure is very poorly marked or not present at all. Cyclopentadiene in isooctane shows no trace of fine

structure[98] and _trans_ piperylene in both vapour and _isooctane_ shows much better developed fine structure than _cis_ piperylene.[98] It is therefore surprising to find that 4-methyl-1,3-pentadiene in solution (Figure 17) and vapour[98] shows little trace of fine structure.

In _all_-_trans_ polyenes with _multiple_ olefinic bonds there is no similar triple peak, but when a _cis_-linkage, and therefore steric hindrance, is introduced the typical structure appears. Published figures[114,118] _cf_.[96] seem to show that $B^-$, B, and $B^+$ are present in _all_-_trans_ compounds, but $B^+$ is more intense than $B^-$. As _cis_ linkages are introduced the intensity of $B^-$ increases and that of $B^+$ decreases until the characteristic triple peak is evident. A highly hindered polyene may not show the triple peak.[77]

1,4-diphenyl-1,3-butadiene in hexane shows the triple peak well when the compound is _trans_-_trans_, but this structure disappears on irradiation with ultra-violet light,[114] presumably owing to the formation of highly hindered _cis_ isomers. The structure is, however, restored on addition of iodine.[114] Similar effects of geometrical isomerism have been observed for 1,4-dinaphthyl-1,3-butadienes.[119]

Dorfman[117] has reviewed the spectral properties of steroids and has pointed out that a similar triple peak is shown by many, but not all, steroids with conjugated olefinic linkages. Here too $B^+$ has a lower intensity than B or $B^-$. According to Dorfman the spacings of the peaks are: in heteroannular dienes, -7 and +8 mμ; in homoannular dienes -10 and +12 mμ, and in trienes - 13 and + 15 mμ. These figures should be compared with the author's of -5 and +6 or 7 mμ. It appears that there are signifi-cant differences between olefinic linkages in ring systems and

those in alicyclic systems, as has been discussed above for 1,3-cyclohexadiene.

In the case of substituted biphenyls[116,120] the triple peak becomes more marked as steric hindrance is increased, suggesting that this band (at about 260 mμ) is due to a transition involving only a part of the benzene ring, since 1,3-cyclohexadiene in hexane absorbs maximally at 256.5 mμ[105].

A triple peak similar to that characteristic of dienes is shown by the C band of p-iodophenol[121] the maxima occuring at 273.5, 279.5 and 288 mμ (the latter as an inflection). The intensities are respectively, 1280, 1430 and 1090. The wide spacing is characteristic of a heteroannular diene[117] but the ratio of intensities is in perfect agreement with that found by the present author for acyclic dienes. This appears to support the ascription of this band to transitions involving only the benzenoid moiety[9].

The presence of fine structure renders comparison of half-band widths difficult, but Table XII shows that half-band widths measured to both long and short wavelength sides shows broadening in the case of compounds thought to be sterically hindered.

## TABLE X

ULTRA-VIOLET ABSORPTION SPECTRA OF CONJUGATED DIENES

| Compound | Solvent: ETHANOL | | | CYCLOHEXANE | | |
|---|---|---|---|---|---|---|
| | $\lambda_{max}(m\mu)$ | $\lambda_{infl}(m\mu)$ | $\varepsilon_{max}$ or $\varepsilon_{infl}$ | $\lambda_{max}(m\mu)$ | $\lambda_{infl}(m\mu)$ | $\varepsilon_{max}$ or $\varepsilon_{infl}$ |
| 1,3-Butadiene | 217.5 | | 22,400 | 218.5 | | 23,000 |
| $CH_2{:}CH.CH{:}CH_2$ | | 212.5 | 19,600 | | 214.5 | 21,000 |
| | | 223.5 | 15,500 | | 225 | 16,000 |
| Isoprene | 222.5 | | 22,800 | 223 | | 26,000 |
| | | 218 | 20,800 | | 218 | 23,400 |
| $CH_2{:}C(CH_3).CH{:}CH_2$ | | | | | 230 | 17,500 |
| Piperylene $CH_3.CH{:}CH.CH{:}CH_2$ | 223 | | 25,500 | 224 | | 26,400 |
| 4-Methyl-1,3-pentadiene | 232.5 | | 22,400 | 234 | | 23,000 |
| $(CH_3)_2C{:}CH.CH{:}CH_2$ | | | | | 229 | 21,400 |
| 2,3-Dimethyl-1,3-butadiene | 226 | | 20,300 | 227.5 | | 22,000 |
| $CH_2{:}C(CH_3).C(CH_3){:}CH_2$ | | 222 | 18,700 | 223 | | 20,000 |
| 2,4-Hexadiene | 226 | | 23,800 | 226.5 | | 24,000 |
| | | 222 | 21,100 | | 222 | 22,200 |
| $CH_3.CH{:}CH.CH{:}CH.CH_3$ | | 232 | 19,800 | | 234 | 17,700 |
| 2,4-Dimethyl-1,3-pentadiene | 232.5 | | 10,000' | 230.5 | | 9,900 |
| $(CH_3)_2C{:}CH.C(CH_3){:}CH_2$ | | 230 | 9,900 | | 228 | 9,800 |
| | | | | | 237 | 9,200 |
| 3,4-Dimethyl-1,3-pentadiene | 231.5 | | 19,200 | 232.5 | | 19,800 |
| | | 227 | 17,700 | | 227.5 | 18,100 |
| $(CH_3)_2C{:}C(CH_3).CH{:}CH_2$ | | 241 | 12,500 | | 240 | 14,000 |
| 2,5-Dimethyl-2-4-hexadiene | 241 | | 24,300 | 242 | | 24,000 |
| | | 236 | 22,400 | | 237 | 22,000 |
| $(CH_3)_2C{:}CH.CH{:}C(CH_3)_2$ | | 247 | 19,000 | | 248 | 18,200 |

