[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

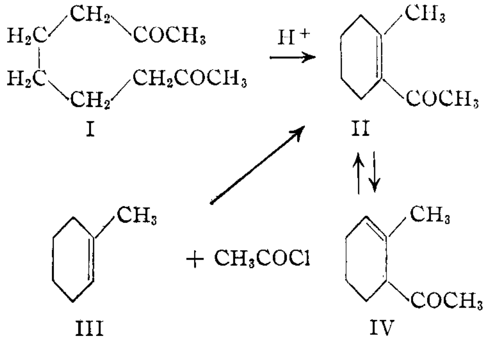
The Structure of 1-Acetyl-2-methylcyclohexene; Spectral Characteristics of *s-cis-α,β*-Unsaturated Ketones[1]

BY RICHARD B. TURNER AND DOROTHY M. VOITLE

Ultraviolet and infrared absorption measurements indicate that 1-acetyl-2-methylcyclohexene, prepared by two different methods, is an equilibrium mixture of Δ^1- and Δ^2-unsaturated forms. Pure 1-acetyl-2-methyl-Δ^1-cyclohexene was obtained by fractional crystallization of the mixed semicarbazones, followed by hydrolysis of the higher melting derivative in the presence of phthalic acid. The resulting product absorbs ultraviolet light of the predicted wave length, but the intensity of absorption is abnormally low. This phenomenon has been attributed by other investigators to steric inhibition of resonance caused by interference between the methyl group of the acetyl residue and the 2-methyl substituent in the *s-trans* (extended) configuration. However, comparison of the absorption properties of 1-acetyl-2-methyl-Δ^1-cyclohexene with those of α,β-unsaturated ketones of the *s-cis* type suggests that the former product also possesses an *s-cis* structure. This conclusion is consistent with the lesser hindrance of the *s-cis* form and is supported by considerations of semicarbazone spectra. Correlation of the spectral characteristics of a number of *s-cis-α,β*-unsaturated ketones reveals no appreciable shift in the position of absorption of these substances as compared with similarly substituted *s-trans* derivatives. The data indicate, however, that compounds of the *s-cis* configuration may be expected to exhibit diminished absorption intensity, owing to the decrease in the distance separating the ends of the conjugated system.

In connection with work described in previous communications[2] we have had occasion to investigate the structure and properties of 1-acetyl-2-methylcyclohexene, first prepared in 1890 by acid-catalyzed cyclization of nonanedione-2,8 (I).[3] A second synthesis, involving condensation of methylcyclohexene with acetyl chloride followed by dehydrochlorination of the resulting β-chloroketone, was reported by Ruzicka, Koolhaas and Wind[4] in 1931. This group employed methylcyclohexene prepared by dehydration of commercial 2-methylcyclohexanol. The latter product contains both *cis* and *trans* isomers, and Raman absorption studies[5] indicate that methylcyclohexene from this source consists of a mixture of Δ^1- and Δ^2-derivatives. No evidence was presented by the Swiss investigators for the purity of the acetylmethylcyclohexene obtained from this intermediate, and the composition of their product is therefore uncertain. Pure 1-methyl-Δ^1-cyclohexene (III) can be obtained by dehydration of 1-methylcyclohexanol.[6] Reaction of this product with acetyl chloride followed by treatment with methanolic sodium hydroxide (or with diethylaniline) furnishes an equilibrium mixture of 1-acetyl-2-methyl-Δ^1-cyclohexene (II) and 1-acetyl-2-methyl-Δ^2-cyclohexene (IV).[5,7] The amounts of other isomers, if present, are negligible.

The following spectroscopic evidence substantiates these views. Maximum absorption in the ultraviolet at 248 mμ (Fig. 1a) is that expected for an α,β,β-trisubstituted-α,β-unsaturated ketone,[8] but is of unusually low intensity (ε 4500) (*cf.* reference 7). The appearance of two bands in the carbonyl region of the infrared (Fig. 2a), one at 5.93 μ and the other at 5.85 μ, indicates the presence of conjugated and of unconjugated ketonic functions, respectively. Significantly, the ultraviolet and infrared spectra of samples derived from nonanedione (I) and from methylcyclohexene (III) are identical.



Treatment of the mixture of unsaturated ketones with semicarbazide acetate at room temperature yields two products, which, in our hands, after repeated fractional crystallization from ethanol, melt at 227–227.5° (dec.) and at 160–162°. Melting points reported for these compounds by Dimroth and Lüderitz[5] are 208° and 158–160°, whereas Braude, Jones and their collaborators[7] record values of 213° and 131–132°.

Some confusion has arisen regarding the constitution of these substances. The German workers formulated their higher melting derivative as a pyrazoline in view of its anomalous light absorption properties (see below). The absorption data can, however, be satisfactorily explained without recourse to this assumption. Since the substance is formed under conditions that with the closely related, but less hindered, acetyl-Δ^1-cyclohexene yield a semicarbazone, and since the pyrazoline derived from the latter product is a liquid, b.p. 160° (14 mm.), there appears no reason to doubt that the compound in question is a true semicarbazone. We have found that a constant melting point is reached only after several recrystallizations and conclude that samples studied previously were impure.

Regeneration of the free ketone by steam distillation in the presence of phthalic acid affords a compound with maximum absorption in the ultraviolet at 249 mμ, ε 6890 (Fig. 1b), and with but a single band in the carbonyl region of the infrared at 5.93 μ

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[1] This work was supported in part by funds provided by the American Cancer Society on recommendation of the Committee on Growth of the National Research Council and by Eli Lilly and Co., Indianapolis.

[2] (a) R. B. Turner, THIS JOURNAL, **72**, 878 (1950); (b) R. B. Turner and Dorothy M. Voitle, *ibid.*, **72**, 4166 (1950).

[3] F. S. Kipping and W. H. Perkin, *J. Chem. Soc.*, **57**, 16 (1890).

[4] L. Ruzicka, D. R. Koolhaas and A. H. Wind, *Helv. Chim. Acta*, **14**, 1151 (1931).

