[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WELLESLEY COLLEGE]

Absorption Spectra of Certain α,β-Unsaturated Ketones. II.[1] Effect of Size of Ring and of Position of Double Bond

BY HELEN S. FRENCH AND LOIS WILEY

Definite and reliable rules have been formulated by Woodward[2] for the relations between structure and absorption spectrum of α,β-unsaturated cyclohexanones. These have been very useful already in determining the structures of complex naturally-occurring compounds. Comparatively little has been done for corresponding compounds of α,β-unsaturated cyclopentanones. Gillam[3] postulated a shift of 110 Å. toward the violet for the high-frequency high-intensity band of such cyclopentenones as compared with that of cyclohexenones based upon experimental results on a small number of such compounds. In our first paper of this series[1] we found indications that the shift occurred in the opposite direction, toward the red, for such α,β-unsaturated cyclopentanones with an exocyclic rather than an endocyclic double bond, and more work on such compounds was promised. Since such five-atom ring ketones also occur frequently in complex naturally-occurring compounds, it seems important to formulate any possible "rules" connecting their structures and absorption spectra.

Closely related and relatively simple derivatives of cyclohexanone and cyclopentanone, with α,β-exocyclic ethylene bonds have therefore been prepared and their absorption spectra studied.

Experimental

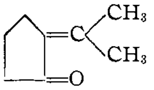
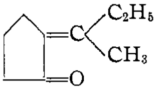
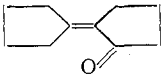
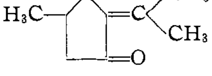
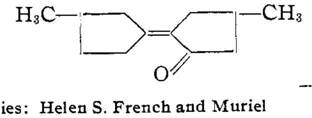
Preparations.—Since all the compounds were prepared according to previously published methods, references to those methods are given in Table I. All compounds were carefully purified by recrystallizations from the appropriate solvents, or by redistillations *in vacuo*, until their melting points (or 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 from this Laboratory,[4] with the substitution of a Spekker photometer for the sector photometer. The results are recorded as curves in Figs. 1–4, and the absorption maxima are listed in Table I.

The first eleven compounds in Table I were prepared and purified as above described. For purposes of comparison, Table I also includes the previously published data for the absorption maxima of nine closely related compounds. The data in the table refer only to the short-wave length, high-intensity bands.

Discussion.—From a study of Fisher–Hirschfelder models, it is clear that 6-atom rings are very little changed by the introduction of one double bond. Cyclohexanone and cyclohexenone are both strainless to about the same degree, since both rings are non-planar. This helps account for the validity of Woodward's[2] rules, which allow very little difference in absorption for equal substitution on an exocyclic double bond and on an endocyclic double bond. The permitted regions for absorption maxima overlap in such cases, *e. g.*, 2350 ± 50 Å. for an endocyclic double bond and 2400 ± 50 Å. for an exocyclic double bond, when two substituents are on the doubly-bound carbons.[2]

TABLE I

Compound	Formula	$\lambda_{max.}$ Å.	$\log_{10} \epsilon$	Solvent
I[5,6]		2520	3.56	Alcohol
II[5,6]		2530	3.52	Alcohol
III[5,6]		2590	4.03	Alcohol
IV[7]		2540	3.98	Alcohol
		2468	3.98	Hexane
V[7]		2590	3.82	Alcohol
		2510	3.92	Hexane

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[1] Previous publication in this series: Helen S. French and Muriel E. T. Holden, THIS JOURNAL, **67**, 1239 (1945).

[2] Woodward, *ibid.*, **64**, 76 (1942).

[3] Gillam and West, *J. Chem. Soc.*, 486 (1942).

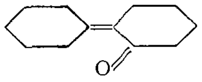
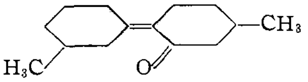
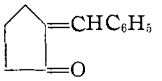
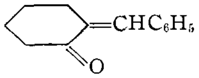
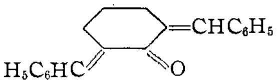
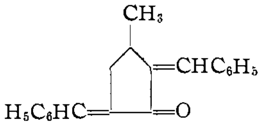
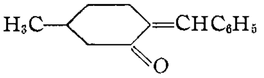
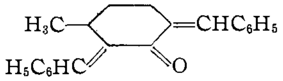
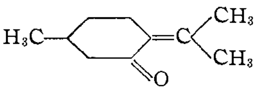
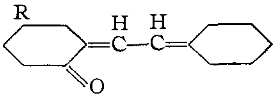
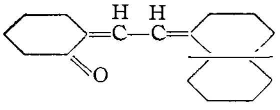
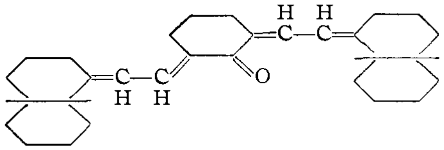
[4] French and Gens, THIS JOURNAL, **59**, 2600 (1937).

