403. *Studies in Light Absorption. Part VI. Steric Inhibition of Resonance in Natural and Synthetic Derivatives of* cyclo*Hexene.*

By E. A. BRAUDE, E. R. H. JONES, H. P. KOCH, R. W. RICHARDSON, F. SONDHEIMER, and J. B. TOOGOOD.

1-Acetyl-2-methyl*cyclo*hexene as prepared by two different methods is shown to be a mixture of the Δ^1- and the Δ^2-isomer, which can be separated either by fractional distillation or through the semicarbazones. No indication of the presence of the unconjugated isomer was obtained with acetyl*cyclo*hexene.

The ultra-violet light absorption properties of 1-acetyl-2-methyl*cyclo*hex-1-ene, β-ionone, dehydro-β-ionone, β-irone, and certain related synthetic compounds are uniformly anomalous in that the intensities of the bands characteristic of the conjugated systems are much lower than for the open-chain analogues. This anomaly is not exhibited by the unsubstituted cyclic homologues and is ascribed to steric inhibition of resonance, the unsaturated side-chain being displaced out of the plane of the *cyclo*hexene ring by the neighbouring methyl groups. The effect is similar to that previously observed by Rodebush and others in *o*-methylacetophenones and related aromatic systems. The general principles underlying the interpretation of steric effect on electronic spectra are discussed and applied qualitatively to the parent compounds named above and to some of their carbonyl derivatives.
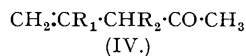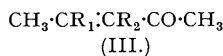
THE work described in this paper was initiated about eight years ago as a result of the observation, briefly discussed in two earlier publications (Koch, *Chem. and Ind.*, 1942, **61**, 273; Braude, Jones, Sondheimer, and Toogood, this vol., p. 607) that 1-acetyl-2-methyl*cyclo*hex-1-ene (I) exhibits ultra-violet light absorption of the expected wave-length but of much lower intensity than that to be expected by analogy with acetyl*cyclo*hexene (a; this and other letters in parentheses refer to the table on p. 1892) and acylic αβ-unsaturated ketones. This apparent anomaly can be satisfactorily explained (see below) in terms of steric interference between the acetyl group and the methyl substituent, and it seemed very probable that an analogous effect was responsible for the anomalous light absorption of certain other conjugated side-chain derivatives of *cyclo*hexene, particularly β-ionone and related compounds. Partly in order to test this hypothesis and partly in view of their potentialities as intermediates in the synthesis of vitamin A analogues, a range of suitable compounds of this type differing in the extent of alkyl substitution has now been prepared (Heilbron, *J.*, 1948, 386; Heilbron, Jones, Richardson, and Sondheimer, this vol., p. 737; Heilbron, Jones, Toogood, and Weedon, this vol., p. 1827), and their spectral properties together with those of some of their derivatives are described and discussed in the present communication.

The data are collected in the table. Acetyl*cyclo*hexene (a) exhibits a band with $\lambda_{max.}$ 2320 A., $\varepsilon_{max.}$ 12,500, entirely analogous to that shown by open-chain αβ-unsaturated ketones with αβ-alkyl substitution (Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123; 1942, **64**, 76; Evans and Gillam, *J.*, 1941, 815). 1-Acetyl-2-methyl*cyclo*hexene, as prepared by the reaction of 1-methyl-*cyclo*hexene with acetyl chloride in the presence of stannic chloride (Ruzicka, Koolhaas, and Wind, *Helv. Chim. Acta*, 1931, **14**, 1151; Huber, *Ber.*, 1938, **71**, 725) as well as by the rearrangement of 2-methyl-1-ethynyl*cyclo*hexanol with formic acid (cf. Hurd and Christ, *J. Amer. Chem. Soc.*, 1937, **59**, 118; Chanley, *ibid.*, 1948, **70**, 244), exhibited a maximum at 2450 A., $\varepsilon_{max.}$ 4000—5000, corresponding to the wave-length displacement expected for the change from αβ-dialkyl to αββ-trialkyl substitution, but also an unexpected decrease in intensity. Moreover, the intensity values differed somewhat in different preparations, and the material obtained by either method proved to be a mixture of the Δ^1-isomer (I) and the less-absorbing Δ^2-isomer (II), which were separated by fractional distillation (b. p.s 89°/12 mm. and 79°/12 mm., respectively).

(I.) [structure: cyclohexene ring with COMe and Me substituents]   [structure: cyclohexene ring with COMe and Me substituents] (II.)

Separation was effected also by fractional crystallisation of the semicarbazones (m. p.s 213° and 132°, respectively). No isomerisation appears to accompany the regeneration of the parent ketones by means of phthalic anhydride or cold dilute sulphuric acid, but the semicarbazone of (II) is converted quantitatively into (I) when distilled in steam in the presence of oxalic acid. A careful examination of acetyl*cyclo*hexene (a), prepared by the rearrangement of ethynyl*cyclo*hexanol with formic acid, failed to yield any evidence of the presence of the corresponding Δ^2-isomer. The prototropic isomerism exhibited by acetylmethyl*cyclo*hexene is closely reminiscent of the behaviour of other alkylated *cyclo*hexene derivatives such as *cyclo*citral,