[5] O. Lüderitz, Dissertation, Göttingen, 1944; K. Dimroth and O. Lüderitz, *Ber.*, **81**, 242 (1948).

[6] W. A. Mosher, THIS JOURNAL, **62**, 552 (1940).

[7] E. A. Braude, E. R. H. Jones, *et al.*, *J. Chem. Soc.*, 1890 (1949).

[8] R. B. Woodward, THIS JOURNAL, **63**, 1123 (1941); *ibid.*, **64**, 76 (1942).

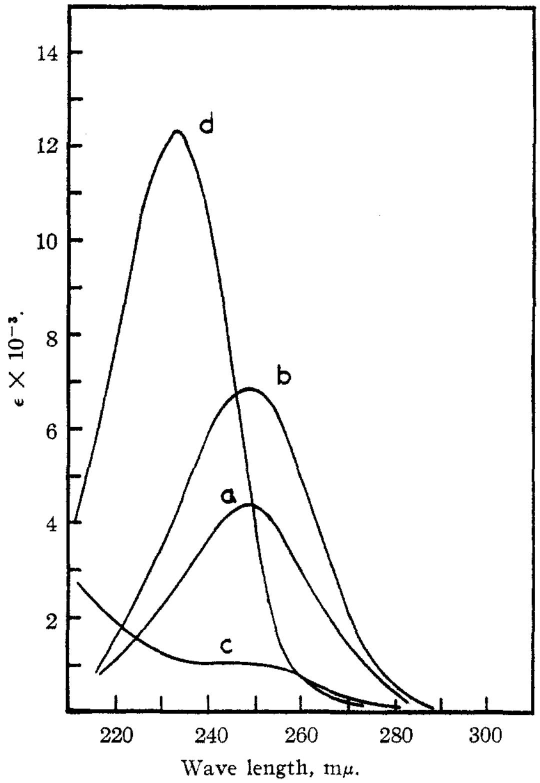


Fig. 1.—Ultraviolet absorption spectra for (a), 1-acetyl-2-methyl-Δ^1(and Δ^2)-cyclohexene (equilibrium mixture from III); (b), 1-acetyl-2-methyl-Δ^1-cyclohexene; (c), 1-acetyl-2-methyl-Δ^2-cyclohexene (containing a small amount of the Δ^1-isomer); (d), acetyl-Δ^1-cyclohexene.

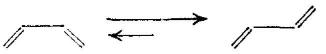
(Fig. 2b). Disappearance of the 5.85 μ band demonstrates the absence of unconjugated ketonic material, and the product is hence assigned structure II.[9]

Similar treatment of the semicarbazone melting at 160–162° leads to the formation of an unsaturated ketone with absorption characteristics shown in curves c of Figs. 1 and 2. The spectral evidence indicates a β,γ-unsaturated structure (IV) for this substance, which however is evidently contaminated by 5–10% of the α,β-unsaturated form (II). In this connection Braude, *et al.*,[7] have observed that the melting point of their semicarbazone (131–132°)—presumably the pure semicarbazone of IV—is raised to about 150° on admixture with a few per cent. of the higher melting derivative. We have not investigated this point further.

The two unsaturated ketones described above are relatively stable toward cold, dilute methanolic sulfuric acid, but each on equilibration with sodium ethoxide furnishes the same product, which is spectroscopically indistinguishable from the original equilibrium mixture (*cf.* Figs. 1a and 2a).

The absorption maximum (249 mμ) of pure 1-acetyl-2-methyl-Δ^1-cyclohexene (II) lies close to the position (247 mμ) predicted by Woodward's rules,[8] but is of abnormally low intensity (ϵ 6890). Acetyl-Δ^1-cyclohexene, which lacks the methyl substituent at C.2, has a molecular extinction coefficient at the maximum (232 mμ) of 12400 (Fig. 1d). The methyl group itself is weakly *hyperchromic*,[10] and Braude, Jones and their associates[7] have attributed the low intensity of the absorption of II to steric inhibition of resonance consequent upon interference between the methyl group of the acetyl residue and the 2-methyl substituent in the *s-trans* form (V).[11] The alternate *s-cis* structure, though less hindered,[12] was rejected on the grounds that (a), the *s-trans* modification (V) is energetically favored over the *s-cis* form (VI) and (b), displacement of the absorption maximum from the predicted position would be expected for the *s-cis*, but not for the *s-trans* structure, if hindrance in the latter were small. The validity of these assumptions is disputable.

Calculations from calorimetric data for the *s-cis*–*s-trans* butadiene equilibrium (VII $\rightleftarrows$ VIII) by Aston and his associates[13] indicate that the two butadiene isomers differ in energy by only 2.3 kcal., the *s-trans* form being more stable, and are separated by an energy barrier of about 2.6 kcal. This value is of the same order of magnitude as the rotational barrier in ethane.[14] If comparable energy relationships apply to α,β-unsaturated ketones, it is clear that other things being equal, the *s-trans* form will predominate at equilibrium. However, the energy changes required for reversal of the stability order are small, and in cases in which the *s-trans* form is more hindered than the corresponding *s-cis* modification, small steric factors will be important.


VII VIII

In considering the spectral characteristics of *s-cis*–*s-trans* isomers and the elements, steric or otherwise, responsible for the low intensity absorption of 1-acetyl-2-methyl-Δ^1-cyclohexene, it will be necessary to summarize briefly certain principles on which correlations of band position and intensity with molecular structure are based.

Absorption of ultraviolet light by organic molecules involves transition from a hybrid ground state, largely homopolar in character, to an excited state in which higher energy resonance forms participate to a greater degree.[15] Whereas the wave length of absorption is determined by the energy of the transition, the integrated intensity of the ab-

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[9] Dr. W. S. Johnson informs us that he and his associates have succeeded in crystallizing this compound and that the molecular extinction coefficient of the crystalline ketone is 6882. The English workers (ref. 7) obtained a value of 6500 for liquid ketone regenerated from their semicarbazone, m. p. 213°.

(10) F. A. Matsen, W. W. Robertson and R. L. Chuoke, *Chem. Revs.*, **41**, 273 (1947), and references cited by these authors.