[5] Vavon and Apchié, *Bull. soc. chim.*, **43**, 667 (1928).

[6] Cornubert and Borrel, *ibid.*, **47**, 958 (1930).

[7] Wallach, *Ann.*, **394**, 362 (1912).

TABLE I (*Continued*)

Compound	Formula	$\lambda_{max.}$, Å.	$\log_{10} \epsilon$	Solvent
VI[8]		2550 2460	3.80 3.90	Alcohol Hexane
VII[8]		2540 2481	3.83 3.90	Alcohol Hexane
VIII[9]		2985	4.23	Alcohol
IX[9]		2900	4.05	Alcohol
X[10]		3300	4.40	Alcohol
XI[11]		3525	4.20	Alcohol
XII[1]		2885	4.20	Alcohol
XIII[1]		3280	4.54	Alcohol
XIV[1]		3440	4.44	Alcohol
XV[12,13]		2520 2420	3.81 3.95	Alcohol Hexane
XVI[14]	 R = H	2970	4.40	Ether
XVII[14]	R = OCH_3	3065 2970	4.39 4,40	Alcohol Ether
XVIII[15]	R = $OCCH_3$	3060	4.14	Alcohol
XIX[14]		3000	4.44	Ether
XX[14]		3420	4.96	Ether

Models show, however, great differences in corresponding five-atom rings. Cyclopentanone and its derivatives with α,β-exocyclic double bonds are planar, with the four conjugated atoms in the same plane. When a double bond is introduced into the ring, the struggle for the ring to be preserved at all upsets the coplanarity of the conjugated atoms. This may account for the shift of absorption maxima of 110 Å. to shorter wave lengths noted by Gillam and West.[3] The complete planarity of the four conjugated atoms in the cyclopentanones with α,β-exocyclic bonds, how-

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(8) Reese, *Ber.*, **75**, 384 (1942).

(9) Vorländer and Kunze, *ibid.*, **59**, 2078 (1926).

(10) Weiss and Ebert, *Monatsh.*, **66**, 399 (1935).

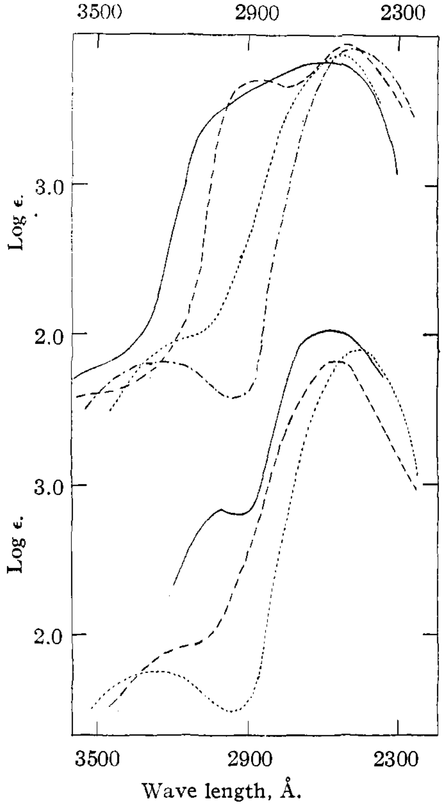
(11) Wallach, *Ber.*, **29**, 1601 (1896).

(12) Gillam, Lynas-Gray, Penfold and Simonsen, *J. Chem. Soc.*, 60 (1941).

(13) Savard, *Bull. soc. chim.*, **43**, 524 (1928).