ionone, and irone, all of which are well known to exist in two so-called β- (Δ^1-) and α- (Δ^2-)forms, readily interconvertible in the presence of suitable catalysts (cf. Köster, *Ber.*, 1944, **77**, *B*, 553; Andrews, Cristol, Lindenbaum, and Young, *J. Amer. Chem. Soc.*, 1945, **67**, 715; Young and Linden, *ibid.*, 1947, **69**, 2072; Ruzicka, Seidel, Schinz, and Tavel, *Helv. Chim. Acta*, 1948, **31**, 257). It is interesting that the experimental details recorded by Evans and Gillam (*loc. cit.*) for the preparation and light absorption of 3 : 4-dimethylpent-3-en-2-one (III; $R_1 = R_2 = $ Me), an acyclic analogue of acetylmethyl*cyclo*hexene, also indicate that the compound is obtained as a mixture of the αβ- and βγ-isomers (III and IV). Again, the lower homologue mesityl oxide (III; $R_1 = $ Me, $R_2 = $ H) as prepared in the ordinary way has been shown to contain *ca.* 10%

$$CH_3 \cdot CR_1 \text{:} CR_2 \cdot CO \cdot CH_3 \qquad\qquad CH_2 \text{:} CR_1 \cdot CHR_2 \cdot CO \cdot CH_3$$
$$\text{(III.)} \qquad\qquad\qquad\qquad\qquad \text{(IV.)}$$

of the βγ-isomer (Stross, Monger, and Finch, *J. Amer. Chem. Soc.*, 1947, **69**, 1627; Gray, Rasmussen, and Tunnicliff, *ibid.*, p. 1630). Ethylideneacetone (III; $R_1 = R_2 = $ H), an open-chain analogue of acetyl*cyclo*hexene, does not appear to have been examined in this respect, but the relatively low ε value which has been recorded (Evans and Gillam, *loc. cit.*) suggests that the non-absorbing βγ-isomer may be present also in this case.

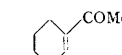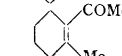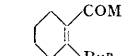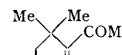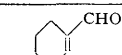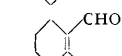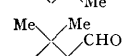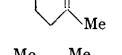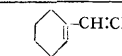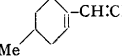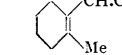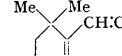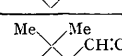Pure 1-acetyl-2-methyl*cyclo*hex-1-ene (b), obtained in the way described above, still exhibits a maximum of abnormally low intensity (ε 6500), in agreement with the data for material prepared by a different route (Braude, Jones, Sondheimer, and Toogood, *loc. cit.*). 1-Acetyl-2-*n*-butyl*cyclo*hexene (c) (*idem, ibid.*) exhibits a maximum of identical location, but of even lower intensity than the methyl homologue. On the other hand, no appreciable lowering in intensity is observed in 1-acetyl-6 : 6-dimethyl*cyclo*hexene (d) (Chanley, *J. Amer. Chem. Soc.*, 1948, **70**, 244), and the anomalous effect is thus produced only when an alkyl substituent occurs in the 2-position.

*cyclo*Hexenealdehyde (e), just as acetyl*cyclo*hexene, exhibits quite normal light absorption, and introduction of a 2-methyl substituent (in f) again leads to the increase in $\lambda_{max.}$ expected for the change from αβ- to αββ-alkyl substitution (cf. Evans and Gillam, *J.*, 1943, 565); no appreciable decrease in intensity is observed in this case and $\varepsilon_{max.}$ remains of the same order as in the acyclic citral (h). β-*cyclo*Citral (g), which contains two additional 6-methyl substituents was originally reported (Burawoy, *J.*, 1941, 20) to absorb with abnormally low intensity, but more recent work by Young and Linden (*loc. cit.*) shows that this was probably due to admixture with the α-isomer, and that pure β-*cyclo*citral, prepared by regeneration from the semicarbazone with sulphuric acid in the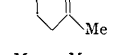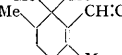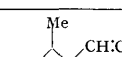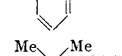 cold, has an $\varepsilon_{max.}$ value almost identical with that of *cyclo*hexenealdehyde and 2-methyl*cyclo*hexenealdehyde. Thus methyl substituents in either the 2- or the 6-position are practically without influence on the intensity of the characteristic band in the *cyclo*hexenealdehyde system.

In *cyclo*hexene derivatives containing the side-chain $-CH\text{:}CH \cdot CO \cdot Me$, *e.g.*, in the series consisting of the β-ionone lower homologues (i), (j), (k), and (l), β-ionone (m), and β-irone (n), as well as in the dehydro-derivatives (p) and (q), yet a different behaviour is encountered. A 2-methyl substituent again displaces the position of the absorption maximum of the dienone system by *ca.* 150 A., but $\varepsilon_{max.}$ is almost unchanged. Introduction of a 6-*gem.*-dimethyl group, however, reduces $\varepsilon_{max.}$ by half; thus, the β-ionone homologue (l), β-ionone and β-irone, unlike β-*cyclo*citral, all exhibit characteristic long-wave-length bands of abnormally low intensity even after the most careful exclusion of the α-isomers. At the same time additional short-wave-length bands near 2200 A. appear. In ψ-ionone (o), in which the *cyclo*hexene ring is opened, the intensity of the band at 2900 A. regains its normal value and no band is observed at 2200 A.