TABLE X (continued)

| | | | | | |
|---|---|---|---|---|---|
| 1,1-Dimethyl-3-t-butyl-1,3-butadiene | 225 | 6,400 | 225 | | 6,600 |
| $(CH_3)_2C{:}CH.C(Bu){:}CH_2$ | | | | | |
| "2-Methyl-2,4-hexadiene" * | 227.5 | 23,300 | 229 | | 24,300 |
| | 222 | 20,700 | | 223.5 | 21,500 |
| | 234 | 17,200 | | 235 | 17,400 |

\* See experimental part.

## TABLE XI

RELATIONSHIPS BETWEEN ABSORPTION MAXIMA AND INFLECTIONS
OF CONJUGATED DIENES

| Compound | Solvent: ETHANOL | | | | CYCLOHEXANE | | | |
|---|---|---|---|---|---|---|---|---|
| | $\lambda_B - \lambda_{B-}$ | $\lambda_{B+} - \lambda_B$ | $\varepsilon_{B-}/\varepsilon_B$ | $\varepsilon_{B+}/\varepsilon_B$ | $\lambda_B - \lambda_{B-}$ | $\lambda_{B+} - \lambda_B$ | $\varepsilon_{B-}/\varepsilon_B$ | $\varepsilon_{B+}/\varepsilon_B$ |
| 1,3-Butadiene | 5 | 6 | 0.88 | 0.69 | 4 | 6.5 | 0.91 | 0.70 |
| Isoprene | 4.5 | - | 0.91 | - | 5 | 7 | 0.90 | 0.7 |
| 4-Methyl-1,3-pentadiene | - | - | - | - | 5 | - | 0.93 | - |
| 2,3-Dimethyl-1,3-butadiene | 4 | - | 0.92 | - | 4.5 | - | 0.91 | - |
| 2,4-Hexadiene | 4 | 6 | 0.89 | 0.83 | 4.5 | 7.5 | 0.93 | 0.74 |
| 2,4-Dimethyl-1,3-pentadiene | 2.5 | - | 0.99 | - | 2.5 | 6.5 | 0.99 | 0.93 |
| 3,4-Dimethyl-1,3-pentadiene | 4.5 | 9.5 | 0.92 | 0.65 | 5 | 7.5 | 0.91 | 0.71 |
| 2,5-Dimethyl-2,4-hexadiene | 5 | 6 | 0.92 | 0.78 | 5 | 6 | 0.92 | 0.76 |
| "2-Methyl-2,4-hexadiene"* | 5.5 | 6.5 | 0.89 | 0.75 | 5.5 | 6 | 0.89 | 0.72 |

* See experimental part.

