

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WELLESLEY COLLEGE]

Absorption Spectra of Certain α,β -Unsaturated Ketones. III.¹ Cross Conjugation of an *exo* and an *endo* Double Bond with the Carbonyl Group

BY HELEN S. FRENCH

In order to increase the usefulness of absorption spectra in determining the structures of complex naturally occurring compounds, the absorption data are reported for thirteen relatively simple cyclic ketones of well established structure containing the chromophore $C=C-C-C=C$, and for the corresponding mother substances without the *exo*-double bond. The

absorption characteristics of the chromophores are discussed, especially to bring out differences between five-atom and six-atom ring compounds.

Complex naturally occurring compounds often contain five- and six-atom ring ketones with the carbonyl groups conjugated simultaneously with an α,β -exocyclic and an α',β' -endocyclic ethylene bond. The study of such structures by means of absorption spectra has been handicapped by the lack of data on the absorption of simpler ketones with well-established constitutions, containing the same chromophore.² Such derivatives, therefore, of both cyclohexanone and cyclopentanone have been prepared and their absorption spectra studied. In order to have a surer basis for generalizations, the preparation and absorption data of the mother substances, containing only α,β -endocyclic double bonds, have been included.

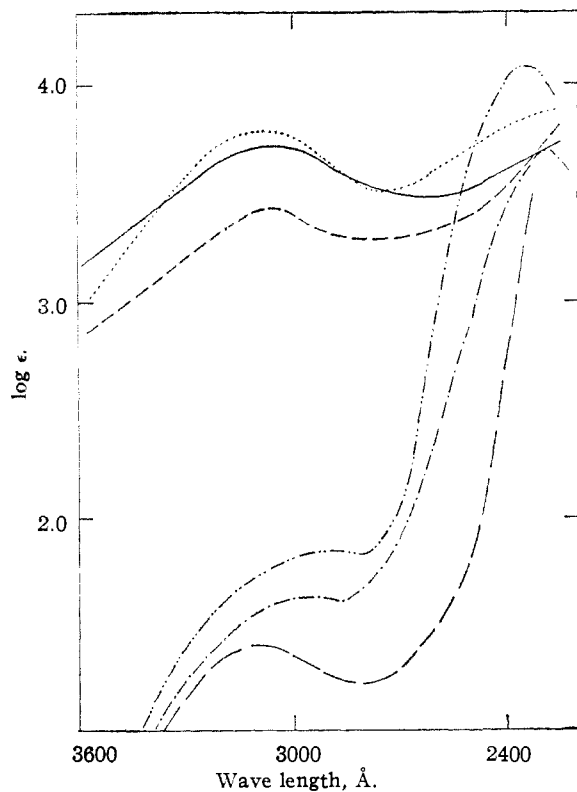


Fig. 1.—Absorption spectra: I, —; II, — — —; III, - - - - -; mother substance of I, — — —; of II, — — —; of III, — — —.

(1) Previous publication in this series: Helen S. French and Lois Wiley, *THIS JOURNAL*, **71**, 3702 (1949).

(2) L. Ruzicka, S. L. Cohen, M. Furter and F. Ch. van der Sluys-Veer, *Helv. Chim. Acta*, **21**, 1738 (1938).

Experimental

Preparations.—Since all the compounds were prepared according to previously published methods, references to those methods are given in the tables only. All compounds were carefully purified by recrystallizations from the appropriate solvents, or by redistillations *in vacuo*, until their melting points (or boiling points) were as recorded in the literature, and until two successive purifications gave identical absorption spectra.

Absorption Measurements.—The method was the same as that previously reported.¹ The solvent used was absolute ethyl alcohol. The results are recorded as curves in Figs. 1-4, and the absorption maxima are listed in Tables I and II.