(11) The terms "*s-cis*" and "*s-trans*" are employed by Mulliken (reference 15b) to designate *cis* and *trans* isomers about a single bond possessing partial double bond character.

(12) The overlap of van der Waals radii of oxygen and of the methyl group in this case is 0.96 Å. as compared with 1.58 Å. for the overlap of methyl radii in V.

(13) J. G. Aston, G. Szasz, H. W. Woolley and F. G. Brickwedde, *J. Chem. Phys.*, **14**, 67 (1946); *cf.* A. D. Walsh, *Nature*, **157**, 768 (1946).

(14) H. Eyring, THIS JOURNAL, **54**, 3191 (1932); J. D. Kemp and K. S. Pitzer, *J. Chem. Phys.*, **4**, 749 (1936); THIS JOURNAL, **59**, 276 (1937); J. B. Conn, G. B. Kistiakowsky and E. A. Smith, *ibid.*, **61**, 1868 (1939).

(15) (a) A. L. Sklar, *J. Chem. Phys.*, **5**, 669 (1937); (b) R. S. Mulliken, *Revs. Mod. Phys.*, **14**, 265 (1942); (c) A. Maccoll, *Quart. Revs.*, **1**, 16 (1947).

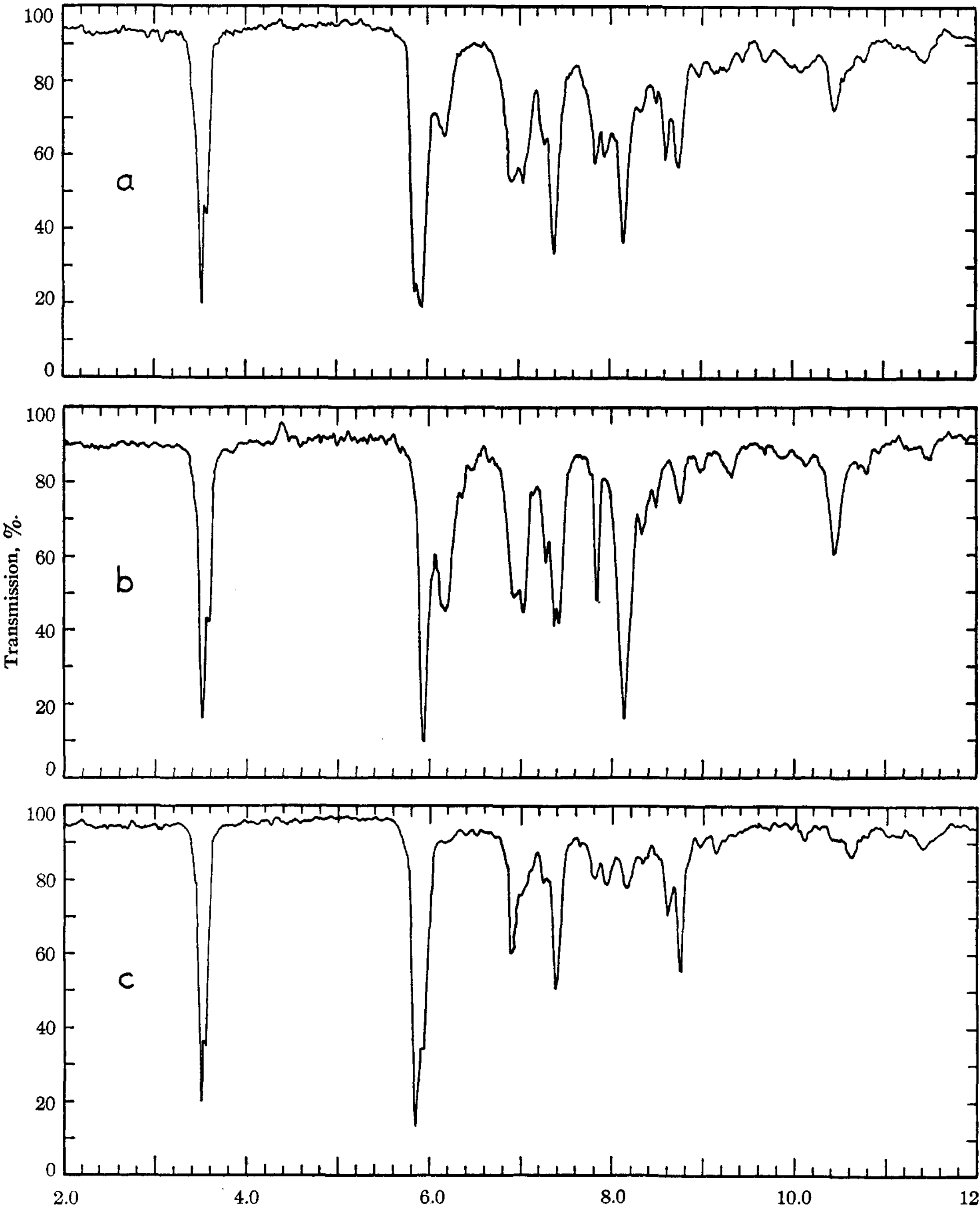


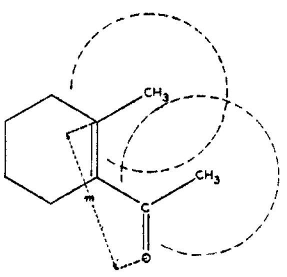
Fig. 2.—Infrared absorption spectra for (a), 1-acetyl-2-methyl-Δ^1(and Δ^2)-cyclohexene (equilibrium mixture from III); (b), 1-acetyl-2-methyl-Δ^1-cyclohexene; (c), 1-acetyl-2-methyl-Δ^2-cyclohexene (containing a small amount of the Δ^1-isomer).

sorption band[16] is related to the *probability* of excitation. This function is proportional to the dipole strength of the chromophoric group and hence essentially to the *square of the distance separating the ends of the absorbing system.*[17]

Since maximum resonance interaction between two groups, as for example between chromophore and auxochrome, is conditioned by approximate coplanarity of the atoms concerned, departures from the planar configuration, owing to steric factors, are accompanied by a decrease in resonance stabilization, which is operative in both the ground and the excited states. As the degree of non-planarity becomes progressively greater, the resultant energy changes may be expected to have the following effects on light absorption.