### TABLE XII

#### HALF-BAND WIDTHS OF CONJUGATED DIENES

| Compound | Half-band width to long wavelength. | Half-band width to short wavelength. |
|---|---|---|
| Butadiene-1,3 | 10 | 13 |
| Piperylene | 9 | 18 |
| Isoprene | 9 | 14 |
| 2,3-Dimethyl-1,3-butadiene | 10 | 15 |
| 4-Methyl-1,3-pentadiene | 10 | 19 |
| 2,4-Hexadiene | 11 | 18 |
| 2,4-Dimethyl-1,3-pentadiene | 15 | 21 |
| 1,1-Dimethyl-3-t-butyl-1,3-butadiene | 18 | (20) |
| 2,5-Dimethyl-2,4-hexadiene | 12 | 19 |
| 3,4-Dimethylpenta,1,3-diene | 12 | 16 |
| "2-Methyl-2,4-hexadiene" * | 10 | 16 |

* See experimental part.

All measurements are in cyclohexane and are to the nearest mµ.

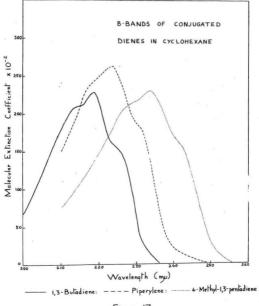All measurements are made from wavelength of maximal absorption.

Figure 17

Figure 18

B-BANDS OF CONJUGATED DIENES IN CYCLOHEXANE

Molecular Extinction Coefficient × 10⁻²

Wavelength (mμ)

—— Isoprene : - - - - 2,3-Dimethyl-1,3-butadiene

· · · · · 2,4-Dimethyl-1,3-pentadiene : –·–·– 1,1-Dimethyl-3-t-butyl-1,3-butadiene
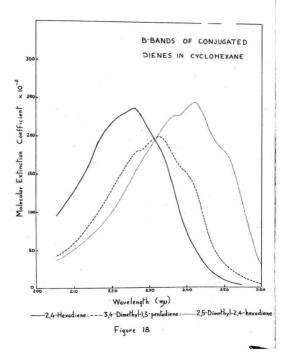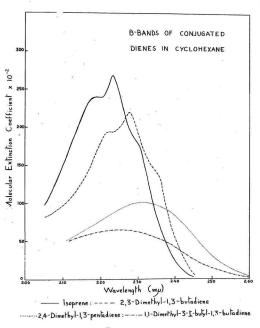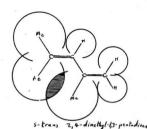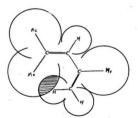
Figure 19

s-trans 2,4-dimethyl-1,3-pentadiene



s-cis 2,4-dimethyl 1,3-pentadiene

Figure 20

PART VI

## Experimental

All ultra-violet spectra were determined at least in duplicate on a Unicam SP500 spectrophotometer, using 1 cm. cells for ethanolic solutions, and 2mm. cells for cyclohexane solutions. Occasional use of 2mm. cells for ethanol solutions and 1 cm. cells for cyclohexane solution showed no difference in the wavelength or intensity of maximal absorption. Replication was continued until values of intensity were in agreement to 5% or better: in most cases agreement to 2% or better could be obtained. Some values were also determined on a Beckman DU spectrophotometer, and good agreement was obtained.

Most of the spectra have been recorded previously, but the present author's values are frequently in disagreement with recorded values: many of the intensities are considerably higher than previously recorded values, particularly in the $\alpha,\beta$-unsaturated aldehydes and ketones. The purity of many compounds was determined by analysis, and the present author's values are in good agreement with recent recorded values when such are available. Molecular extinction coefficients are believed to be accurate to $\pm$ 2%, and wavelengths of maximal absorption are precise to 0.5 m$\mu$. The accuracy of wavelength, by comparison with figures of other authors, appears to be $\pm$ 1 m$\mu$.

Weighing into a stoppered weighing bottle was found to give variable results. The technique finally adopted was a modification of that of Forbes and Mueller.[52] A stoppered 50 ml. volumetric flask containing approximately 15 mls. solvent was weighed, then one drop (8-12 mgm.) of liquid added and the flask and contents reweighed. The flask was then filled to the graduation mark and shaken vigorously. Appropriate portions (1,2,5,10, or 25 mls.) were withdrawn and made up to 100 mls. with solvent, the concentration being chosen so as to give an optical density between 0.3 and 0.7. In order to minimise errors due to unmatched cells all spectra were determined with cells reversed and mean optical densities taken.

