THE SPECTRA OF ENONES AND CONJUGATED DIENES

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PREFACE

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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* conformations 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.

CONTENTS

Contents (continued)

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 spectrophotometers 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 mμ 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 α-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 mμ 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 mμ. 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 mμ, with molecular extinction coefficient (ε_{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--> V transition, that is a transition in which a π electron in a bonding orbital undergoes excitation to a π 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 σ 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 λ_{max} or ε_{max} or both. For example, acetophenone in ethanol absorbs maximally at 240 mμ, ε_{max} 12,500 and o-methylacetophenone in ethanol at 242 mμ, ε_{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 λ_{max}237-238 mμ, ε_{max}12,500^{10}; *o*-fluoroacetophenone λ_{max}233 mμ ε_{max}9, 500^{10}; *o*-chloroacetophenone λ_{max}235 mμ, ε_{max}5, 700^{10}; and *o*-bromoacetophenone λ_{max}234-236 mμ, ε_{max}4,900^{10}. Another example is provided by *o*-nitroanisole in ethanol (λ_{max}249 mμ, ε_{max}3,400)^{14}, *o*-nitroacetophenone in ethanol (λ_{max}254 mμ, ε_{max}6,000)^{10}, and nitrobenzene in ethanol (λ_{max}260 mμ, ε_{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 *para*nitroanilines 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* methoxyl 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 ultraviolet 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 ± 5 mμ 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 (<u>cf</u>.[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 λ_{max} 240 mμ, ε_{max} 12,500[2] and 2,6-dimethylacetophenone λ_{infl} 241 mμ, ε_{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 (λ_{max} 251 mμ, ε_{max} 13,000 [29]) 2,6-dimethylacetophenone 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 1-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 (Δp_{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_θ related to the angle of twist θ. Therefore, to a first approximation $\Delta\lambda = K\Delta p_{xy} \cdot M_\theta$. Thus the sign of the wavelength displacement will depend on Δp_{xy}. Heilbronner and Gerdil give figures showing that for acetophenones, bond order difference in going from ground state to excited state is positive, for α,β-unsaturated ketones Δp 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 α,β-unsaturated ketones, and bathochromic wavelength displacements 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_θ. When θ 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 θ is small, leading to a small value of $\Delta\lambda$. In type II effects Δp and θ 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 π 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 π 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 α,β-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 α,β-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 hypothetical 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-methylnitrobenzene, (ε_{max} 6,070), 2-ethylnitrobenzene (ε_{max} 5,300), 2-*iso*-propylnitrobenzene (ε_{max} 4,150) and 2-*t*-butylnitrobenzene (ε_{max} 1,540).[41] In the latter case the largest decrease is observed between the *iso*propyl 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 *iso*propyl 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 ortho substituent gives a decreased extinction coefficient with only a slight change in wavelength. Again there is a great decrease in intensity between the isopropyl and tert-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 s-cis and s-trans 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 spectroscopically. 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 $A \rightleftharpoons B$, 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 ΔF,

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

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

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 ΔF. In each case the value of ΔF is in reasonable agreement with the values of ΔE 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 (ΔE), since $\Delta F = \Delta E - T\Delta S$, where ΔS 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 <u>ortho</u> 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 ± 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 ± 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 wavelength of maximal absorption of a polar solute is dependent on the polarity of the solvent. For α,β-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 λ_{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]

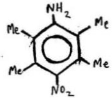
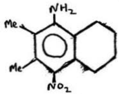
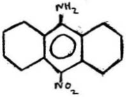
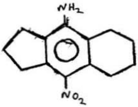
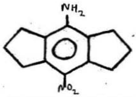
Compound	λ_{max}(mμ)	$\varepsilon_{max} \times 10^{-3}$
	395	1.57
	393	1.97
	397	2.24
	385	7.3
	372	12.8

TABLE II

ULTRA-VIOLET ABSORPTION SPECTRA OF NN-DIMETHYLANILINES

Substituent	Solvent	λ_{max}(mμ)	ε_{max}	Reference
None	n-heptane	250	13,750	a
o-Methyl	"	247.5	6,300	a
oo'-Dimethyl	"	259	2,200	a
p-Methyl	"	254	15,100	a
o-Fluoro	"	250	11,600	a
o-Chloro	"	256	7,600	a
o-Bromo	"	254	5,900	a
2,4,6-Trimethyl	isooctane	257	2,500	b
2-t-Butyl	"	250*	630	b

* Inflection

a) Refs.[150,151] Wavelengths recalculated in mμ by the present author.

b) Ref. 152

TABLE III

ULTRA-VIOLET ABSORPTION SPECTRA OF SUBSTITUTED BIPHENYLS

Substituent	Solvent	λ_{max}(mμ)	ε_{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-*Iso*propyl	"	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

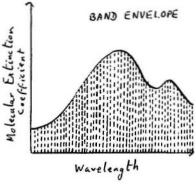
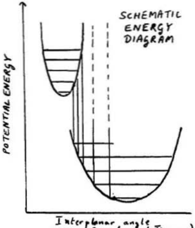
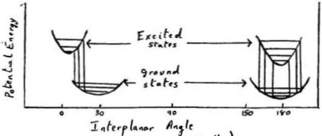


Figure 1.