The differing influence of 2- and 6-alkyl substituents in the three systems is again brought out in the light absorption of the semicarbazones and 2 : 4-dinitrophenylhydrazones of the parent carbonyl compounds. The spectra of these derivatives are also given in the annexed table and need not be described in detail, but may be summarised as follows : (i) The absorption data of the derivatives of the unsubstituted carbonyl compounds are the same as for the derivatives of the corresponding open-chain analogues (cf. Evans and Gillam, *J.*, 1943, 565; Braude and Jones, *J.*, 1945, 498), (ii) the introduction of a methyl substituent which increases $\lambda_{max.}$ without reducing $\varepsilon_{max.}$ of the parent carbonyl compound, has the same effect for the derivative, and (iii) the introduction of a methyl substituent which reduces $\varepsilon_{max.}$ of the parent carbonyl compound, reduces both $\varepsilon_{max.}$ and $\lambda_{max.}$ of the derivative.

	Carbonyl compound.[†]		Semicarbazone.[†]		2 : 4-Dinitrophenyl-hydrazone.[‡]	
	$\lambda_{max.}$, A.*	$\varepsilon_{max.}$	$\lambda_{max.}$, A.	$\varepsilon_{max.}$	$\lambda_{max.}$, A.	$\varepsilon_{max.}$
(a) [COMe]	2320	12,500	2600	24,600	3870	27,500
(b) [COMe, Me]	2450 *2490*	6,500 *6,000*	2330 2420 2510	9,800	3750	24,000
(c) [COMe, Bu^n]	2450	4,000 [1]	2260	12,000 [1]	3690	25,500 [1]
(d) [Me, Me, COMe]	2320	12,000 [2]	2550	15,600 [2]		
(e) [CHO]	2290	12,100 [3]	2600 2650	28,500 [3] 31,700	3770	27,800 [3]
(f) [CHO, Me]	2420 2510	11,200 [3]	2740 *2800*	23,200 [3] *21,700*	3870	29,500 [3]
(g) [Me, Me, CHO, Me]	2490	11,600 [4]	2730	24,500 [5]	3890	28,000 [6]
(h) [Me, Me, CHO, Me]	2380	13,500 [7]	2720	31,400 [7]	3850	3,1000 [6]
(i) [CH:CH·COMe]	2810	20,800 [3]	2900 *3000*	35,000 [3] *32,000*	3950	32,000 [3]
(j) [CH:CH·COMe, Me]	2790 2730	23,000 23,000	2910 3000	37,000 32,000	3930	34,500
(k) [CH:CH·COMe, Me]	2200 2960	4,000 [3] 20,300	3030	40,900 [3] ‡	4020	39,900 [3]
(l) [Me, Me, CH:CH·COMe]	2280 2810 *2900*	4,100 [8] 13,000 12,500	2820 2910	29,500 30,500	3920	31,000
(m) [Me, Me, CH:CH·COMe, Me]	2230 2960	6,500 [9] 10,700	2820	22,300 [9]	3880	27,500 [6]
(n) [Me, Me, Me, CH:CH·COMe, Me]	2950	11,200 [10]				
(o) [Me, Me, CH:CH·COMe, Me]	2910	21,800 [7]	3000	45,400 [7]	4070	34,500 [5]
(p) [Me, CH:CH·COMe]	3370	17,700 [3]	2550 3190 3340 3500	13,200 [3] 19,100 25,000 20,200	4120	34,900 [3]
(q) [Me, Me, CH:CH·COMe, Me]	2210 3380	7,200 [11] 9,100	2600 3150 *3240*	12,400 [11] 16,500 *16,000*	3980 and 4050	27,800 [11] 28,900

* Data in italics refer to inflexions.   † In ethanol.   ‡ In chloroform.

[1] Braude, Jones, Sondheimer, and Toogood, this vol., p. 607.   [2] Chanley, *J. Amer. Chem. Soc.,* 1948, **70**, 244.   [3] Heilbron, Jones, Richardson, and Sondheimer, this vol., p. 737.   [4] Young and Linden, *J. Amer. Chem. Soc.,* 1947, **69**, 2072.   [5] Andrews, Cristol, Lindenbaum, and Young, *ibid.,* 1945, **67**, 715. [6] Braude and Jones, *J.,* 1945, 498.   [7] Burawoy, *J.,* 1941, 20.   [8] Heilbron, Jones, Toogood, and Weedon, this vol., p. 1827.   [9] Young, Cristol, Andrews, and Lindenbaum, *J. Amer. Chem. Soc.,* 1944, **66**, 855 (data for shorter-wave-length band of β-ionone determined by present authors).   [10] Ruzicka, Seidel, Schinz, and Tavel, *Helv. Chim. Acta,* 1948, **31**, 257; Naves, *ibid.,* p. 893.   [11] Henbest, *Nature,* 1948, **161**, 481, and private communication.   [12] Naves and Ardizio, *Helv. Chim. Acta,* 1949, **32**, 1228.

DISCUSSION.