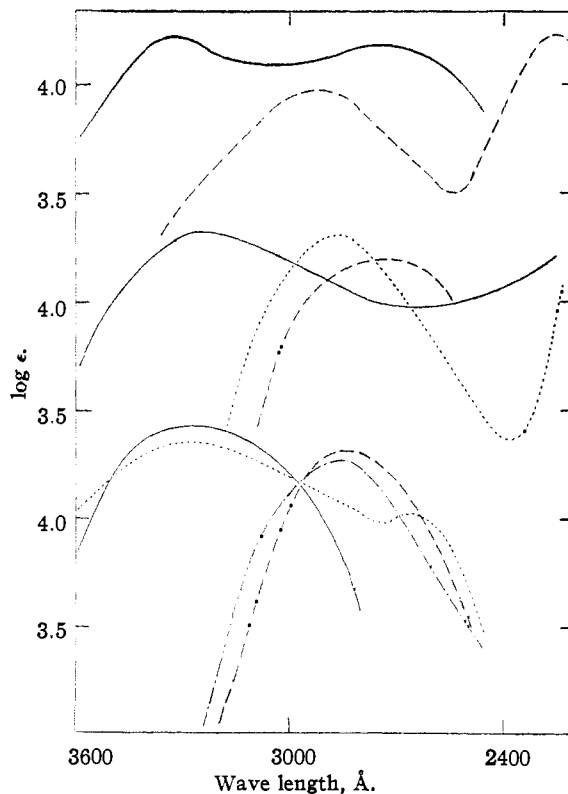


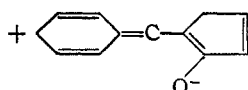
Fig. 2.—Absorption spectra: lower, IV, —; V, - - - - -; mother substance of IV, — — —; of V, — — —; middle, VI, —; VIa, - - - - -; mother substance of VI, — — — upper, VII, — — —; mother substance of VII, — — —.

Discussion

Study of the curves and the tables reveals a general characteristic of the absorption of the chromophore $C=C-C-C=C$ in cyclic ketones. Whether



from the ground state to the excited form



requiring two double bonds in the ring. The six atom ring can sterically contain two double bonds much more easily. This difference is shown by I, II, III ($\log \epsilon$ about 3.7) as compared with VIII and IX ($\log \epsilon$ about 4.5), all compounds with no aromatic substituents on the *endo*-bond. Turner and Voitle¹⁶ find a similar difference in intensities, and ascribe it to the difference in length of the absorbing system, which may also contribute to the intensity differences here. Their compounds are not complicated by the presence of an *endo*-double bond. The *shift* of wave length in the cyclopentenones is about the same as in the cyclohexenones, as far as the present data can show, being less than 200 Å. But when aromatic substituents are present on the endocyclic double bond of the cyclopentenones, the shift increases greatly and is fairly uniform, being greater than 400 Å.

Comparison of $\text{C}=\text{C}-\text{C}(\text{O})-\text{C}=\text{C}$ with $\text{C}=\text{C}-\text{C}(\text{O})-\text{C}=\text{C}$

More interesting differences in effect of ring size are shown by consideration of the effect of adding the *endo* double bond to the ketone already containing the *exo* double bond.^{1,17} For cyclohexanones, the result is a shift of more than 300 Å. toward the red (2900 Å. to 3220 or 3258 Å.), and the pulling of a previously unmeasurable short wave length band into the measurable region (2380 Å.) For cyclopentanones the shift of the long wave length band is only 100 Å. or less (2985 Å. to 3095 or 3070 or 3060 Å.), and the unmeasurable short wave length band is still in the difficultly measurable region. The greater shift in the six-atom ring is natural. The *exo*-compound absorbs farther from the red in the first place.¹ Also the introduction of the *endo*-bond into a six-atom ring increases greatly the coplanarity¹⁸ of the conjugated systems, while the five-atom ring is planar both in the saturated and unsaturated states.¹⁹ It is interesting to note the entirely to be expected effect of the presence of the phenyl group beta to the ketone group. Its presence in the saturated part of the ring gives a negligible effect, as is shown by comparing the absorption maxima of IV and V. Both the mother substances and the benzal derivatives differ only by a phenyl group and a hydroxyl in the saturated part of the ring, and the differences in absorption maxima are only 35 Å. in each case.²⁰

(16) R. B. Turner and D. M. Voitle, *THIS JOURNAL*, **73**, 1407 (1951).

(17) We use here the data for compounds VIII, IX, XII, from that 1949 article.

(18) G. W. Wheland, "The Theory of Resonance and its Application to Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 161.

(19) "Planar" is more or less a relative term, since Pitzer (K. S. Pitzer, *Science*, **101**, 672 (1945)) has shown that cyclopentane itself is non-planar by deformation of the tetrahedral angles, and that cyclopentene (K. S. Pitzer, *THIS JOURNAL*, **70**, 4227 (1948)) may be puckered.