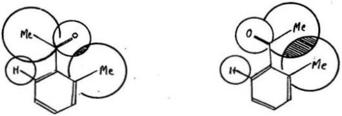
(After Braude and Timmons)

Figure 2.



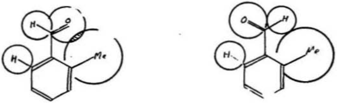
(After Forbes and Mueller)

Figure 3



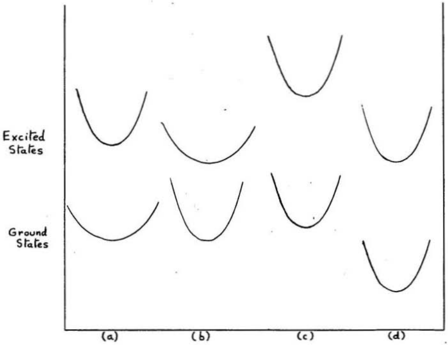
o-methylacetophenone

Figure 4



o- tolualdehyde

Figure 5



(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

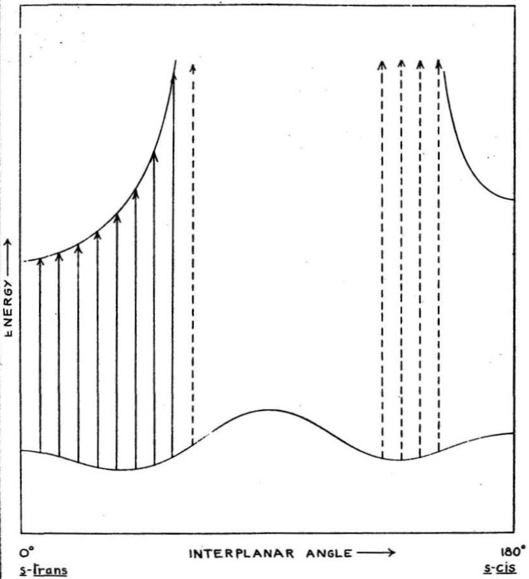


Figure 7.

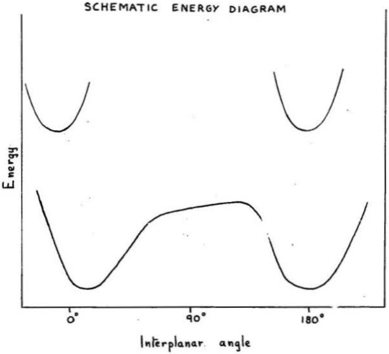
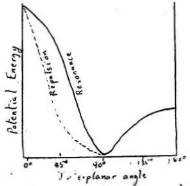
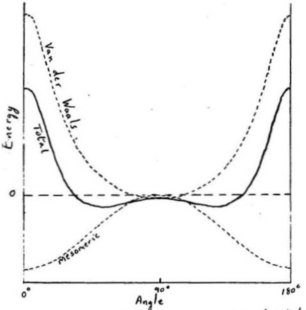

SCHEMATIC ENERGY DIAGRAM
Energy
0°
90°
180°
Interplanar angle

Figure 8



(After Braude and Timmons)

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. Nevertheless 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 ± 5 mμ, a disubstituted α,β-unsaturated ketone at 239 ± 5 mμ, and a trisubstituted α,β-unsaturated ketone at 254 ± 5 mμ.

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

The value of the rules was shown immediately by their application to show that α-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-Δ^5 (6)-norcholestene-7-carboxylic acid must be incorrect, since the compound did not show the absorption characteristic of an α,β-unsaturated ketone. This conclusion was again in accordance with strictly chemical evidence.

Later, Gillam and Evans[66] carried out a more comprehensiv investigation on the spectra of α,β-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-dimethylpent-3-en-2-one. They also found that although the displacement per alkyl group varied from 5 mμ to 19 mμ the displacement was greater for a β group than an α group. Fieser[67] has quoted values of, on average, 10 mμ for an alkyl group in the α position, and 12 mμ for an alkyl group in the β position. In a conjugated dienone each alkyl group in the γ or δ position gives a displacemen of 18 mμ.[67]