It has been claimed[33] that unsaturated aldehydes react rapidly with ethanol to form hemiacetal. A solution of croton-aldehyde in ethanol showed no loss in intensity on standing for 24 hours, and only 3% loss of intensity on standing for 14 days. This would suggest that either no formation of hemiacetal takes place, or that reaction takes place very rapidly and proceeds to equilibrium within a few minutes. The former explanation is favoured, since addition of one drop of dilute hydrochloric acid gave an immediate decrease of intensity. Addition of further drops of acid gave a small increase in intensity. On the other hand, a solution of acrolein in ethanol showed a great drop in intensity after 7 days, as found also by Buswell, Dunlop, Rodebush and Swartz.[123]

The determination of the absorption spectra of α,β-unsaturated ketones is rendered more difficult by the observations that many exist as a mixture of conjugated and unconjugated isomers which are very difficult to separate on the laboratory scale. (e.g. mesityl oxide). Cf.[73,124,125]

Sources of chemicals are given below. All except β-methylcrotonaldehyde were distilled from hydroquinone immediately before use. Constants after distillation were in good agreement with recorded data except where otherwise stated.

## α,β-Unsaturated Aldehydes

Acrolein. Eastman Kodak Co. product was used. B.p. 51°, 769 mm.; $n_D^{24.5}$ 1.3974

Crotonaldehyde. Eastman Kodak Co. product. B.p. 26°, 30 mm., $n_D^{25}$ 1.4347

β-Methylcrotonaldehyde. Kindly supplied by Messrs. Hoffman-La-Roche and Co., Basle, Switzerland. $n_D^{20}$ 1.4548
This compound furnished a 2,4-dinitrophenylhydrazone in over 90% yield.

α-Methacrolein. Carbide and Carbon Chemicals Co. product.
After quick distillation from hydroquinone it had b.p. 62°, 752 mm., $n_D^{22}$ 1.4100. Slow distillation appeared to give polymeric material. Reported constants vary widely, Rogers[82] reports b.p. 66.5°, 752 mm., $n_D^{25}$ 1.4098.

<u>Tiglaldehyde</u>. (Tiglinaldehyde). Eastman Kodak Co. product.
B.p. 49°, 76 mm., $n_D^{20}$ 1.4480. The present author's
value for $\varepsilon_{max}$ is much higher than that recorded by
Gillam and Evans[68] ($\varepsilon_{max}$ >5,000) but the latter authors
admitted the compound used to be impure.

<u>2,3-Dimethylbut-2-enal</u>. This compound was prepared by the method
of Braude and Evans.[126] Only impure material could be
isolated. The material was converted into semicarbazone
which after crystallisation from methanol had m.p.
229-231° (Braude and Evans[126] give 239-240°). This was
steam distilled with potassium hydrogen phthalate, but
no aldehyde could be recovered from the distillate.

   The absorption spectrum of the impure material was
determined, and found to be, in ethanol, $\varepsilon_{max}$ 10,700 and
in cyclohexane $\varepsilon_{max}$ 11,200. Formation of 2,4-dinitro-
phenylhydrazone followed by chromatographic analysis
showed the material to be 82% pure. Values of $\varepsilon_{max}$
given by Braude and Evans,[126] and also by Waight and
Erskine[39] indicate the material to be 83% pure. Values
given in Table V and Figure 11 are estimated using this
figure.

<u>Cyclohexylideneacetaldehyde</u>. This compound was kindly supplied
by Professor M. Viscontini, of Zürich University.
Redistillation afforded material b.p. 104°, 25 mm.,
$n_D^{22}$ 1.4980. Dimroth[127] gives b.p. 86-92°, 13.5 mm.,
but no comparison figure for refractive index was

available. 2,4-Dinitrophenylhydrazone analysis showed
the redistilled material to be 75% pure, from which it
was concluded that the material had partly decomposed
during transit. Comparison of the observed value of $\varepsilon_{max}$
in ethanol, (12,600) with the figure given by Aldersley,
Burkhardt, Gillam and Hindley[128] ($\varepsilon_{max}$ 15,900) indicates
the material to have been 79% pure. The values of $\varepsilon_{max}$
in Table V are calculated using the latter figure, and
hence may be a little low.

## α,β-Unsaturated Ketones

**Methylvinyl ketone.** Fluka stab. purissimum grade was used.
B.p. 32°, 122 mm., $n_D^{21}$ 1.4098.

**Methylisopropenyl Ketone.** An azeotrope generously donated by Messrs.
Celanese Corporation was dried over anhydrous sodium
sulphate, then fractionated. A little azeotrope distilled
over, followed by pure methylisopropenyl ketone,
b.p. 94-96°. On refractionation this had b.p. 96°, $n_D^{25}$
1.4257. This compound showed a serious drop in absorption
intensity after storage for three days at 5°C.