The abnormal light-absorption properties of β-ionone and its semicarbazone were first noted by Burawoy (*loc. cit.*) who ascribed the low intensity values to a " ring-closure effect " and the low value of $\lambda_{max.}$ of the semicarbazone to a " steric-hindrance effect " of the methyl groups. However, the data now available show that ring closure as such evidently does not lead to any reduction in intensity since *cyclo*hexenealdehyde, acetyl*cyclo*hexene, and the β-ionone homologues (i), (j), and (k) all exhibit absorption of the same intensity as their acyclic analogues, and there is no obvious reason why steric hindrance should be operative in the semcarbazone and not in the parent carbonyl compound.

Many examples of the effects of steric factors on electronic spectra have been described, relating mostly to aromatic systems. They fall into three categories : (*a*) differences in light absorption between *cis*- and *trans*-isomers, *e.g.*, in the stilbenes, cinnamic acids, azobenzenes, and carotenoids (Smakula and Wasserman, *Z. physikal. Chem.*, 1931, *A*, **155**, 353; Cook, Jones, and Polya, *J.*, 1939, 1315; Zechmeister, *Chem. Reviews*, 1944, **34**, 267); (*b*) large changes in light absorption consequent upon the introduction of substituents normally producing only small spectral effects, but in positions where they may be expected to decrease the planarity of the conjugated system, *e.g.*, in *o*-methyl-diphenyls, -styrenes, -stilbenes, -acetophenones, and -dialkylanilines (Pickett, Walter, and France, *J. Amer. Chem. Soc.*, 1936, **58**, 2296; Rodebush *et al.*, *ibid.*, 1940, **62**, 2906; 1941, **63**, 3018; 1946, **68**, 896; Carlin and Constantine, *ibid.*, 1947, **69**, 50; Remington, *ibid.*, 1945, **67**, 1838); and (*c*) lack of spectral interaction, in large molecules, between conjugated chromophores expected to be non-coplanar, *e.g.*, in certain polyarylethylenes and diaryls (Jones, *J. Amer. Chem. Soc.*, 1941, **63**, 1658; 1943, **65**, 1818; 1945, **67**, 2127; *Chem. Reviews*, 1947, **41**, 353; Friedel, Orchin, and Reggel, *J. Amer. Chem. Soc.*, 1948, **70**, 199).

The present observations are clearly of the type described under (*b*) and there can be little doubt that the abnormalities observed are mainly steric in origin and that they arise through the displacement of the unsaturated side-chains out of the plane of the *cyclo*hexene ring owing to interference with the methyl substituents.

It is now well recognised that the near-ultra-violet and visible light absorption of conjugated systems is closely related to the occurrence of valence-bond resonance (for references see Pauling in Gilman, " Organic Chemistry," Wiley, 1943; Braude, *Ann. Reports*, 1945, **42**, 105; Maccoll, *Quart. Reviews*, 1947, **1**, 16) and that an essential requirement for maximum resonance is a co-planar configuration of all the bonds concerned. The relations which might, however, be expected between steric inhibition of resonance and electronic spectra have been variously interpreted and the following is an attempt to restate the basic principles involved.

(i) Light absorption in the near ultra-violet region can be regarded as resulting in transitions from a hybrid ground state, to which resonance forms (particularly ionic resonance forms) of higher energy content than classical structures make a relatively small contribution, to excited states to which resonance forms of higher energy content make a larger contribution.

(ii) A structural change which increases the conjugation and thereby lowers the energy content of the higher resonance forms will normally decrease the energy of the excited state more than that of the ground state (since the contribution of non-classical resonance forms is greater in the excited than in the ground state) and therefore decrease the excitation energy; *i.e.*, this change increases the wavelength associated with the electronic transition. Differences in the light absorption of *cis*- and *trans*-isomers will be at least partly of this type (quite independently of any steric interference in the *cis*-form) since the actual configuration of the chromophore is different in the two cases.

(iii) A structural change which tends to decrease the planarity of the conjugated system might be expected to influence ultra-violet absorption properties in the following ways. If the steric interference resulting in non-planarity is relatively small, then the characteristic transition of the chromophore might be restricted to vibrational states in which appropriate bonds are sufficiently extended to allow a large degree of co-planarity. Solution spectra representing band envelopes rather than discrete bands will then show little change in wave-length location, but the intensity of absorption will be decreased since the transition will be restricted to a smaller number of vibrational states. At the same time, bands characteristic of the partial chromophore present in the non-planar configuration will appear, increasing in intensity as the intensity of the main band decreases. If, however, steric interference is large and resonance interaction takes place despite non-planarity, the energy content of the contributing resonance forms will be increased and the energy level of the excited state will therefore be raised relatively to that of the ground state; *i.e.*, the characteristic band itself will be displaced towards shorter wave-lengths. If the expected wave-length locations of the full and partial chromophore

bands do not lie far apart, *e.g.*, in multiple conjugated systems, it will not always be a simple matter to decide between the two interpretations.

The present observations appear to receive satisfactory explanation in terms of the principles formulated above. Dealing first with the parent carbonyl compounds, it will be noted that the wave-length locations of the maxima in any one group bear no direct relation to the intensities, but are constant in the absence of 2-alkyl substituents and uniformly displaced by *ca.* 150 A. towards higher wave-lengths in their presence. These displacements can therefore be regarded as simple bathochromic effects due to the interaction of the alkyl groups with the conjugated system, entirely analogous to the effect observed with acyclic ethylenic carbonyl compounds (Woodward, *loc. cit.*; Evans and Gillam, *loc. cit.*).