Gillam and Evans extended[68] their studies to α,β-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 ± 5 mμ, a disubstituted compound at 230 ± 5 mμ, and a trisubstituted compound at 242 ± 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, ε_{max}9,500, whereas cyclohexen-3-one under the same conditions has λ_{max} 224.5 mμ, ε_{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 λ_{max}239 mμ, ε_{max}13,000, 1-acetylcyclohexene with λ_{max}232-3 mμ, ε_{max}13,000, 1-acetylcycloheptene with λ_{max}236 mμ ε_{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-~~3n~~en-2-one (see Table VII). A similar example from the same authors is equally surprising: 2-cyclopentylidenecyclopentanone absorbs with λ_{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 ε_{max} about 10,000. A saturated ketone shows a high intensity band below 200 mμ and an additional weak band at 270-290 mμ, ε_{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, ε_{max} approx. 10,000: this is often called the K band.[71] A weak band also appears at about 320 mμ, with ε_{max} about 50: this is called the R band.[71] The position of each band is dependent a on the solvent, and as solvent polarity increases the two b~~o~~ands 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 π 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 σ antibonding orbital, but the wavelength of the transition is shorter than that of the N--> V transition, and the position ~~at~~ 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 (λ_{max}232 mμ, ε_{max}13,000) and 1-acetyl-2-methylcyclohexene (λ_{max}249 mμ, ε_{max}6890) in ethanol in both cases.[74] Even for these compounds very variable values of ε_{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 interplanar 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 ε_o and its interplanar angle be θ_1. Let the corresponding values for a similar but hindered compound be ε and θ_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-methylcyclohexene 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 arguement 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 π 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 $\varepsilon/\varepsilon_o = \frac{1}{2}[\cos^2(\theta_2 - \theta_1) + \cos^2(\theta_4 - \theta_3)]$ where θ_1 is the interplanar angle in one unhindered conformation, θ_2 the angle in the same hindered conformation, θ_4 and θ_3 the angles in the other conformation, hindered and unhindered respectively. Assuming θ_1 and θ_3 to be approximately zero this reduces to $\varepsilon/\varepsilon_o = \frac{1}{2}[\cos^2\theta_2 + \cos^2\theta_4]$ In the case of a symmetrically substituted compound their equation reduces to $\varepsilon/\varepsilon_o = \cos^2\theta$, 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 ~~in~~ 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 α,β-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 cis-crotonaldehyde and angelaldehyde. Values of λ_{max} and ε_{max} are given in Table V. Many of the values of ε_{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

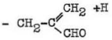
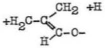
*Half-band widths should be in wave-numbers for this purpose, but for small ranges of wavelength the differences are qualitatively similar.

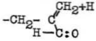
the order of intensities of the methyl- substituted acroleins.

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]

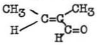
In β-methylcrotonaldehyde [$(CH_3)_2C:CH.CHO$] the introduction of a second β-methyl group relative to crotonaldehyde might lead to steric interaction between the methyl group and the formyl hydrogen atom, but diagrams drawn using the proposed interference radii of Forbes and Mueller[52] show very little difference in steric hindrance between the <u>s</u>-<u>cis</u> and <u>s</u>-<u>trans</u> conformations. (See Figure 12). Resonance stabilisation will therefore tend to maintain the molecule in a planar <u>s</u>-<u>trans</u> 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 <u>s</u>-<u>cis</u>, <u>s</u>-<u>trans</u> 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 <u>s</u>-<u>cis</u> compound than <u>s</u>-<u>trans</u>. 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  $-CH_2-C(=CH_2\ {+H})-CHO$ 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  $+H_2C-C(CH_2\ {+H})=C(H)-O-$

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 effect 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 π bonding electrons become more weakly bound, and all transitions move to longer wavelength. Resonance structures of the type  $-CH_2-\overset{CH_2+H}{\underset{H-C:O}{C}}$ 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 π electron system facilitates excitation. The latter hypothesis permits the greater displacement shown by a β-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.[13] The present author suggests that on account of the very different nature of the π 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 mμ) on introducing an <u>ortho</u> methyl group into acetophenone[10] compared with the figure for aliphatic compounds. A displacement of 12 mμ is observed[10] on introducing a <u>para</u> methyl group, whereas comparison with δ substituents in aliphatic dienones would lead one to expect a displacement of 18 mμ.

Returning to the question of the conformation of α-methacrolein, the carbonyl frequency in carbon tetrachloride is 1702 cm.$^{-1}$ (ε^a 240) and the olefinic frequency 1637 cm.$^{-1}$ (ε^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 crotonaldehyde (3.39 Debye compared with 3.54 Debye[78]) and ε_{max} for tiglaldehyde compared with that for α-methacrolein is less than ε_{max} for crotonaldehyde compared with ε_{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 ϵ_{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] ($\epsilon_{c=o}/\epsilon_{c=c} = 374/122$) 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 ε_{max} for crotonaldehyde to ε_{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 cyclohexylideneacetaldehyde (see Table V). It should be pointed out that some assumptions are implicit in this treatment, since the interfering system in β-methylcrotonaldehyde is a gem dimethyl group, and not two buttressed methyl groups.

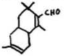
Table VIa shows that in compounds thought to be sterically hindered there is slight but distinct band widening. This may be compared with the similar effect in infra-red spectra of s-cis compounds (see Part II) and may prove to be general (see Parts IV and V).