**Pent-3-en-2-one.** Prepared by the method of Rapson.[129] Yield = 39%.
B.p. 120°, 760 mm., $n_D^{23}$ 1.4343.

**3-Methylpent-3-en-2-one.** Prepared by the method of Kyrides[130] in 11%
yield. After purification via semicarbazone it had b.p.
136°, $n_D^{24}$ 1.4462.
A sample prepared by the method of Hinkel, Ayling, Dippy
and Angel[131] in 12% yield had b.p. 134-138°, $n_D^{20}$ 1.4503
and slightly lower absorption.

**Mesityl oxide.** Eastman Kodak Co. product. On vacuum distillation

it afforded a fraction b.p. 50°, 48 mm.; 53°, 65 mm.,

$n_D^{22}$ 1.4410, $n_D^{13}$ 1.4450. (Heilbron's Dictionary[122] gives

$n_D^{13}$ 1.4484). Mesityl oxide is known[124] to contain 9%

unconjugated isomer which cannot be separated easily on

a laboratory scale. Infra-red analysis showed the

material to contain about 10% unconjugated isomer, and

values of intensity in Table VII and Figure 13 are

calculated using that figure. Gray, Rasmussen and

Tunnicliff[124] give, in isooctane, $\lambda_{max}$ = 231 mμ, $\varepsilon_{max}$ =

12000.

**3,4-Dimethylpent-3-en-2-one.** Numerous attempts to repeat the

preparation of Colonge and Mostafavi[132] failed to give a

halogen-free product using either NN-dimethylaniline or

collidine as dehydrochlorinating agent. (Cf.[48] for a

similar case). The following modification was adopted.

2-Methyl-2-butene (85.4 gms) was placed in a three

necked flask equipped with dropping funnel, stirrer,

and reflux condenser. Acetyl bromide (100 gms) was

added, then anhydrous stannic chloride (8.1 gms) added

dropwise. After a few moments reaction set in and the

mixture became dark red. Stirring was continued for one

hour, then the mixture was cooled and 15% hydrochloric

acid (325 mls.) added. The lower layer of bromoketone

was separated then washed with successive portions of

dilute hydrochloric acid, water, sodium bicarbonate

solution, and water. The dark red liquid was then dried

over anhydrous sodium sulphate. Distillation afforded unreacted hydrocarbon, 2-methyl-3-bromobutane (cf.[132]) 4-chloro-3,4-dimethylpentan-2-one (13.4 gms.) and the hitherto unreported compound 4-bromo-3,4-dimethylpentan-2-one (51.3 gms.), b.p. 57-61°, 11 mm., $n_D^{24}$ 1.4608. Refractionation gave material b.p. 74°, 40 mm., $n_D^{22}$ 1.4600. The liquid was colourless on first distilling, but rapidly turned dark red and lost hydrogen bromide. Attempts to prepare a 2,4-dinitrophenylhydrazone gave only the 2,4-dinitrophenylhydrazone of 3,4-dimethylpent-3-en-2-one, m.p. 131°, not depressed by an authentic specimen. (Cf.[133]). (See also below).

4-Bromo-3,4-dimethylpentan-2-one (40 gms) was refluxed for 30 minutes with NN-dimethylaniline (25 gms) and then allowed to cool. The mixture was washed with successive portions of dilute hydrochloric acid, water, sodium bicarbonate solution, and water, then dried over sodium sulphate. Distillation gave 3,4-dimethylpent-3-en-2-one (11.6 gms) in 50% yield on bromoketone. The heart cut, b.p. 149.5°, $n_D^{24}$ 1.4473 was used for spectral investigation. This product gave a 2,4-dinitrophenyl-hydrazone in quantitative yield.

4-Bromo-3,4-dimethylpentan-2-one.    (With D.L. Coffen). A repetition of the preparation using the appropriate molecular ratio of stannic bromide in place of stannic chloride gave bromoketone in 52% yield, b.p. 68-69°,

23 mm., $n_D^{24}$ 1.4607. Analytical figures for this material showed Br = 30.8 % (Calc. for $C_7H_{13}OBr$: Br, 41.4 % ). However, three weeks elapsed between preparation and microanalysis, so loss of hydrogen bromide was expected. This material afforded a bromine-free 2,4-dinitrophenylhydrazone in red needles from methanol, m.p. 126°, depressed by authentic 2,4-dinitrophenylhydrazone of 3, 4-dimethylpent-3-en-2-one and by that prepared from the previous sample of bromoketone. Microanalysis showed N, 19.3 % (Calc. for the 2,4-dinitrophenylhydrazone of 3, 4-dimethylpent-3-en-2-one, $C_{13}H_{16}N_4O_4$ : N, 19.2 %). In 10% chloroform in ethanol the spectra were identical (The author thanks Miss F. Jackman for determining these spectra). Hence the reason for the discrepancy is obscure.