[16] Integrated intensity is measured by the area under the band envelope and is often expressed as "oscillator strength," $f = 4.32 \times 10^{-9}\int \epsilon d\nu$, where ν is the frequency in cm.$^{-1}$ and ϵ, the molecular extinction coefficient.

[17] N. Q. Chako, *J. Chem. Phys.*, **2**, 644 (1934); R. S. Mulliken, *ibid.*, **7**, 14 (1939), and subsequent papers; L. Pauling, *Proc. Nat. Acad. Sci.*, **25**, 577 (1939).



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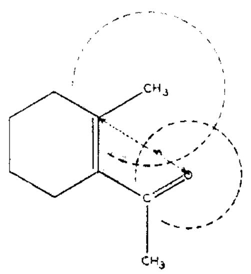
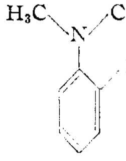


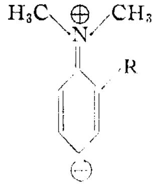
VI

Fig. 3.—Dimensions are as follows: C–CH$_3$ 1.54 Å.; C=C, 1.35 Å.; =C—C=, 1.46 Å.; C=O, 1.25 Å.; C—C=C and C—C=O angles, 120°; van der Waals' radii of -CH$_3$, 2.00 Å., of the carbonyl oxygen atom, 1.40 Å.

In the event that steric repulsions are sufficiently small to permit an essentially planar, though strained, configuration, the effect on the position of maximum absorption may be negligible, for differences in steric energy of the ground and of the excited states, represented for the N-dimethylanilines by extreme forms IX and X, respectively, will probably not be large. The intensity of absorption, however, will in general be diminished, since the configuration most favorable for excitation is attained less frequently in a hindered than in an unhindered molecule. Thus *o*-chloro-N-dimethylaniline (IX, R = Cl) absorbs maximally at 256 mμ (ε 7600) as compared with 258 mμ (ε 17000) for the *p*-chloro isomer.[18]



IX



X

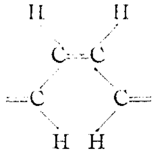
As repulsive interactions opposing coplanarity increase, the energy of the excited state, to which forms of type X make a comparatively large contribution, will increase relative to that of the ground state, in which these forms are less important, owing to strain imparted by rotation of the carbon–nitrogen partial double bond. Absorption in such non-planar systems will be characterized by diminished intensity (diminished polarity of the excited state) and by hypsochromic displacement of the absorption band. These effects may be illustrated by the following comparisons.[18,19]

p-Methyl-N-dimethylaniline	254 mμ (ε 15000)
o-Methyl-N-dimethylaniline	247 mμ (ε 6200)
trans-Stilbene	294 mμ (ε 23400)
α-Methyl-*trans*-stilbene	275 mμ (ε 18000)
α,β-Dimethyl-*trans*-stilbene	243 mμ (ε 11700)

When deviation from the planar configuration becomes so large that the energy required for excitation of the conjugated system is prohibitive, absorption owing to conjugation reverts to that of the isolated chromophores. The spectra of bimesityl[20] and of isodurene,[21] for example, are nearly identical, with the exception that bimesityl absorbs with greater intensity owing to the presence of two benzenoid rings.

Departures from coplanarity are brought about, not only by introduction of bulky substituents, but also in certain instances by changes in molecular geometry. X-Ray analyses of *cis*- and of *trans*-azobenzene[22] show that whereas the *trans* compound can assume a strainless planar configuration, repulsions between *o*- and *o'*-hydrogen atoms in the *cis* isomer cause a rotation of the benzene rings of about 50° from the planar position. Similar properties have been attributed to *cis*-stilbene,[23] and Zechmeister and LeRosen[24] have estimated that out-of-the-plane rotation in diphenylpolyenes in which a phenyl group is joined to a *cis*-ethylenic linkage is about 52°. Although *cis*-azobenzene itself is exceptional, various substituted *cis*-azobenzenes,[25] *cis*-stilbene[26] and *cis*-cinnamic acid[26] absorb at somewhat shorter wave length and with lower intensity than do the respective *trans* isomers. Analogous relationships appear in the series *trans*-*trans*-diphenylbutadiene (328 mμ, ε 56200), *cis*-*trans*-diphenylbutadiene (313 mμ, ε 30600), *cis*-*cis*-diphenylbutadiene (299 mμ, ε 29500).[27]

Intensity losses associated with the *cis* compounds in this group are only partly attributable to steric hindrance, for shortening of the chromophore by incorporation of a *cis*-ethylenic linkage also contributes to reduction of the electric moment. The latter effect is most easily studied in geometric isomers in which hindrance of the *cis* form is negligible. The unit



of the carotenoids constitutes such a system.[28] Correlation of spectra with structure in this series has been extensively investigated by Zechmeister and his associates,[29] who showed that the principal absorption band, which in these compounds occurs in the visible, is shifted only about 5 mμ to shorter wave length by one *trans* → *cis* conversion.[30] If this change involves the central double bond as in lycopene (XI) → neolycopene A (XII), the reduction of intensity is appreciable. The ratio of the integrated absorption coefficient of neolycopene A to

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[18] W. R. Remington, THIS JOURNAL, **67**, 1838 (1945).

[19] R. N. Jones, *ibid.*, **65**, 1818 (1943).

[20] L. W. Pickett, G. F. Walter and H. France, *ibid.*, **58**, 2296 (1936).

[21] H. Conrad-Billroth, *Z. physik. Chem.*, **29B**, 170 (1935).

[22] J. M. Robertson, *J. Chem. Soc.*, 232 (1939).

[23] G. N. Lewis, T. T. Magel and D. Lipkin, THIS JOURNAL, **62**, 2973 (1940).

[24] L. Zechmeister and A. L. LeRosen, *ibid.*, **64**, 2755 (1942).