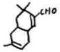
If the assignment of spectral effects to steric interaction is correct there must be some interaction between a cis methyl group and the formyl hydrogen atom in the s-trans conformation. Scale diagrams indicate the distance between the centres of the methyl group and the formyl hydrogen atom to be 2.48A in the s-trans conformation, and the distance between the centres of the methyl group and carbonyl oxygen atom in the s-cis conformation 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 λ_{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 (λ_{max}215.5 mμ, ε_{max}9,400 and tiglic acid (λ_{max}212.5 mμ, ε_{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 comparab pair of isomers examined appears to be *cis* and *trans* piperylene, for which Jacobs and Platt[59] found λ_{max}226 and 223 mμ, respectively, and ε_{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 of 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 

(λ_{max} 240 mμ) compared with 

(λ_{max} 235 mμ)[4]

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	λ_{max}(mμ)	ε_{max}	λ_{max}(mμ)	ε_{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.

TABLE VI a

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

- -

All measurements are in cyclohexane.

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

TABLE VI b

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.

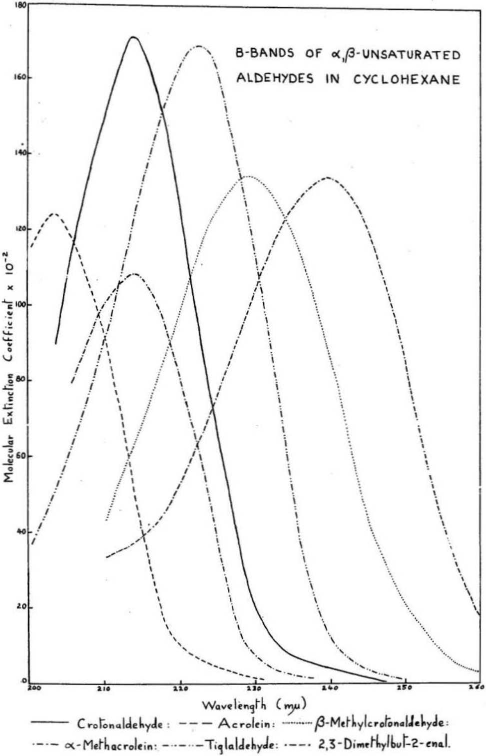
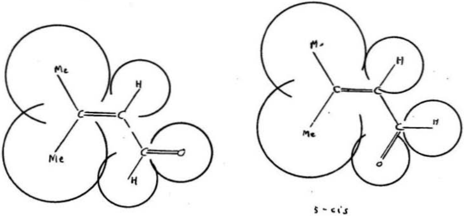

B-BANDS OF α,β-UNSATURATED ALDEHYDES IN CYCLOHEXANE
Molecular Extinction Coefficient x 10⁻²
180
160
140
120
100
80
60
40
20
0
200
210
220
230
240
250
260
Wavelength (mμ)
Crotonaldehyde:
Acrolein:
β-Methylcrotonaldehyde:
α-Methacrolein:
Tiglaldehyde:
2,3-Dimethylbut-2-enal.

Figure II

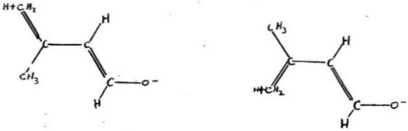


s-cis

s-trans

β-methylcrotonaldehyde

Figure 12



Resonance Forms of β-methylcrotonaldehyde

Figure 13

PART IV.

The Spectra of α,β-Unsaturated Ketones

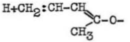
Saturated ketones and unsaturated ketones in which the olefinic bond and carbonyl group are not in conjugation show very weak absorption (ε_{max} about 100, λ_{max} about 260 mμ). On the other hand, when the olefinic link and the carbonyl group are in conjugation, two bands appear (see Part II), one 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-methylacetophenone (3.20 Debye)[80] in which s-cis s-trans isomerism cannot occur. Hence it is probable that both acrolein and methylvinyl 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. Hyperconjugation 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 ε_{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} (ε^a 320), and the olefinic frequency at 1631 cm^{-1}(ε^a 140). Since $\Delta\nu = 46$ cm^{-1} these figures also support the assignment of an s-trans conformation.

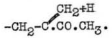
Estok and Dehn[80] have ascribed equal proportions of s-cis and s-trans conformations to pent-3-en-2-one, since, although acrolein and methylvinyl ketone have almost identical dipole moments, the moment of pent-3-en-2-one is less than that of crotonaldehyde (3.58 Debye in dioxan, as measured by the authors 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° ± 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=0 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, $\nu_{C=O} = 1677$ $cm.^{-1}$, ε^{a} 320; $\nu_{C=C} = 1631$ $cm.^{-1}$ ε^{a} 140. These figures support an s-trans conformation.