In the *cyclo*hexenealdehydes, the intensities are practically unaffected by 2- or 6-methyl substituents, and any steric interference between the methyl and the aldehyde groups is therefore not sufficiently great to be manifested in the light-absorption properties. On examining scale models, it is found that, in configurations in which the aldehyde group is co-planar with the *cyclo*hexene ring, the distance between the oxygen atom and the methyl substituents is considerably smaller than the sum of the van der Waals radii, but slightly larger than the sum of the covalent radii. It is now generally accepted that van der Waals radii are probably too large a measure of the intra-molecular interference properties of atoms. On the other hand, covalent radii, though almost certainly too small, represent a reliable measure of the *minimum* interference properties of non-bonded atoms and appear to afford a better indication of the degree of interference necessary to produce anomalous ultra-violet-light absorption properties, possibly because a certain extent of non-planarity can be tolerated before resonance is seriously inhibited. Projections of the two co-planar *s-cis-* and *s-trans*-configurations * of β-*cyclo*citral, employing covalent radii, are shown in Figs. 1*a* and 1*b*. It will be seen that no overlap between the aldehyde group and either the 2- or 6-methyl substituents is apparent on this basis.

The corresponding scale diagrams for acetylmethyl*cyclo*hexene are shown in Figs. 2*a* and 2*b*. No overlap occurs in the *s-cis*-configuration but, as a result of the replacement of the aldehyde by an acetyl group, interference is indicated in the *s-trans*-configuration between the acetyl-methyl group and the 2-methyl substituent. Similarly, the diagrams (Figs. 3*a* and 3*b*) for 6 : 6-di-methylacetyl*cyclo*hexene indicate intereference for the co-planar *s-cis-* but not for the *s-trans*-configuration of this compound. The fact that an intensity reduction of the band characteristic of the enone system is shown by the 2-methyl but not by the 6 : 6-dimethyl derivative would therefore appear to suggest that in both compounds the *s-trans*-configuration is preferred. This is in harmony with the fact that, in general, the most elongated configuration of a conjugated system appears to be the most stable; thus, butadiene is believed to exist predominantly in the *s-trans*-configuration at room temperature, and the energies of the ground levels of the *s-trans-* and *s-cis*-forms are thought to differ by as much as 6 kcals./mol. (Mulliken, *J. Chem. Physics*, 1939, **7**, 121; Sugden and Walsh, *Trans. Faraday Soc.*, 1945, **41**, 76). This difference is of the same order of magnitude as that found with stable *cis-* and *trans*-isomers about ethylenic bonds. The fact that the only variations in wave-length location of the maxima in the *cyclo*hexene-aldehydes and acetyl*cyclo*hexenes are those to be expected from the differences in alkyl substitution supports the tentative conclusion that all these compounds tend to assume identical *s-trans*-configurations. This conclusion, if correct, implies that in the case of acetyl-methyl*cyclo*hexene and other acetyl-2-alkyl*cyclo*hexenes the preference for the *s-trans*-configuration over the *s-cis*-configuration outweighs the steric hindrance to co-planarity in the former. The potential energy difference between the *s-cis-* and *s-trans*-forms might be expected to be of the same order as in butadiene, *i.e.*, *ca.* 5—6 kcals./mol., so that the steric hindrance effect, which would have to be smaller than this, could amount to, at most, *ca.* 4 kcals./mol. It was pointed out in the general discussion (p. 1893) that steric interference, if relatively small, might be expected to produce only decreases in intensity without any wave-length displacements. The acetyl-2-alkyl*cyclo*hexenes and the ionones discussed below appear to be examples of this type (an energy difference of 4 kcals./mol. corresponds to a wave-length displacement of less than 100 A. in this region). The same applies to the related *o*-methyldiphenyls and *o*-methyl-acetophenones (Rodebush *et al.*, *loc. cit.*) which also exhibit intensity reductions without any appreciable changes in the wave-length locations of the maxima.

In the ionones, the number of feasible co-planar configurations is multiplied by the possibility

---

* The nomenclature employed is that introduced by Mulliken (*Rev. Mod. Physics*, 1942, **14**, 265) for distinguishing between geometrical isomers about conventional single bonds which possess some double-bond character.

of *cis-trans*-isomerism about the ethylenic bond, and of *s-cis*- or *s-trans*-orientation about the two carbon–carbon single bonds in the side-chain. A *cis*-configuration of the ethylenic bond in

FIG. 1.
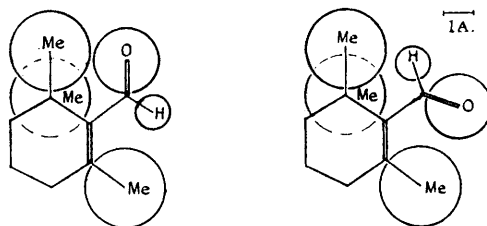
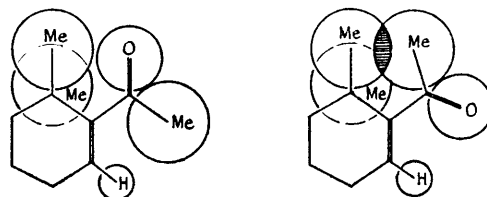(a) s-trans-*Configuration.*   (b) s-cis-*Configuration.*

β-cyclo*Citral.*

Dimensions used in Figs. 1–4 : C—C bond length 1·54 A., C═C bond length 1·33 A., C—H bond length 1·08 A., C═O bond length 1·22 A., H covalent-bond radius 0·31 A., Me covalent-bond radius 1·39 A., ═O covalent-bond radius 1·10 A.