[25] A. H. Cook, D. G. Jones and J. B. Polya, *J. Chem. Soc.*, 1315 (1939).

[26] A. Smakula and A. Wasserman, *Z. physik. Chem.*, **155A**, 353 (1931).

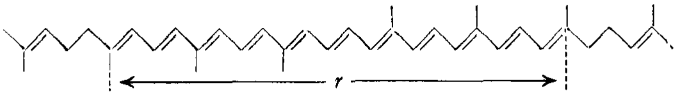
[27] J. H. Pinckard, B. Wille and L. Zechmeister, THIS JOURNAL, **70**, 1938 (1948).

[28] L. Pauling, *Fortschr. Chem. organ. Naturstoffe*, **3**, 203 (1939); *Helv. Chim. Acta*, **32**, 2241 (1949).

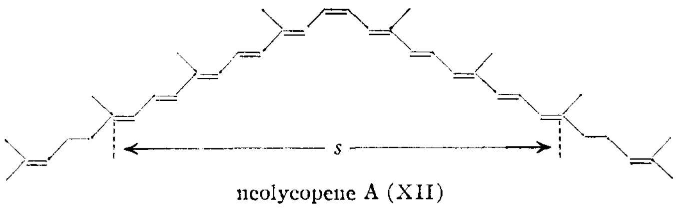
[29] L. Zechmeister, *Chem. Revs.*, **34**, 267 (1944).

[30] A shift of 5 mμ in this region corresponds to a difference in excitation energy of 600–700 cal., and represents a shift of only 1–2 mμ in the region of 250 mμ.

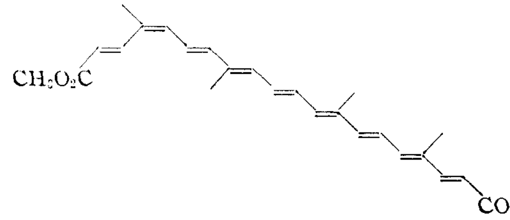
that of lycopene is 0.67 as compared with 0.61 for the ratio of squares of the respective lengths (s^2:r^2).[28] Inversion of a peripheral double bond will, of course, have much less effect. Thus the intensity ratio, natural methylbixin (XIII):all-*trans*-methylbixin, is 0.93.[31]



lycopene (XI)



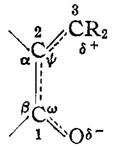
neolycopene A (XII)



natural methylbixin (XIII)

In view of structural similarities between *s-cis*–*s-trans* isomers and *cis–trans* isomers of the conventional type, analogous absorption properties might be anticipated. It is clear that, owing to the low barrier opposing interconversion, independent existence of structural modifications of the former type will be possible only in ring-stabilized systems or in compounds in which, for steric reasons, one configuration is greatly favored. Although the spectral characteristics of *s-trans* compounds (*e.g.*, cholesterylene, cholestenone, etc.) have been thoroughly investigated, information relating to *s-cis* derivatives is not extensive. Molecular orbital treatment of *s-cis-* and of *s-trans*-butadiene (VII and VIII, respectively) led Mulliken[32] to conclude that the wave lengths of absorption should differ very little for the two isomers, but that the intensity of the long wave length band (217 mμ) should be reduced in the *s-cis* form. Although the number of dienes for which the *s-cis* configuration has been unequivocally established is insufficient to permit verification of this point,[33] several α,β-unsaturated ketones of this type are known. Absorption data for these compounds are recorded in Table I.

It will be observed that the position of maximum absorption in all cases lies close to that predicted by Woodward's rules,[8] the greatest deviation being 4 mμ. The compounds listed may be divided into two groups: I, those with carbonyl group and double bond exocyclic to a six-membered ring (no. 1–8) and II, compounds in which these functions are exocyclic to a five-membered ring (no. 9–14). Whereas extinction coefficients of α,β-unsaturated ketones of the *s-trans* type normally range from about 12000 to 20000, those for compounds in group I lie in a narrow region between 4700 and 7200, the average value being 6360. The spread in group II is somewhat larger—7950 to 12800 if no. 10 is omitted—and the average extinction coefficient for derivatives in this class is 10730. If, as seems probable, the diminished intensity of absorption exhibited by *s-cis* compounds is related to the decreased length of the absorbing system, the difference between compounds of group I and of group II is readily explained. In the resonance hybrid XIV the valency angles about carbon atoms 1 and 2 will normally lie close to 120°. These angles, in particular α and β, can be accommodated in a six-membered ring with minimum distortion, but must suffer contraction in a five-membered ring, as can be shown by simple geometric calculations. The consequent expansion of the external angles will be distributed in part over the angles ψ and ω and will result in increased separation of the oxygen atom and carbon atom 3.



XIV

Similarities in the spectra of *s-cis* ketones of group I and of 1-acetyl-2-methyl-Δ^1-cyclohexene suggest that the latter compound may also possess the *s-cis* structure (VI). Comparison of the integrated intensities of 1-acetyl-2-methyl-Δ^1-cyclohexene and of acetyl-Δ^1-cyclohexene, for which the *s-trans* configuration is assumed, is consistent with this view. The intensity factor obtained from the ratio of areas under curves b and d (extrapolated to the base line) of Fig. 1 is 0.65 and is in close agreement with the value 0.68 for the ratio of squares of the respective chromophore lengths (n^2:m^2, Fig. 3).[34] Acceptance of the alternate *s-trans* configuration (V) proposed by Braude, *et al.*,[7] requires that hindrance between the two methyl groups be sufficiently small to permit a high degree of coplanarity (*cf.* preceding discussion). That such is not the case can be deduced from consideration of semicarbazone spectra.

Data of Evans and Gillam[35] indicate that conversion of an α,β-unsaturated ketone into the semicarbazone is normally accompanied by intensification of the principal absorption maximum (K-band) and a shift in the position of this band of about 30 mμ toward longer wave lengths. In these respects acetyl-Δ^1-cyclohexene semicarbazone may be re-

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[31] L. Zechmeister and R. B. Escue, THIS JOURNAL, **66**, 322 (1944).