As in the case of crotonaldehyde, the wavelength displacement may be attributed to the participation of resonance forms such as



$$\mathrm{H{+}CH_2{:}CH{-}CH{=}C(CH_3){-}O{-}}$$

In methyl*iso*propenyl ketone [$CH_2{:}C(CH_3).CO.CH_3$] the wavelength displacement, relative to methylvinyl ketone, is 9 mμ in ethanol and 9.5 mμ in cyclohexane. The difference between these figures and those for pent-3-en-2-one (11.5 and 10 mμ respectively) is significant. The low value of ε_{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 α-methacrolein and would not be inconsistent with the low dipole moment of methyl*iso*propenyl ketone (2.74 Debye in benzene, 2.80 Debye in dioxan[89]). These figures are close to the dipole moments of the saturated ketones methyl*iso*propyl 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



$$\mathrm{{-}CH_2{-}C(CH_2{+}H).CO.CH_3.}$$

Lamb and de Groot[47] have also shown from ultra-sonic absorption data that a proportion of methyl*iso*propenyl ketone exists in the higher energy form.

The low dipole moment, compared with that of methylvinyl ketone, would lead one to expect methyl<u>iso</u>propenyl ketone to have a lower extinction coefficient than methylvinyl ketone. Since ε_{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<u>iso</u>propenyl ketone occurs at 1681 cm^{-1} (ε^a 400) and the olefinic frequency at 1631 cm^{-1} (ε^a 36). These figures favour an <u>s</u>-<u>trans</u> conformation.

In mesityl oxide the wavelength displacement relative to pent-3-en-2-one is 16 mμ 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 <u>s</u>-<u>trans</u> conformation. The <u>s</u>-<u>cis</u> 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 <u>s</u>-<u>cis</u> isomer to be the only stable isomer at room temperature. The carbonyl frequency is 1690 cm^{-1}, ε^a 270 and the olefinic frequency 1620 cm^{-1}, ε^a 220. These figures are consistent with an <u>s</u>-<u>cis</u> conformation, though $\Delta\nu$ is not as large as in compounds with a fixed <u>s</u>-<u>cis</u> 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 mμ in both ethanol and cyclohexane. Relative to methyl<u>iso</u>propenyl ketone the displacements are 10.5 mμ in ethanol, and 8.5 mμ 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 <u>s-cis</u> conformations in 3-methylpent-3-en-2-one. The carbonyl frequency is 1672 $cm.^{-1}$, ε^{a} 410, and the olefinic frequency 1644 $cm.^{-1}$, ε^{a} 85, whence $\Delta\nu$ = 28 $cm.^{-1}$, favouring an <u>s-trans</u> 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 <u>s-cis</u> and <u>s-trans</u> conformers in approximately equal amounts. A buttressing effect similar to that postulated for tiglaldehyde would be expected to give an increased proportion of <u>s-cis</u> conformations. The present author favours a mixture of <u>s-cis</u> and <u>s-trans</u> 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<u>iso</u>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 λ_{max} 249 mμ, ε_{max}4,000, and concluded that the compound was impure. The present figures (λ_{max}245.5 mμ, ε_{max}5,800 in ethanol, and λ_{max}238.5 mμ, ε_{max}6,400 in cyclohexane) are in agreement with those given by Erskine and Waight[39] (λ_{max} 245.5 mμ, ε_{max}6,000 [in ethanol or cyclohexane]) and may be regarded as established. The very low value of ε_{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}, ε^{a}200; $\nu_{c=c}$1622 cm^{-1}, ε^{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 α,β-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 respectively).[89] In an s-cis compound addition of an α-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 (λ_{max}239 mμ), and 2-methyl-1-acetylcyclopentene (λ_{max} 253 mμ) also 1-acetylcyclohexene (λ_{max}232-3 mμ) and 2-methyl-1-acetylcyclohexene (λ_{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 ε_{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, excitatio 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 displacement. 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

Solvent:	ETHANOL		CYCLOHEXANE	
Compound	λ_{max} (mμ)	ε_{max}	λ_{max} (mμ)	ε_{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 VIIIa

HALF-BAND WIDTHS OF α,β-UNSATURATED KETONES

Compound	Half-band width (mμ)
Methylvinyl ketone	10
Methyl*iso*propenyl 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
Methyl*iso*propenyl 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

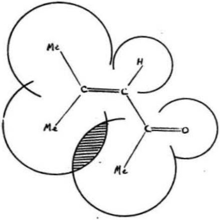
Intensity units are arbitrary, taking methylvinyl ketone as 9,500

TABLE IX

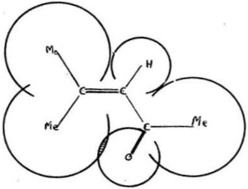
RELATIONSHIPS BETWEEN ABSORPTION INTENSITY AND DIPOLE MOMENT

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			
Methyl<u>isop</u>ropenyl 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. μ_0 is the dipole moment of the reference compound, μ that of the compound considered. ε_0 is the molecular extinction coefficient of the reference compound, ε that of the compound considered.