FIG. 2.
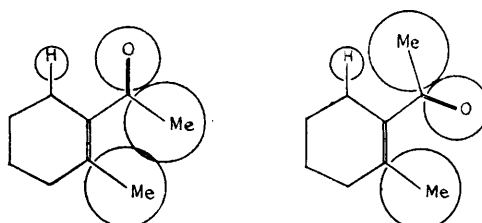
(a) s-trans-*Configuration.*   (b) s-cis-*Configuration.*

1-*Acetyl-2-methyl*cyclohexene.

FIG. 3.

(a) s-trans-*Configuration.*   (b) s-cis-*Configuration.*

1-*Acetyl-6 : 6-dimethyl*cyclohexene.

FIG. 4.
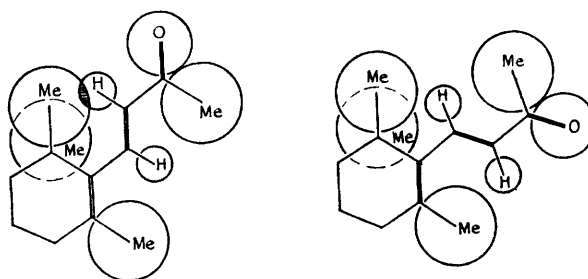
(a) trans-*Configuration.*   (b) s-cis-*Configuration.*

β-*Ionone.*

β-ionone has been advocated (Naves and Bachmann, *Helv. Chim. Acta.*, 1943, **26**, 2153), though on rather ambiguous evidence, and is not incompatible with the method of preparation of the synthetic analogues. It would, however, imply strong steric interference between the acetyl

6 H

group and one of the ring-hydrogen atoms in the completely demethylated analogue (i). The intensity and wave-length location of the 2800 A. maximum exhibited by this compound are very similar to those shown by the acyclic ψ-ionone (o), and a *cis*-configuration of the side-chain ethylenic bond therefore appears unlikely. If a *trans*-configuration is assumed for this bond, no interference with the acetyl group is indicated by diagrams employing covalent radii, even in the presence of 2- or 6-methyl substituents. There is, however, a significant overlap between a 6-methyl substituent and a hydrogen atom of the side-chain, provided that the orientation about the single bond between the *cyclo*hexene ring and the side-chain is *s-trans* (Figs. 4*a* and 4*b*). This would be expected to be the preferred orientation by analogy with that suggested for the other diene and enone systems. No overlap is shown with a 2-methyl substituent in either the *s-trans-* or *s-cis*-configurations. This is in agreement with the experimental data which show that a large intensity reduction of the dienone band at 2800 A. is produced by 6-*gem*-dimethyl substituents whilst 2-methyl substituents have only a small effect. The increase in the intensity of the 2200 A. band which is observed also in the former case may be ascribed to the partial enone chromophore in the side-chain (in the case of the acetyl*cyclo*hexenes, the characteristic wave-length bands of the partial $-C\dvtri C-$ and $-C\dvtri O$ chromophores fall ouside the observational range).

We shall now turn to the semicarbazones and dinitrophenylhydrazones of the parent carbonyl compounds. Increases in $\lambda_{max.}$ due to 2-methyl substituents without changes in $\varepsilon_{max.}$ are clearly simple alkylation effects as before. In those cases where 2-methyl substituents result in a decrease in $\lambda_{max.}$ as well as in $\varepsilon_{max.}$, the positions of the maxima are displaced towards those expected for the partial chromophore represented by the side-chain and not involving the unsaturation in the ring. The displacement is greater the greater the steric interference, as indicated by the intensity decrease in the parent carbonyl compound, and the derivatives of 1-acetyl-2-*n*-butyl*cyclo*hexene show absorption practically identical with that of derivatives of an unconjugated ketone, *e.g.*, 1-acetyl-2-methyl*cyclo*hex-2-ene (II). The decreases in $\lambda_{max.}$ in the sterically " hindered " derivatives is presumably due to the fact that, unlike those in the parent carbonyl compounds, the bands of the fully conjugated and partial side-chain chromophores are situated fairly closely together in wave-length and do not differ greatly in intensity, and that the appearance of the " partial " bands masks the much reduced longer-wave-length bands due to full conjugation. This is borne out by the fact that the bands in the sterically hindered derivatives are unusually wide, and, especially in the semicarbazones, often show subsidiary inflections. In these cases there may be, in addition to purely geometrical superposition, some additional resonance degeneracy owing to the proximity of the energy levels.

Experimental.

(Absorption spectra, unless stated otherwise, were determined in alcoholic solutions).