[32] R. S. Mulliken, *J. Chem. Phys.*, **7**, 121 (1939); *cf.* W. C. Price and A. D. Walsh, *Proc. Roy. Soc.* (*London*), **A174**, 220 (1940).

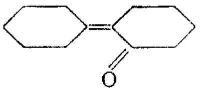
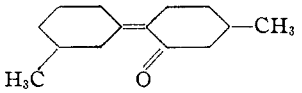
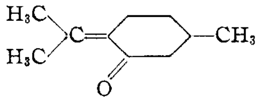
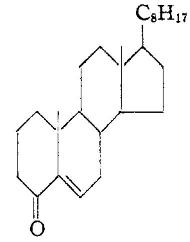
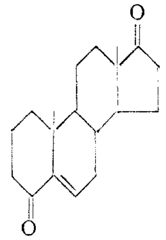
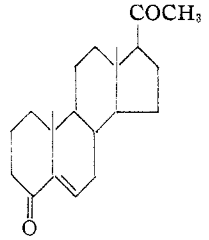
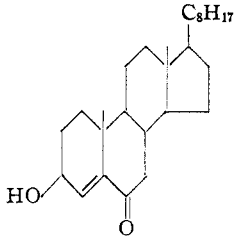
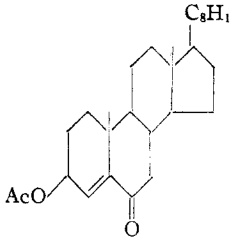
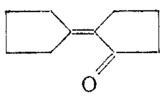
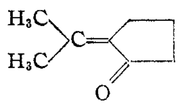
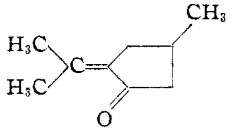
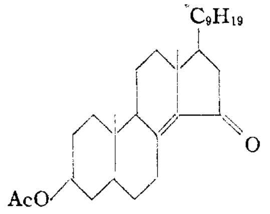
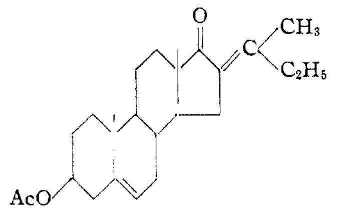
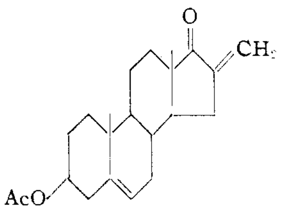
[33] Homoannular dienes, for example cyclohexadiene, constitute a special class not considered here, since in these cases complications arise from hyperconjugation and/or charge transfer involving the intervening methylene groups [R. S. Mulliken, C. A. Rieke and W. G. Brown, THIS JOURNAL, **63**, 41 (1941); T. M. Sugden and A. D. Walsh, *Trans. Faraday Soc.*, **41**, 76 (1945)].

[34] Correction of the intensity ratio for the weak hyperchromic effect of the methyl group would lead to a value slightly lower than 0.65. The present evidence cannot be interpreted as excluding the possibility that hindrance of a low order between the carbonyl oxygen atom and the methyl group may also contribute to the reduction of intensity.

[35] L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 565 (1943).

TABLE I[g]

ABSORPTION SPECTRA OF *s-cis*-α,β-UNSATURATED KETONES

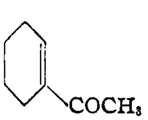
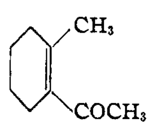
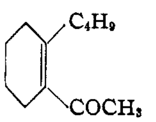
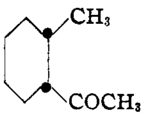
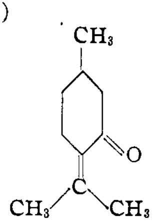
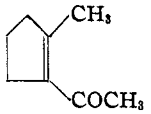
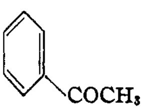
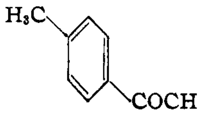
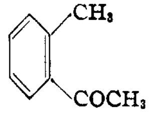
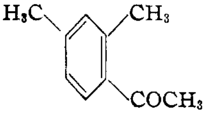
				
Compound no.	1	2	3	4
$\lambda^{calcd.}_{max.}$, mμ	257	257	252	240
$\lambda^{obsd.}_{max.}$, mμ	255	254	252	241
$\epsilon_{max.}$	6300	6760	6500	7200
Ref.	*a*	*a*	*a*	*b*
				
Compound no.	5	6	7	8
$\lambda^{calcd.}_{max.}$, mμ	240	240	240	240
$\lambda^{obsd.}_{max.}$, mμ	239[h]	241[i]	239	236
$\epsilon_{max.}$	6900	4700	6300	6300
Ref.	*b*	*b*	*c*	*c*
				
Compound no.	9	10	11	
$\lambda^{calcd.}_{max.}$, mμ	257	252	252	
$\lambda^{obsd.}_{max.}$, mμ	259	252	254	
$\epsilon_{max.}$	10790	3640(?)	9550	
Ref.	*a*	*a*	*a*	
				
Compound no.	12	13	14	
$\lambda^{calcd.}_{max.}$, mμ	257	252	230	
$\lambda^{obsd.}_{max.}$, mμ	259	252[i]	228	
$\epsilon_{max.}$	12,600	12,800	7950	
Ref.	*d*	*e*	*f*	

[a] H. S. French and L. Wiley, THIS JOURNAL, **71**, 3702 (1949). [b] H. Dannenberg, *Abhandl. preuss. Akad. Wiss.*, **21**, 2 (1939); *cf.* A. Butenandt and G. Ruhenstroth-Bauer, *Ber.*, **77**, 397 (1944). [c] I. M. Heilbron, E. R. H. Jones and F. S. Spring, *J. Chem. Soc.*, 801 (1937). [d] H. E. Stavely and G. N. Bollenback, THIS JOURNAL, **65**, 1285, 1290 (1943). [e] A. Butenandt, J. Schmidt-Thomé and T. Weiss, *Ber.*, **72**, 417 (1939). [f] P. L. Julian, E. W. Meyer and H. C. Printy, THIS JOURNAL, **70**, 3872 (1948). [g] The solvent is ethanol unless otherwise indicated. [h] Measured in chloroform and corrected to ethanol as solvent [*cf.* L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1949, 3rd ed., p. 184]. [i] Measured in ether and corrected to ethanol as solvent (Fieser and Fieser, *loc. cit.*).