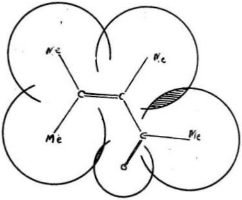


s-trans mesityl oxide

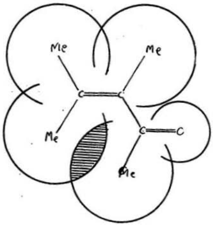


s-cis mesityl oxide

Figure 14



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



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

Figure 15

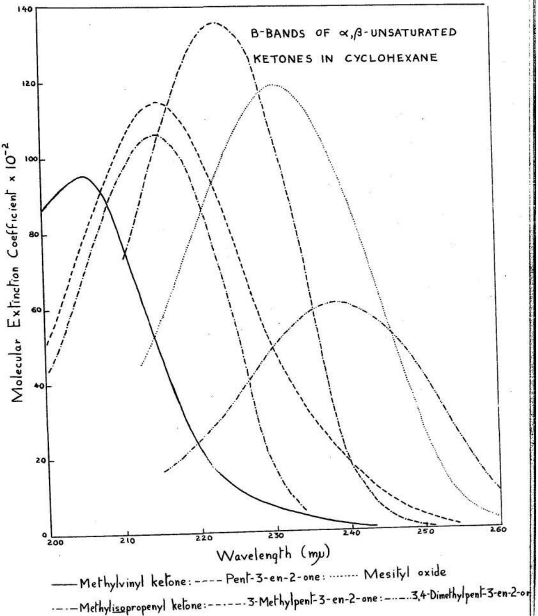

B-BANDS OF α,β-UNSATURATED
KETONES IN CYCLOHEXANE
Molecular Extinction Coefficient × 10⁻²
140
120
100
80
60
40
20
0
200
210
220
230
240
250
260
Wavelength (mμ)
——Methylvinyl ketone: ---- Pent-3-en-2-one: ······· Mesityl oxide
-·-—Methylisopropenyl ketone: -·-·-·-3-Methylpent-3-en-2-one: —··—3,4-Dimethylpent-3-en-2-on

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 mμ, but a compound containing two conjugated olefinic linkages exhibits intense absorption in the region 215-270 mμ.

The ultra-violet spectrum of butadiene has been discussed by Mulliken[1] who identified the band at 217 mμ with an N-->V transition. Molecular orbital calculations showed that four transitions were possible, N-->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-->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 conformations 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 containing 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 ε_{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. Woodwoard 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 α,β-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 $CH_3.\bar{C}H\ .CH{:}CH.CH_2+$. Some evidence in support of this mechanism is provided by the large wavelength displacement on introducing a second methyl group on the [illegible]-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 α,β-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 mμ, piperylene in ethanol at 223 mμ, and 4-methyl-1,3-pentadiene in ethanol at 232.5 mμ. 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 λ_{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 <u>trans</u>-piperylene in the vapour phase has λ_{max} 213 mμ, <u>cis</u>-piperylene 216 mμ, and 4-methyl-1,3-pentadiene λ_{max} about 222 mμ. 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 β-methylcrotonaldehyde (Part III).

If the interpretation given above in terms of dipole moments is correct there should be only a small wavelength displacement 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 diple 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 interference 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 [$CH_3.CH:CH.C(CH_3):CH$] for which λ_{max} in isooctane[98] is 227 mμ, ε_{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-pentadiene. Assuming 4-methyl-1,3-pentadiene to be essentially planar,

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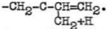
* Zingiberine, usually formulated  might be thought to provide an acceptable approximation but this is vitiated by the demonstration (Refs.99,100) that its formula is actually

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  $-CH_2-C-\underset{CH_2+H}{\underset{|}{C}}H=CH_2$. 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 ε_{max} would suggest that the compound exists predominantly in the _s-trans_ conformation. It is surprising that λ_{max} for this compound is the same as that for 4-methyl-1,3-pentadiene. 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 trisubstituted α,β-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 hyperconjugativ effects. Some support is afforded by the observation that 1-_t_-butyl -1,3-butadiene in ethanol has λ_{max} 224 mμ, ε_{max}25,000 [102] only 1 mμ 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 tetramethylethylene 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 hydrogenation,[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.$^{-1}$ ε^a 48; and 1652 cm.$^{-1}$ ε^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.$^{-1}$, ε^a 12; 1628 cm.$^{-1}$ ε^a 31; and 1653 cm.$^{-1}$, ε^a 18. There appears to be no ready explanation for the presence of three frequencies, but the low values of ε^a are consistent with steric hindrance of resonance.

Hexa-2,4-diene showed a band in the infra-red at 1653 cm.$^{-1}$ ε^a9. 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 ultraviolet 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 π electron system by electrons, but no more quantitative conclusions can be drawn at present.