Condensation of 1-*Methyl*cyclo*hexene with Acetyl Chloride* (Ruzicka, Koolhaas, and Wind, *loc. cit.*).— The reaction was carried out by the recorded method with 1-methyl*cyclo*hexene (130 g.; prepared according to Mosher, *J. Amer. Chem. Soc.*, 1940, **62**, 552), acetyl chloride (106 g.), and stannic chloride (345 g.) in carbon disulphide (825 g.). After treatment with diethylaniline (130 g.), the crude ketone (75 g.; 40% yield) had b. p. 95—100°/23 mm., and on distillation through a Widmer column at 16 mm. the following fractions were collected : (i) b. p. 82—83° (7·5 g.), $n_D^{20°}$ 1·4715; (ii) 83—84° (8·2 g.), $n_D^{20°}$ 1·4715; (iii) 85—86° (3·7 g.), $n_D^{20°}$ 1·4751; (iv) 86—87° (9·2 g.), $n_D^{19°}$ 1·4788; (v) 87—88° (7·0 g.), $n_D^{19°}$ 1·4805; (vi) 88—89° (8·2 g.), $n_D^{18°}$ 1·4832; (vii) 89—90° (4·4 g.), $n_D^{17°}$ 1·4841. Light absorption of (i); Maximum, 2450 A.; ε, 1600. Light absorption of (vii) : Maximum, 2450 A.; ε, 5600.

Treatment of 2-*Methyl*-1-*ethynyl*cyclo*hexanol with Formic Acid.*—A solution of 2-methyl-1-ethynyl-*cyclo*hexanol (83 g.; prepared from the ketone with sodium acetylide in liquid ammonia) in formic acid (750 g.; 90%) was heated under reflux for 2½ hours; the bulk of the acid was removed through a column under reduced pressure, and after the residue had been neutralised with sodium carbonate solution the product was isolated by means of ether; the crude ketone (62 g.; 76%) had b. p. 80—90°/11 mm. Light absorption : Maximum, 2450 A.; ε, 4000. Distillation through a fractionating column containing a 40 × 1·5-cm. section packed with single-turn glass halices, fitted with a total condensation variable take-off head operating at a reflux ratio of about 8 : 1, gave the following fractions : (i) b. p. 78—84°/12 mm. (1·7 g.), $n_D^{15°}$ 1·4704; (ii) 84—86° (5·8 g.), $n_D^{15°}$ 1·4783; (iii) 86—88° (9·2 g.), $n_D^{15°}$ 1·4827; (iv) 88—89° (10·1 g.), $n_D^{12°}$ 1·4870; and (v) 89° (8·4 g.), $n_D^{13°}$ 1·4887. Light absorption of (v); Maximum, 2450 A.; ε, 6400. The residue remaining after the crude ketone mixture had been distilled partly solidified. Crystallisation from light petroleum (b. p. 40—60°) gave plates (1·6 g.), m. p. 47°, which were shown to consist of nonane-2 : 8-dione, probably formed from the acetylmethyl*cyclo*hexene by a reversed aldol condensation (Found : C, 69·7; H, 10·65. Calc. for $C_9H_{16}O_2$: C, 69·2; H, 10·35%). The bisdinitrophenylhydrazone had m. p. 160° (Found : C, 48·55; H, 5·1. Calc. for $C_{21}H_{24}O_8N_8$: C, 48·8; H, 4·7%) (Alder, Pascher, and Schmitz, *Ber.*, 1943, **76**, 27, give m. p. 49° for the diketone and m. p. 156° for the bisdinitrophenylhydrazone).

1-*Acetyl*-2-*methyl*cyclo*hex*-1-*ene* (I).—(*a*) The crude ketone (46·5 g.; $n_D^{20°}$ 1·478), prepared by the first method described above, on treatment with semicarbazide acetate solution in the normal manner

deposited a crystalline mass (*A*) (36 g.), m. p. 180—200°. Two recrystallisations from ethanol, followed by a recrystallisation from benzene, which did not alter the m. p., gave the semicarbazone of 1-acetyl-2-methyl*cyclo*hex-1-ene as plates, m. p. 212—214° (Ruzicka, Koolhaas, and Wind, *loc. cit.*, give m. p. 213°). Light absorption : see table.

(*b*) The crude ketone (36·5 g.; $n_D^{28°}$ 1·474), prepared by the second method described above, on treatment with semicarbazide acetate solution deposited a powder (*B*), m. p. 195—200°. Crystallisation from ethanol gave the semicarbazone of 1-acetyl-2-methyl*cyclo*hex-1-ene (23 g.) as shining plates, m. p. 213°, undepressed on admixture with the material obtained in (*a*).

The ketone was regenerated from the pure semicarbazone (22 g.) by boiling under reflux a stirred suspension in light petroleum (b. p. 60—80°) and 2N-sulphuric acid for 48 hours. This gave 1-acetyl-2-methyl*cyclo*hex-1-ene (14 g.; 90%), b. p. 98—98·5°/25 mm., $n_D^{25°}$ 1·4852. Light absorption : see table (Braude, Jones, Sondheimer, and Toogood, *loc. cit.*, for a sample obtained by the partial hydrogenation of 6-methyl-2 : 5-dihydroacetophenone, give b. p. 89—91°/14 mm., $n_D^{21°}$ 1·4842. Light absorption : Maximum, 2440 A.; ε, 6000). Alternatively, the ketone could be regenerated from the semicarbazone by steam-distillation with phthalic anhydride, whereafter the product had physical properties identical with those above. On treament with semicarbazide acetate, the pure ketone gave the semicarbazone described above [m. p. (crude) 208—214°] ; it gave an oily oxime and was recovered unchanged on treatment with sodamide in ether (cf. Jones and Koch, *J.*, 1942, 393). It was similarly recovered unchanged after heating under reflux with 90% formic acid, no rearrangement to the Δ²-isomer being observed. The 2 : 4-dinitrophenylhydrazone crystallised from ethanol in bright red plates, m. p. 125°, undepressed on admixture with the sample (m. p. 124—125°) prepared by Braude, Jones, Sondheimer, and Toogood (*loc. cit.*). Light absorption : see table.