garded as typical (see Table II). The semicarbazone of 1-acetyl-2-methyl-Δ^1-cyclohexene, on the other hand, absorbs at *shorter* wave length than does the parent ketone and is in fact more nearly comparable with the semicarbazone of a saturated ketone (no. 4) than with that of an α,β-unsaturated derivative. The case of 1-acetyl-2-*n*-butyl-Δ^1-cyclohexene semicarbazone (no. 3) reported by

TABLE II

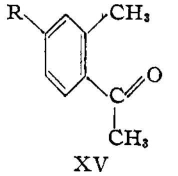
SPECTRA OF KETONES AND DERIVED SEMICARBAZONES (ALL SPECTRA MEASURED IN ETHANOL)

						
Compound no.		1	2	3	4	5
Ketone	$\lambda_{max.}$, mμ	232	249	245	...	252
	$\epsilon_{max.}$	12400	6890	4000	...	6500
Semicarbazone	$\lambda_{max.}$, mμ	260	240	226	225	253
	$\epsilon_{max.}$	24000	10360	12000	12300	11000
						
Compound no.		6	7	8	9	10
Ketone	$\lambda_{max.}$, mμ	253	242	252	243	252
	$\epsilon_{max.}$	10010	12800	15100	8850	14100
Semicarbazone	$\lambda_{max.}$, mμ	268	272	275	250	255
	$\epsilon_{max.}$	18120	15810	19900	12480	11030

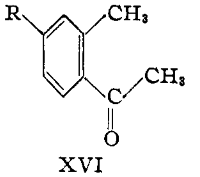
Braude, *et al.*,[7] is even more striking. We see no rational explanation for this phenomenon in terms of an *s-trans* structure (V), in which hindrance of the ketone and of the semicarbazone should be nearly equivalent. The facts are, however, compatible with the *s-cis* configuration. In this case replacement of the carbonyl oxygen atom by the somewhat larger nitrogen atom may be expected to result in increased hindrance and rotation from the planar configuration. It is of some interest in this connection that the spectrum of pulegone semicarbazone (no. 5)[35,36] is also abnormal. Relief of strain in this substance by rotation about the bond joining the two unsaturated functions may account for the observed displacement to shorter wave lengths. The effects noted above should be less pronounced in 1-acetyl-2-methyl-Δ^1-cyclopentene semicarbazone, in which separation of substituents is greater than in the corresponding cyclohexene derivative, and such is found to be the case (no. 6, Table II).

In an effort to obtain confirmation of the position adopted in the foregoing discussion, we have measured the spectra of the four acetophenones listed in Table II together with the spectra of the corresponding semicarbazones. Acetophenone and 2,4-dimethylacetophenone have been examined previously[37]; our results agree with those of the earlier investigators.

Two planar structures, XV and XVI, corresponding in a steric sense to the *s-cis* and *s-trans* configurations of acetylmethylcyclohexene are theoretically possible for the ortho-substituted derivatives. Kadesch and Weller[38] have concluded from dipole moment measurements on a series of substituted aldehydes and ketones that structure XV is the preferred form. That this structure is, nevertheless, not entirely strain-free is suggested by comparison of the spectra of ketones 7 and 8 with those of ketones 9 and 10, in which hypsochromic displacements (about 10 mμ) of the absorption maxima from the expected positions are observed. Of somewhat greater interest, however, are the spectra of the corresponding semicarbazones. Whereas absorption of acetophenone semicarbazone and of *p*-methylacetophenone semicarbazone is normal in all respects, large displacements of the maxima of *o*-methylacetophenone semicarbazone and of *o,p*-dimethylacetophenone semicarbazone are observed. These shifts are comparable with that noted for 1-acetyl-2-methyl-Δ^1-cyclohexene semicarbazone and indicate a considerably larger degree of hindrance for the ortho-substituted semicarbazones than for the corresponding ortho-substituted ketones.



XV



XVI

Acknowledgment.—We wish to express our appreciation for advice given us in connection with certain aspects of this work by Dr. Martin G. Ettlinger and Dr. R. B. Woodward.

Experimental[39]

1-Acetyl-2-methyl-Δ^1(and Δ^2)-cyclohexene. (1) From Nonanedione-2,8 (I).—The procedure employed was substantially that of Kipping and Perkin.[2] A mixture of 9.0 g. of nonanedione-2,8 (m.p. 45–47°)[40] and 40 ml. of 20%

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[36] W. Menschick, I. H. Page and K. Bossert, *Ann.*, **495**, 225 (1932).

[37] M. T. O'Shaughnessy and W. H. Rodebush, THIS JOURNAL, **62**, 2906 (1940).

[38] R. G. Kadesch and S. W. Weller, *ibid.*, **63**, 1310 (1941).

[39] All melting points are corrected. Ultraviolet absorption spectra were measured in ethanol with the Beckman quartz spectrophotometer, model DU. Infrared absorption curves were obtained with the Baird Infrared Recording Spectrophotometer, Model B, on samples in carbon tetrachloride solution.

[40] F. S. Kipping and W. H. Perkin, *J. Chem. Soc.*, **55**, 330 (1889).

sulfuric acid was refluxed for 15 hours under an atmosphere of nitrogen. The reaction mixture was then cooled and extracted with ether. The ether extracts were combined, washed with water, dilute sodium hydroxide solution, saturated sodium chloride, and filtered through anhydrous sodium sulfate. The solvent was finally removed, and the product purified by distillation. The yield of material boiling at 85–88° (16 mm.) was 5.8 g. (73%); $\lambda_{\max.}$ 248 mμ (ϵ 4450).

Essentially the same results were obtained when ethyl α,ω-diacetylcaproate was similarly treated.