Dehydrobromination was effected more easily with collidine than with NN-dimethylaniline.

2-Methylhex-2-en-4-one.   (With D.L. Coffen).  This compound was prepared according to the general method of Colonge and Mostafavi[132] though with modification of experimental technique.  Isobutylene, generated from t-butyl alcohol and 30% sulphuric acid, was condensed in a freezing mixture of ice and salt and the liquid passed under pressure of the evolved gas or nitrogen into a stirred mixture of propionyl chloride and stannic chloride.  The product was isolated and dehydrochlorinated as for

3,4-dimethylpent-3-en-2-one. Yield of 2-chloro-2-methylhexan-4-one (yellow liquid turning green b.p. about 100°, 75 mm., $n_D^{25.5}$ 1.4325) = 30% on propionyl chloride. Yield of 2-methylhex-2-en-one = 15% on propionyl chloride. B.p. 146°, $n_D^{24}$ 1.4392. (Colonge and Mostafavi[134] give b.p. 147-148°, $n_D^{15}$ 1.4496, but their analytical figures show the compound to have been impure).

<u>2,3,5-Trimethylhex-2-en-4-one</u>. (With D.L. Coffen). This was prepared according to the general method of Colonge and Mostafavi,[132] from 2-methyl-2-butene, <u>iso</u>butyryl chloride and stannic chloride. Yield = 35% on intermediate chloroketone. B.p. 175°; 91°, 44 mm., $n_D^{26}$ 1.4401.

Some unreported 2,4-dinitrophenylhydrazones were prepared and purified by solution in chloroform, chromatography on activated alumina using benzene or benzene-chloroform as eluent, followed by crystallisation from ethyl acetate.

2,4-Dinitrophenylhydrazone of:

| Compound | M.p. | Found | | Calculated |
|---|---|---|---|---|
| cyclohexylideneacetaldehyde | 197-199° | C | 56.97% | 55.25% |
| | | H | 5.45% | 5.3% |
| | | N | 22.14% | 18.41% |
| 3-methylpent-3-en-2-one | 195-196° | C | 51.61% | 51.79% |
| | | H | 5.22% | 5.07% |
| | | N | 20.35% | 20.14% |
| methyl<u>iso</u>propenyl ketone | 192-193.5° | C | 50.03% | 50.00% |
| | | H | 4.93% | 4.58% |
| | | N | 20.95% | 21.20% |

| Compound | M.p. | Found | | Calculated |
|---|---|---|---|---|
| pent-3-en-2-one | 136–138° | C 49.73% | | 50.00% |
| | | H 4.97% | | 4.58% |
| | | N 20.80% | | 21.20% |
| β-methylcrotonaldehyde | 183–185° | C 47.06% | | 50.00% |
| | | H 5.03% | | 4.58% |
| | | N 19.56% | | 21.20% |

Some of the above 2,4-dinitrophenylhydrazones sublimed under reduced pressure, or even under atmospheric pressure.

## CONJUGATED DIENES

**1,3-Butadiene.** Material from Messrs. Petro-Tex was condensed in solid carbon dioxide, then redistilled from iced-water and condensed in solid carbon dioxide. The liquid was then weighed out quickly.

**Isoprene.** Eastman Kodak Co. product. B.p. 35°, $n_D^{22}$ 1.4217. (Heilbron's Dictionary[122] gives b.p. 34.5–35°, 762 mm., $n_D^{20}$ 1.4194.

**1,1-Dimethyl-3-$t$-butyl-1,3-butadiene.** Prepared (by D.L. Coffen) by the method of Fieser and Wieghard.[135] B.p. 145°, $n_D^{24}$ 1.4439.

**2,3-Dimethyl-1,3-butadiene.** Prepared from pinacol by the method given by Vogel.[136] Yield = 10%. B.p. 68–69°, 755 mm., $n_D^{24}$ 1.4369.