Precisely as in the case of α,β-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 λ_{max}226 mμ, ε_{max}22,000, and trans piperylene (in n-heptane) with λ_{max}223 mμ, ε_{max}26,000. These figures, together with Dreiding 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 ε_{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 (λ_{max}230 mμ) and 2-methyl-1-vinylcyclohexene (λ_{max}233 mμ),[95] where the methyl group is cis to the vinyl group and the wavelength displacement is only 3 mμ. The present author believes a re-examination 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 λ_{max}236.5 mμ, ε_{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 mμ, and with the surprisingly low intensity of 3,400.[51,104] Cyclohexa-1,3-diene in hexane has λ_{max} 256 mμ (in hexane) ε_{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 interplana 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 π 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, λ_{max} moves to shorter wavelength and ε_{max} decreases: as the ring size then increases λ_{max} moves to longer wavelengths and ε_{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 λ_{max} (in hexane) is 237 mμ, ε_{max} 9,750, in 1,2-dimethylenecyclopentane (in hexane) $\lambda_{max} < 220$ mμ, and in 1,2-dimethylenecyclohexane (in hexane) $\lambda_{max} = 220$ mμ, $\varepsilon_{max} = 10{,}000$.[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 ehtanol, 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-pentadiene; 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 significant 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

Solvent:	ETHANOL			CYCLOHEXANE		
Compound	λ_{max}(mμ)	λ_{infl}(mμ)	ε_{max} or infl	λ_{max}(mμ)	λ_{infl}(mμ)	ε_{max} or infl
1,3-Butadiene	217.5		22,400	218.5		23,000
		212.5	19,600		214.5	21,000
CH_2:CH.CH:CH_2		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
$(CH_3)_2$C: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
		230	9,900		228	9,800
$(CH_3)_2$C:CH.C(CH_3):CH_2					237	9,200
3,4-Dimethyl-1,3-pentadiene	231.5		19,200	232.5		19,800
		227	17,700		227.5	18,100
		241	12,500		240	14,000
$(CH_3)_2$C:C(CH_3).CH:CH_2						
2,5-Dimethyl-2-4-hexadiene	241		24,300	242		24,000
		236	22,400		237	22,000
		247	19,000		248	18,200
$(CH_3)_2$C:CH.CH:C$(CH_3)_2$						

TABLE X (continued)

1,1-Dimethyl-3-*t*-butyl-1,3-butadiene $(CH_3)_2C{:}CH.C(Bu^t){:}CH_2$	225		6,400	225		6,600
"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

	Solvent: ETHANOL				CYCLOHEXANE			
Compound	$\lambda_B-\lambda_{B-}$	$\lambda_{B+}-\lambda_B$	$\varepsilon_{B-}/\varepsilon_B$	$\varepsilon_{B+}/\varepsilon_B$	$\lambda_B-\lambda_{B-}$	$\lambda_{B+}-\lambda_B$	$\varepsilon_{B-}/\varepsilon_B$	$\varepsilon_{B+}/\varepsilon_B$
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
ℓ 2,5-Dimethyl-2, 4-hexadine	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 wave-length.	Half-band width to short wave-length.
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.

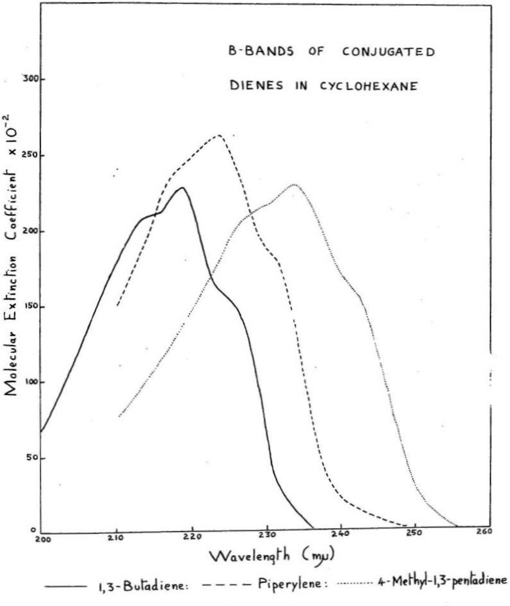

B-BANDS OF CONJUGATED
DIENES IN CYCLOHEXANE
Molecular Extinction Coefficient x 10⁻²
300
250
200
150
100
50
0
200
210
220
230
240
250
260
Wavelength (mμ)
1,3-Butadiene:
Piperylene:
4-Methyl-1,3-pentadiene

Figure 17

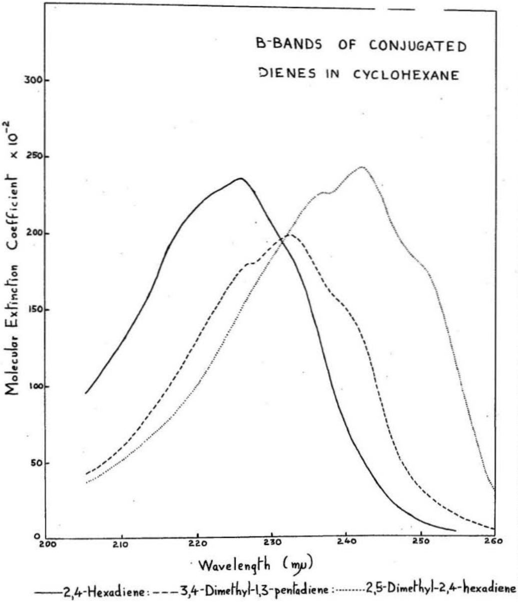

B-BANDS OF CONJUGATED DIENES IN CYCLOHEXANE
Molecular Extinction Coefficient × 10^{-2}
300
250
200
150
100
50
0
200
210
220
230
240
250
260
Wavelength (mμ)
——2,4-Hexadiene : ---3,4-Dimethyl-1,3-pentadiene : 2,5-Dimethyl-2,4-hexadiene