1-*Acetyl-2-methylcyclohex-2-ene* (II).—(*a*) The mother-liquors obtained after separation of the crude semicarbazone (*A*) described above gave a solid (11 g.) on dilution with water. Repeated crystallisation from aqueous alcohol, neglecting the more insoluble fractions, followed by crystallisation from benzene, gave the *semicarbazone* of 1-acetyl-2-methyl*cyclo*hex-2-ene (5 g.) as stout prisms, m. p. 148—150° (mixed with semicarbazone of Δ¹-form, m. p. 154—190°) (Found : N, 21·7. $C_{10}H_{17}ON_3$ requires N, 21·5%). Light absorption : Maximum, 2300 A.; ε, 13,000.

(*b*) The mother-liquors obtained after separation of the crude semicarbazone (*B*) described above, gave a solid (8·9 g.) on dilution with water. Repeated crystallisation as before gave the semicarbazone of 1-acetyl-2-methyl*cyclo*hex-2-ene, m. p. 131—132° (the m. p. depends on the rate of heating and is raised to *ca.* 150° by admixture with a few % of the Δ¹-isomer. This probably explains the higher m. p. recorded above, (Found : N, 21·0. Calc. for $C_{10}H_{17}ON_3$: N, 21·5%). Light absorption : Maximum, 2270 A.; ε, 12,000.

The ketone was regenerated from the semicarbazone (4·9 g.) by steam-distillation with phthalic anhydride (10 g.) in water (100 c.c.). This yielded 1-*acetyl-2-methyl*cyclohex-2-ene (2·9 g.), b. p. 83—85°/18 mm., $n_D^{20°}$ 1·4695 (Found : C, 78·1; H, 10·2. $C_9H_{14}O$ requires C, 78·3; H, 10·1%). Light absorption : ε, <600 at 2450 A. On treatment with semicarbazide acetate it gave the semicarbazone described above [m. p. (crude) 140—144°]. After treatment with sodamide in ethereal solution the ketone was recovered unchanged. When this regeneration was carried out by steam-distillation with oxalic acid instead of phthalic anhydride, complete isomerisation to the Δ¹-isomer occurred and the product had $n_D^{15°}$ 1·4891. Light absorption : Maximum, 2490 A.; ε, 6500.

In a recent paper, Dimroth and Lüderitz (*Ber.*, 1948, **81**, 242) state that the reaction of 1-methyl-*cyclo*hexene furnishes both 2-methyl-1-acetyl*cyclo*hex-1-ene and the Δ²-isomer, but the light-absorption properties recorded for the former show that the material was not obtained pure. The m. p.s of the semicarbazones are given as 206° and 158—160°, respectively. From the rearrangement of 2-methyl-1-ethynyl*cyclo*hexanol with formic acid, Dimroth and Lüderitz report having obtained a third isomer, formulated as 1-acetyl-2-methyl*cyclo*hex-5-ene, which gives a semicarbazone, m. p. 208°. Dimroth and Lüderitz formulate the semicarbazone, m. p. 208°, as a pyrazoline derivative. This formulation is almost certainly erroneous, however, since in all analogous cases the pyrazoline derivative is obtained as a *liquid* from the semicarbazone itself, and since the derivative exhibits the expected light absorption properties (the data in the table on p. 245 appear to be transposed).

Acetylcyclohexene.—The ketone was prepared by methods analogous to those used for preparing the acetylmethyl*cyclo*hexene (cf., *inter al.*, Hurd and Christ, *J. Amer. Chem. Soc.*, 1937, **59**, 118; Chanley, *ibid.*, 1948, **70**, 244). The pure ketone was obtained from the semicarbazone (see below) by heating the latter under reflux with light petroleum (b. p. 60—80°) and dilute sulphuric acid. It had b. p. 90°/16 mm., $n_D^{15°}$ 1·4910. Light absorption : see table. The semicarbazone had m. p. 218—219° (Chanley, *loc. cit.*, gives m. p. 220—221°). Light absorption : see table. The 2 : 4-dinitrophenyl-hydrazone had m. p. 202°, undepressed on admixture with a sample (m. p. 202°) obtained by partly hydrogenating 2 : 5-dihydroacetophenone (Braude, Jones, Sondheimer, and Toogood, *loc. cit.*). Light absorption : see table. Dimroth and Lüderitz (*loc. cit.*) record light-absorption properties for the ketone and its semicarbazone almost identical with our own and also state that the semicarbazone, m. p. 210°, can be converted, by melting, into a liquid pyrazoline derivative with a maximum at 2400 A., ε, 9600.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W.7.