**2,5-Dimethyl-2,4-hexadiene.** Borden Chemical Co. product. B.p. 134°, $n_D^{22}$ 1.4742.

<u>2,4-Dimethyl-1,3-pentadiene</u>. Prepared by the method of Jitkow and Bogert.[137] Yield = 39% overall. This was shown by infra-red analysis to contain a carbonyl compound as impurity. The hydrocarbon was treated with Brady's reagent, the precipitate filtered off, and excess water added. The upper layer was separated and dried over calcium chloride. The product was then distilled from sodium. The hydrocarbon had b.p. 95°, $n_D^{20}$ 1.4412.

<u>2,4-Hexadiene</u>. Prepared according to the method of Adams and Geissmann.[138] Yield (on hex-2-en-4-ol) = 20%. B.p. 79-81°, $n_D^{21}$ 1.4502. Figures quoted in the literature for the refractive index vary widely, from $n_D^{20}$ 1.4469[139] to $n_D^{20}$ 1.4544.[140]

<u>Piperylene</u>. (1,3-pentadiene). A Grignard reaction between methylmagnesium iodide and crotonaldehyde gave pent-2-en-4-ol in 47% yield, b.p. 47°, 18 mm., $n_D^{24}$ 1.4270. 5 gms. carbinol were heated with 48% hydrobromic acid to yield piperylene, b.p. 41-42°, 756 mm., $n_D^{23}$ 1.4297. Heilbron's Dictionary[122] gives b.p. 42°, $n_D^{20}$ 1.4280.

<u>4-Methyl-1,3-pentadiene</u>. Prepared by the method of Bachman and Goebel.[141] Yield = 7.3% overall, B.p. 74-75°, $n_D^{19}$ 1.4528

<u>3,4-Dimethyl-1,3-pentadiene</u>. This compound has been described in the literature[142,143] but neither method of preparation was convenient.

3,4-Dimethylpent-3-en-2-one (9.5 gms) in anhydrous ether (20 mls ), was added drop by drop to a stirred

suspension of excess (4 gms) lithium aluminium hydride
in ether (80 mls). After stirring for half an hour water
was added drop by drop with cooling. The ether refluxed
and a white precipitate was formed. The contents were
poured into 250 mls 10% sulphuric acid and the ethereal
layer separated. The aqueous layer was saturated with
ammonium sulphate then extracted with three 75 mls
portions of ether. The combined ethereal extracts were
dried over magnesium sulphate. Ether was removed by
distillation and the carbinol distilled at 85-125°. The
impure carbinol was dried over anhydrous sodium sulphate,
then redistilled, b.p. 109-134°, $n_D^{22}$ 1.4560. This
appeared to have undergone spontaneous dehydration.
Beilstein's "Handbuch der Organischen Chemie", 4th
edition, Zweites Erganzungswerk, vol. 3 gives b.p.
137-140°. Yield of carbinol = 3.7 gms. The carbinol
(3.7 gms) was distilled with potassium bisulphate and
the distillate collected from 85-104°. Yield (2.3 gms)=
28% on 3,4-dimethylpent-3-en-2-one.

On redistillation the diene had b.p. 103-106°,
757 mm., $n_D^{20}$ 1.4624. Naves and Ardizio give b.p.
104-108°, $n_D^{20}$ 1.45600 for impure material.[143]

<u>2-Methyl-2,4-hexadiene</u>. (With D.L. Coffen). An attempt was made
to prepare this compound by the method of Ziegler.[144]
Dimethyl-<u>n</u>-butylcarbinol was made by the method given