(2) **From Methyl-Δ^1-cyclohexene (III).**—A mixture of 122 g. of acetyl chloride and 147 g. of methyl-Δ^1-cyclohexene[6] was added to a cooled solution of 400 g. of stannic chloride in 750 ml. of carbon disulfide at such a rate that the temperature of the reaction mixture did not rise above −5° during the addition.

After standing at room temperature overnight, the dark solution was cooled to 0° and treated with ice. The layers were separated, and the aqueous phase was extracted with ether. The organic fractions were then combined, washed several times with water, and dried over anhydrous sodium sulfate. Removal of the solvents was carried out under reduced pressure, and the residual oil was then allowed to stand overnight at room temperature with 61.0 g. of sodium hydroxide in dilute methanol solution. The product was extracted with ether after dilution of the reaction mixture with a large volume of water. The ether solution was finally washed with water, dried, and concentrated under diminished pressure. Distillation of the residue furnished 102 g. (48%) of 1-acetyl-2-methylcyclohexene, b.p. 82–85° (14 mm.), $\lambda_{\max.}$ 248 mμ (ϵ 4500). The infrared spectrum of this material (Fig. 2a) was identical with that of the product from nonanedione.

1-Acetyl-2-methyl-Δ^1-cyclohexene (II).—Twenty grams of the product obtained in the preceding experiment was converted into semicarbazone by treatment with 20.0 g. of semicarbazide hydrochloride and 15.0 g. of sodium acetate in 50 ml. of water and 150 ml. of methanol. The first crop of crystalline material melted at 201–204° (dec.). After seven recrystallizations from ethanol, the substance melted constantly at 227–227.5° (dec.).

A 4.0-g. sample of this product was steam distilled in the presence of 4.0 g. of phthalic anhydride until no further oil appeared in the distillate. The free ketone was taken into ether, dried over anhydrous sodium sulfate, and fractionated. 1-Acetyl-2-methyl-Δ^1-cyclohexene, b.p. 89.5–90° (17 mm.), was obtained in this way and possessed the following constants: d^{25} 0.9484, $n^{25}\text{D}$ 1.4872, $\lambda_{\max.}$ 249 mμ (ϵ 6890). Reconversion into the semicarbazone gave material melting at 225–226° (dec.) after one recrystallization.

From the mother liquor obtained from the separation of the crude semicarbazone, m.p. 201–204° (dec.), a second semicarbazone was obtained, which, after several recrystallizations from ethanol, melted at 160–162°. The ketone regenerated from this derivative by the procedure described above represented a slightly impure sample of 1-acetyl-2-methyl-Δ^2-cyclohexene (IV), b.p. 83–83.5° (17 mm.), d^{25} 0.9463, $n^{25}\text{D}$ 1.4740. The ultraviolet absorption spectrum (Fig. 1c) was characterized by a plateau at 240–250 mμ (ϵ 1020).

Equilibration of II and IV.—Samples of the α,β- and β,γ-unsaturated ketones (II and IV, respectively) described above were dissolved in dilute methanol and treated with a few drops of concentrated sulfuric acid. After standing overnight at room temperature, the solutions were further diluted with water, and the ketones recovered by ether extraction. The products showed no significant changes in ultraviolet absorption.

Samples of II and IV were then allowed to stand overnight with sodium ethoxide in absolute ethanol under a nitrogen atmosphere. The product obtained from II ($\lambda_{\max.}$ 249 mμ, ϵ 6890) absorbed at 249 mμ, ϵ 4470; the ketone from IV (plateau 240–250 mμ, ϵ 1020) exhibited an absorption maximum at 248 mμ, ϵ 4450. The infrared spectra of the two products were identical with that of the original mixture derived from methylcyclohexene or from nonanedione (Fig. 2a).

Preparation of Ketones and Semicarbazones (Table II).—The following ketones and semicarbazones, listed in Table II, were prepared for ultraviolet absorption measurements. In all cases the ketone was regenerated (steam distillation in the presence of phthalic acid) from the purified semicarbazone and distilled through a short Podbielniak column.

Acetyl-Δ^1-cyclohexene, b.p. 82–84° (14 mm.), was prepared from cyclohexene and acetyl chloride by the procedure of Ruzicka, Koolhaas and Wind[4] with the exception that dehydrochlorination was effected with sodium hydroxide instead of with diethylaniline. The semicarbazone melted at 219–221° (dec.); literature value,[41] 220–221°.

***cis*-1-Acetyl-2-methylcyclohexane semicarbazone**, m.p. 182–182.5°, was prepared from the free ketone formed on hydrogenation of acetylmethylcyclohexene.[2a]

1-Acetyl-2-methyl-Δ^1-cyclopentene, b.p. 75.5–76.5° (15 mm.), was synthesized by the method of Marshall and Perkin.[42] The semicarbazone melted at 223–224° (dec.); literature value,[43] 221°.

Acetophenone, b.p. 85.5–86.5° (16 mm.), was obtained from purified semicarbazone, m.p. 204.5–205.5°.

***p*-Methylacetophenone**, b.p. 94–95° (12 mm.), was obtained from purified semicarbazone, m.p. 212–213.5°.

***o*-Methylacetophenone**, b.p. 93–94° (16 mm.) was prepared by treatment of *o*-toluyl chloride with dimethylcadmium.[44] The melting point of the semicarbazone was 210–211°; best literature value,[45] 212°.

***o,p*-Dimethylacetophenone.**—Semicarbazone melting at 200–201° (literature value,[45] 202°) was derived from ketone supplied by Mr. R. T. Loring of these laboratories. The regenerated ketone boiled at 110–110.5° (15 mm.).

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[41] O. Wallach and E. Evans, *Ann.*, **360**, 46 (1908).

[42] T. R. Marshall and W. H. Perkin, *J. Chem. Soc.*, **57**, 242 (1890).

[43] E. H. Farmer and A. Sundralingam, *ibid.*, 121 (1942).

[44] J. W. Baker, *ibid.*, 445 (1938).

[45] G. Baddeley, *ibid.*, 232 (1944).