Figure 18

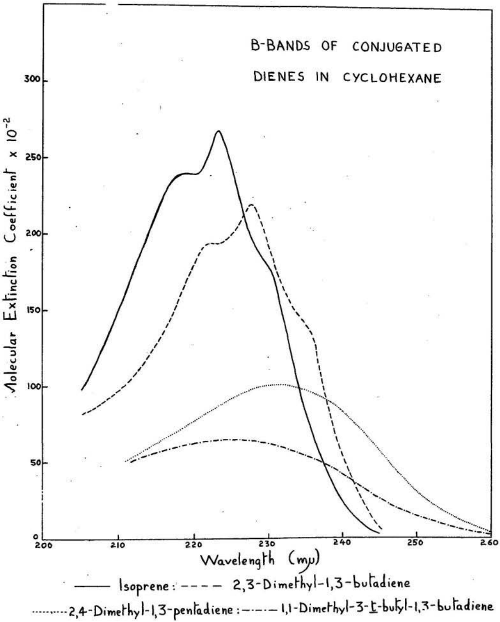
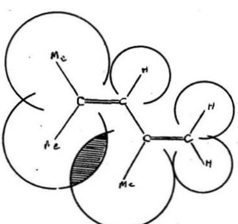
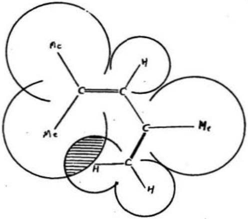

B-BANDS OF CONJUGATED
DIENES IN CYCLOHEXANE
Molecular Extinction Coefficient x 10^{-2}
300
250
200
150
100
50
0
200
210
220
230
240
250
260
Wavelength (mμ)
—— Isoprene: - - - - 2,3-Dimethyl-1,3-butadiene
.... 2,4-Dimethyl-1,3-pentadiene: —·—·— 1,1-Dimethyl-3-t-butyl-1,3-butadiene

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 α,β-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 ± 2%, and wavelengths of maximal absorption are precise to 0.5 mμ. The accuracy of wavelength, by comparison with figures of other authors, appears to be ± 1 mμ.

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 crotonaldehyde 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.

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

2,3-Dimethylbut-2-enal. 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, ε_{max} 10,700 and in cyclohexane ε_{max} 11,200. Formation of 2,4-dinitrophenylhydrazone followed by chromatographic analysis showed the material to be 82% pure. Values of ε_{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.

Cyclohexylideneacetaldehyde. This compound was kindly supplied by Professor M. Viscontini, of Zürich University. Redistillation afforded material b.p. 104°, 25 mm., n_D22 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 ε_{max} in ethanol, (12,600) with the figure given by Aldersley, Burkhardt, Gillam and Hindley[128] (ε_{max} 15,900) indicates the material to have been 79% pure. The values of ε_{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, λ_{max} = 231 mμ, ε_{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-dinitrophenylhydrazone 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).

2,3,5-Trimethylhex-2-en-4-one. (With D.L. Coffen). This was prepared according to the general method of Colonge and Mostafavi,[132] from 2-methyl-2-butene, isobutyryl chloride and stannic chloride. Yield = 35% on intermediat 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%
methylisopropenyl 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% H 4.97% N 20.80%	50.00% 4.58% 21.20%
β-methylcrotonaldehyde	183-185°	C 47.06% H 5.03% N 19.56%	50.00% 4.58% 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.

2,4-Dimethyl-1,3-pentadiene. 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.

2,4-Hexadiene. 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]

Piperylene. (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.

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

3,4-Dimethyl-1,3-pentadiene. 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 Ergänzungswerk, 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]

2-Methyl-2,4-hexadiene. (With D.L. Coffen). An attempt was made to prepare this compound by the method of Ziegler.[144] Dimethyl-*n*-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 λ_{max} 228.5 mμ ε_{max} 11,200, with λ_{infl} 222.5 mμ, ε_{infl} 9,900 and λ_{infl} 235 m ε_{infl} 9,000. In cyclohexane it had λ_{max} 229.5 mμ, ε_{max} 11,100, with λ_{infl} 224.5 mμ, ε_{infl} 9,800, and λ_{infl} 236 m ε_{infl} 8,400. In each case the spectral curve was of the typical conjugated diene form. The values of λ_{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 λ_{max}233.5 mμ, ε_{max}9,700, and in cyclohexane λ_{max} 236 mμ, ε_{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 crotonaldehyde 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 λ_{max}225 mμ, ε_{max} 17,600, and in cyclohexane λ_{max}226 mμ, ε_{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 ε_{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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