(20) That the hydroxyl in the saturated part of the ring also has no effect on the absorption is indicated by the work of F. B. La Forge and S. B. Soloway, *THIS JOURNAL*, **69**, 186 (1947), and of A. L. Wilds, *et al.*⁹

TABLE II

Compound	Formula	λ_{max} , Å.		Mother subs. λ_{max} , Å.	
		Å.	$\log \epsilon$	Å.	$\log \epsilon$
X ^{11,10}		3020	4.15	2865	4.30
XI ⁸		3650	4.20	2830	4.31
		3095	4.30		
XII ¹¹		3580	4.10	2830	4.31
		2675	4.20		
XIII ¹¹		4000	3.90	No mother substance	
		3055	4.17		
		2350	4.21		

Hence the benzal derivative of 3-phenylcyclopentanone can be assumed to show an intense maximum not far from 2985 Å. (the maximum for 2-benzal-cyclopentanone itself). The introduction of the *endo*-double bond, however, brings the phenyl group into conjugation with the chromophore, and the absorption maxima are shifted almost 300 Å. to the red (from about 2985 Å. to 3265 or 3300 or 3255 or 3320 Å. in compounds IV through VII). Presumably a similar effect would be shown in the six-atom ring compounds. We have not yet been able to obtain such a compound in pure condition, but a slightly impure sample of 3-phenyl-5,5-dimethyl-6-benzal-2-cyclohexenone shows an absorption band at about 3500 Å., a shift of 600 Å. from the 6-benzal-2-cyclohexanone. This may indeed indicate the 300 Å. shift for the increase in coplanarity and another 300 Å. shift for the added conjugation of the phenyl group. More work is necessary to establish this point.

Effect of Substitution on $\text{C}=\text{C}-\text{C}(\text{O})-\text{C}=\text{C}$.—It

would be interesting to study the relations between structure and absorption spectra of the chromophore $\text{C}=\text{C}-\text{C}(\text{O})-\text{C}=\text{C}$ with varying numbers

of substituents in these cyclic compounds. There are, however, an insufficient number of different types of substituted derivatives to make such a study profitable. For most of the compounds reported here, the exocyclic double bond is disubstituted, one substituent being the phenyl group and the other a ring carbon. Considering the exocyclic substitution as constant, then, the effect of substitution on the endocyclic double bond follows the general pattern expected for substitution in the simpler chromophore $\text{C}=\text{C}-\text{C}=\text{O}$, with the dif-

(21) F. R. Japp and J. Knox, *J. Chem. Soc.*, 673 (1905).

(22) O. Widman, *Ber.*, **52**, 1652 (1919).

(23) C. F. H. Allen and E. W. Spanagel, *THIS JOURNAL*, **55**, 3773 (1933); C. F. H. Allen and J. W. Gates, *ibid.*, **64**, 2120 (1942); *ref. 24*.

(24) C. F. H. Allen, *Chem. Revs.*, **37**, 209 (1945).

ference that the shifting absorption band of course starts at about 3000 Å. instead of 2300 Å. (Note especially compounds I, II, III, IV and VII in Table I.)

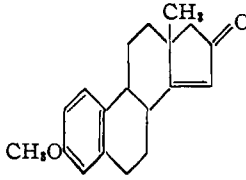
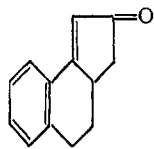
Effect of Substitution for and on the Benzal Group.—The compounds in Table II together with IV and V in Table I offer a story in themselves, although admittedly data for more compounds would be desirable. The change from two saturated substituents on the exocyclic double bond to one aromatic substituent shifts the absorption maximum almost 300 Å. to the red (compare X with V). This is comparable to the 375 ± 25 Å. shift for the change of a saturated ring to a phenyl ring.¹ The effect of an ortho-hydroxyl radical on the benzal group in XI is at first surprising, since it apparently splits the 3265 Å. band of IV into two almost equally intense bands at 3650 and 3905 Å. in XI. From a study of Fisher-Taylor-Hirschfelder models it is clear that the hydroxyl hydrogen can easily coordinate with the carbonyl oxygen and the resulting eight-atom ring, although puckered, can be stabilized by resonance. By the closing of the eight-atom ring, however, the coplanarity of the five-atom ring with the aromatic benzal ring is no longer possible. The upsetting of coplanarity of the two previously conjugated rings would tend to shift the band of IV at 3265 Å. toward the blue, while the chelation and resonance of the eight-atom ring would tend to shift the same band toward the red, thus accounting for the two slightly less intense bands at 3650 and 3905 Å. in XI. An isomer of XI (XII) also has two intense bands, but at quite different wave lengths, 3580 and 2615 Å. The models show that the chelated ring is quite impossible in this compound, and this is borne out by the presence of the band at 2615 Å., characteristic of the free phenolic hydroxyl. The coplanarity of the aromatic benzal ring with the five-atom ring can be fully maintained, thus extending the endocyclic C=C—C=O conjugation by the equivalent of one more double bond; the 3265 Å. band of IV is thereby shifted to the red by more than 300 Å., as would be expected.²⁵ If the hydroxy-phenyl group is on the side of the ethylene double bond away from the other phenyl group in the molecule, models show that all three rings can be coplanar. Otherwise there is interference. Hence there may be a *cis-trans* effect involved, but further evidence would be necessary for confirmation of this point. Compound XIII may offer a bit of further evidence. Its mother substance might be considered to be 2,3-diphenyl-2-cyclopentenone. The absorption spectrum of this compound has not been determined, but by a comparison of the absorption of IV, V, VII and of their mother substances, it can be deduced that 2,3-diphenyl-2-cyclopentenone should give an intense absorption band at approximately 3300 Å. XIII resembles this last compound in structure, except that the substituted group on the doubly-bound CH is not phenyl but C=C—C₆H₅, held by the ring rigidly away from the ketone group. Again the form of the absorption curve, with two intense maxima, is very similar to that of XI, but with the longest wave length band shifted even far-