by Vogel.[136] The carbinol was dehydrated by potassium bisulphate, followed by washing with water, separation, drying with calcium chloride and redistillation to give 2-methyl-2-hexene (36.3%) b.p. 92–97°, $n_D^{28}$ 1.4050. This was brominated with N-bromosuccinimide in carbon tetrachloride, and succinimide recovered in 100% yield. After removal of carbon tetrachloride by distillation the residue had very variable boiling point, including a fraction b.p. 59°, 12 mm, $n_D^{22}$ 1.4928 (Ziegler[144] gives b.p. 54°, 12 mm. for 2-methyl-4-bromo-2-hexene). This fraction was distilled from collidine, the distillate washed with dilute hydrochloric acid and dried over calcium chloride. On distillation from sodium 1 gm. material was obtained, b.p. 94°, $n_D^{20}$ 1.4383 (Ziegler[144] gives b.p. 107°, $n_{He}^{20}$ 1.46080; Reif[145] gives b.p. 97–99°, $n_D^{24.5}$ 1.4266). On redistillation this had b.p. 97–99°, $n_D^{25}$ 1.4277. In ethanol this compound showed $\lambda_{max}$ 228.5 mμ $\varepsilon_{max}$ 11,200, with $\lambda_{infl}$ 222.5 mμ, $\varepsilon_{infl}$ 9,900 and $\lambda_{infl}$ 235 mμ $\varepsilon_{infl}$ 9,000. In cyclohexane it had $\lambda_{max}$ 229.5 mμ, $\varepsilon_{max}$ 11,100, with $\lambda_{infl}$ 224.5 mμ, $\varepsilon_{infl}$ 9,800, and $\lambda_{infl}$ 236 mμ $\varepsilon_{infl}$ 8,400. In each case the spectral curve was of the typical conjugated diene form. The values of $\lambda_{max}$ appear to be at too short wavelengths for 2-methyl-2,4-hexadiene, and the low intensities indicate the compound to be very impure. The spectrum appears more likely to be that of 2-methyl-1,3-hexadiene.

In a repetition of the preparation a fraction was
obtained b.p. 101-103°, $n_D^{21}$ 1.4358. In ethanol this had
$\lambda_{max}$233.5 m$\mu$, $\varepsilon_{max}$9,700, and in cyclohexane $\lambda_{max}$ 236 m$\mu$,
$\varepsilon_{max}$10,000. These figures are closer to those expected
for 2-methyl-2,4-hexadiene though the compound must still
be very impure. The curves were not clearly defined
diene curves and had poorly defined maxima. Found:
C,87.29%, H,12.52%. Calc. for $C_7H_{12}$; C,87.43%, H,12.57%.

Preparation of 2-methylhex-2-en-4-ol from croton-
aldehyde and isopropylmagnesium bromide, followed by
dehydration of the carbinol with potassium bisulphate
gave only material b.p. 94°, 750 mm., $n_D^{23}$ 1.4430. In
ethanol this showed $\lambda_{max}$225 m$\mu$, $\varepsilon_{max}$ 17,600, and in
cyclohexane $\lambda_{max}$226 m$\mu$, $\varepsilon_{max}$19,200. Farmer and Bacon[146]
have claimed that dehydration of the alcohol used in this
preparation gives an inseparable mixture of 2-methyl-2,
4-hexadiene and 1-isopropyl-1,3-butadiene. In the
present work an attempt was made to separate the isomers
by reaction with maleic anhydride in dioxan (cf.[141]) but
only gummy material could be prepared which is, according
to Farmer and Bacon[146], also Henne and Turk[147], the
product from maleic anhydride and 2-methyl-2,4-hexadiene.
According to Farmer and Bacon the isomeric 1-isopropyl-
1,3-butadiene furnishes a maleic anhydride adduct which

crystallises from petrol as colourless plates, m.p. 90°.

Another route was tried. 2-Methylhex-2-en-4-one (see above) was reduced with lithium aluminium hydride in ether. After removing ether by distillation the crude carbinol was dehydrated with potassium bisulphate to yield a hydrocarbon b.p. 101-102°, $n_D^{22}$ 1.4517. Both boiling point and refractive index are somewhat lower than the figures given by Ziegler,[144] and the refractive index is very different from that given by Reif. Found: C,87.36; H,12.53. Calc: for $C_7H_{12}$: C,87.43; H,12.57%. In both ethanol and cyclohexane the compound showed very well-marked triple peaks, and this is the compound given in Table X.

The high values of $\varepsilon_{max}$ indicate the material to be nearly pure diene, but the wavelengths of maximal absorption still seem to be more in accord with 2-methyl-1,3-hexadiene. This material, in dioxan, formed a maleic anhydride adduct m.p. (from ligroin) 166-167°. The high boiling residue from the hydrocarbon gave a maleic anhydride adduct m.p. 60°, dehydrogenated by sulphur to a compound m.p. 118°. 2-Methyl-2,4-hexadiene would be expected to give 3,6-dimethylphthalic anhydride, m.p. 143.5°. The identity of all products is doubtful, and an attempt to prepare 2-methyl-2,4-hexadiene unambiguously would be desirable. The author suggests

that some other method of dehydration, such as the
Tschugaeff method should be tried.

All melting and boiling points are uncorrected.  Micro-analyses
were performed by Mr. A. Bernhardt, Max-Planck Institut für
Kohlenforschung, Muelheim, Ruhr.

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