(25) L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 482 (1945).

ther to the red. This would be expected from the longer conjugation.

Further Analysis of Spectra.—Further analysis of the absorption spectra of these compounds would be desirable, in an attempt to assign one of the two maxima to the endocyclic conjugation and the other to the exocyclic. Such an attempt seems reasonable when applied to VIII and IX, for example. The intense band of the mother substance with its endocyclic conjugation is in each case preserved with only a slight shift to the red.

TABLE III

α, β -UNSATURATED CYCLOPENTANONES		λ_{\max} , Å.
<i>endo</i> -Bond, all substituents saturated		
Monosubstituted		
2-cyclopentenone		<2220 ²⁶
5-hexyl-2-cyclopentenone		2120 ²⁷
4,5,5-trimethyl-2-cyclopentenone		2210 ²⁸
Disubstituted		
2-hexyl-2-cyclopentenone		2290 ²⁹
		2270 ³⁰
Trisubstituted		
2-propyl-3-methyl-2-cyclopentenone		2350 ³¹
2,3-dimethyl-4-isopropyl-2-cyclopentenone		2375 ³¹
2-pentyl-3-methyl-2-cyclopentenone		2350 ³¹
2,3-dimethyl-2-cyclopentenone		2370 ³¹
2350 ³¹		2350 ³¹
<i>endo</i> -Bond, aromatic substituents		
Disubstituted (one aromatic)		
3-phenyl-2-cyclopentenone		2830 ³²
3,4-diphenyl-4-hydroxy-2-cyclopentenone		2865 ³⁴
		2865 ³⁵
5-methyl-3,4-diphenyl-4-hydroxy-2-cyclopentenone		2875 ³⁶
Trisubstituted (two aromatic)		
2,3,4-triphenyl-4-hydroxy-2-cyclopentenone		2905 ³⁷
α, β -UNSATURATED CYCLOHEXANONES		
<i>endo</i> -Bond, one aromatic substituent		
3-phenyl-2-cyclohexenone ³⁷		2847
3-phenyl-5,5-dimethyl-2-cyclohexenone ³⁷		2837
3,5-diphenyl-6-carbethoxy-2-cyclohexenone		2870 ³⁸

(26) See mother substance of I in Table I.

(27) See mother substance of II in Table I.

(28) A. L. Wilds, *THIS JOURNAL*, **70**, 1168 (1948).

(29) See mother substance of III in Table I.

(30) L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 816 (1941).

(31) R. L. Frank, P. G. Arvan, J. W. Richter and C. R. Vannemas, *THIS JOURNAL*, **66**, 4 (1944).

(32) A. E. Gillam and T. F. West, *J. Chem. Soc.*, 486 (1942).

(33) See mother substance of IV in Table I.

(34) See mother substance of V in Table I.

(35) See VIa in Table I.

(36) See mother substance of VII in Table I.

(37) We are indebted to Prof. G. Forrest Woods of the University of Maryland for a generous sample of this compound.

(38) D. L. Turner, *THIS JOURNAL*, **73**, 1284 (1951).

The intense long wave length band is new and is logically assigned to the exocyclic conjugation. This argument is strengthened by a study of models, which shows the interference of the extra methyl group in IX with the phenyl group, thus causing either greater strain or forcing the phenyl group to the other side of the double bond. Either would explain the slight shift of maximum from 3220 to 3258 Å. It is difficult to carry the same argument to all the compounds studied. It appears preferable to consider the chromophore $C=C-C=C$ as



a whole. Just as the chromophore $C=C-C=O$ has one intense absorption band within definite limits of the spectrum, so this more complicated chromophore has its intense long wave length absorption band within definite limits of the spectrum. For five-atom rings with saturated substituents only on the endocyclic bond this band lies at 3075 ± 25 Å., for corresponding six-atom rings at 3240 ± 25 Å., and for five-atom rings with aromatic substituents at 3290 ± 25 Å.

Rules for α,β -Unsaturated Cyclopentanones.—Our final point is incidental to the main purpose of this study, but is important. It is concerned with the "mother substances" listed in Tables I and II, derivatives of cyclopentanones with an α,β -endocyclic ethylene bond. Although the number of such compounds whose absorption spectra have been determined is still much smaller than the number of six-atom ring ketones upon which Woodward³⁹ based his reliable rules for the relations between structure and absorption spectra of such α,β -unsaturated cyclohexanones, we believe that the number justifies the attempt now to formulate

(39) R. B. Woodward, *THIS JOURNAL*, **64**, 76 (1942).

similar rules for the α,β -unsaturated cyclopentanones. We include in the following list three six-atom-ring ketones with aromatic substituents on the double bond, since such compounds were not included in Woodward's²⁵ survey.

The data given in Table III are summarized roughly in Table IV, and at the same time compared with the data for cyclohexenones.²⁵

TABLE IV

	2-Cyclohexenones	2-Cyclopentenones
<i>endo</i> -Bonds		
Saturated substituents		
Monosubstituted	2250 \pm 50	2170 \pm 50
Disubstituted	2350 \pm 50	2270 \pm 50
Trisubstituted	2470 \pm 50	2360 \pm 50
<i>exo</i> -Bonds		
Aromatic substituents		
Disubstituted	2850 \pm 50	2860 \pm 50
Saturated substituents		
Trisubstituted	2520 \pm 50	2550 \pm 50 ¹

In general, the conclusion is obvious that the five-atom ring ketones have their absorption maxima at shorter wave lengths than do the six-atom ring ketones when the ethylene bond is in the ring and all substituents are saturated. The reverse is true when the ethylene bond is outside the ring. When the substituents are phenyl groups, the size of the ring makes negligible difference.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Ultraviolet Absorption Spectra of Alicyclic Compounds. II. Methyl Cycloalkyl Ketones¹

BY RAYMOND P. MARIELLA AND RICHARD R. RAUBE

The ultraviolet absorption spectra of methyl vinyl, methyl cyclopropyl, methyl cyclobutyl, methyl cyclopentyl, methyl cyclohexyl and several methyl alkyl ketones were measured in alcohol and isoöctane solutions. In this series, as the polarity of the solvent is increased the main maxima are shifted to shorter wave lengths. There is no simple gradation in the spectra as the ring size is increased.

The second order conjugation effect (hyperconjugation) of the cyclopropyl ring in conjugation with aromatic nuclei, ketone groups, and double bonds has been observed by several investigators.¹⁻⁷

The present work was undertaken to determine whether other alicyclic systems exhibit this hyperconjugation phenomenon, and to see if there is any

correlation between ring size and ability to hyperconjugate.

There have been several reports in the literature concerning the different effects of the cyclopentyl and cyclohexyl rings.⁸ There have been two independent correlations of four, five and six membered rings⁹ (cyclobutanone, cyclopentanone and cyclohexanone). Comparing the maxima with the highest intensity in each case, we get the following figures:

(8) See L. N. Ferguson, *Chem. Revs.*, **43**, 392 (1948), for some leading references.

(9) (a) G. Forster, R. Skrabal and J. Wagner, *Z. Elektrochem.*, **43**, 290 (1937); (b) S. W. Benson and G. B. Kistiakowsky, *THIS JOURNAL*, **64**, 80 (1942).

(1) For the previous paper in this series see R. P. Mariella, L. F. A. Peterson and R. C. Ferris, *THIS JOURNAL*, **70**, 1494 (1948).

(2) E. P. Carr and C. P. Burt, *ibid.*, **40**, 1590 (1918).

(3) I. M. Klotz, *ibid.*, **66**, 88 (1944).

(4) J. D. Roberts and C. Green, *ibid.*, **68**, 214 (1946).

(5) M. Rogers, *ibid.*, **69**, 2544 (1947).

(6) J. F. Music and F. A. Matsen, *ibid.*, **72**, 5256 (1950).

(7) W. W. Robertson, J. F. Music and F. A. Matsen, *ibid.*, **72**, 5260 (1950).