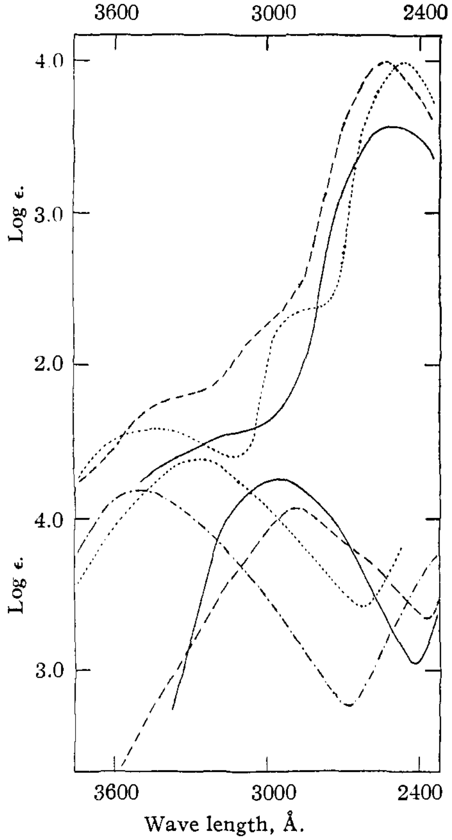
(14) Dimroth and Jonsson, *Ber.*, **71**, 2658 (1938).

(15) Aldersley and Burkhardt, *J. Chem. Soc.*, 545 (1938).



Figs. 1, 2.—Upper, absorption spectra: V in alcohol —; V in hexane — — —; VII in alcohol - - - - - -; VII in hexane —·—·—; lower, absorption spectra: III in alcohol —; VI in alcohol — — —; VI in hexane - - - - - -.

ever (more complete than in either of the 6-atom ring types), results in a shift of the absorption toward the red. The relations among (1) co-planarity of conjugated atoms, (2) the completeness of the resonance of the system and (3) the region of maximum absorption are well-known, and have been frequently emphasized.[16] Our results show this shift to be small and to vary from 20 to 50 Å. when the substituents on the exocyclic double bonds are saturated groups. Note the corresponding cyclohexanone and cyclopentanone pairs of compounds VI and III, VII and V, XV and IV, the latter two pairs in both alcohol and hexane. The shift to the red is greater when the phenyl group is a substituent, 85 Å. for IX and VIII, 140 Å. for X and XIV, and 250 Å. for XIII and XI. The smallest shift (20 Å.) means a difference of approximately 130 Å. between the effects of an exocyclic and an endocyclic double bond in cyclopentanones, which is admittedly within the largest limit (150 Å.) allowed for cyclohexanones. However, if the absorption maxima of four corresponding compounds are considered, those of *both* cyclohexanones lie between those of the two more widely differing cyclopentanones.



Figs. 3, 4.—Upper, absorption spectra: I and II in alcohol —; IV in alcohol — — —; IV in hexane - - - - - -. Lower, absorption spectra in alcohol: VIII —; IX — — —; X - - - - - -; XI —·—·—.

An unexplained but consistent shift to the red is caused by the change from two alkyl radicals to an alicyclic ring on the exocyclic double bond in both cyclopentanones and cyclohexanones. The models show less tendency to steric interference when the alicyclic rings are present, which may be a sufficient explanation. (Compare the pairs I and III, IV and V, XV and VII.)

The very large shifts to the red caused by extending the conjugation are to be expected, and show consistent regularities. (1) When one α-sidechain is extended to include a second double bond conjugated with the first, but with only saturated substituents, the shift is about 500 Å. to the red. (Compare VI with XVI, XVII, XVIII, and XIX.) (2) When the conjugation is extended by the substitution of a phenyl group for a saturated ring, the shift to the red is 375 ± 25 Å. (Compare VI and IX, VII and XII, III and VIII.) The phenyl group has been variously described under such circumstances as being equivalent to one double bond[17] and to 1.5 double bonds.[18] From these few examples, it would seem

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(16) Wheland, "Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 161.

(17) Wilds, Beck, Close, Djerassi, Johnson, Johnson and Shunk, THIS JOURNAL, **69**, 1991 (1947).

(18) Dimroth, *Angew. Chem.*, **52**, 545 (1939).

to be not quite equivalent to one double bond in these compounds. (3) When the conjugation is crossed by the introduction of a second exo-α,β-double bond on the other side of the ketone group, the shift to the red is 400–450 Å. (Compare IX and X, XII and XIII, VIII and XIV, XIX and XX.) This *shift* is independent of whether the substituted groups are saturated or aromatic.

Finally, several pairs of compounds (III and V, I and IV, VI and VII, IX and XII, X and XIII, XI and XIV) differ only by a methyl radical which is on the ring but not on a doubly-bound carbon. The effect of this methyl group on the absorption maxima is negligible with the exception of the last pair. The shift of 85 Å. to the red on the introduction of the methyl group into the 2,5-dibenzalcyclopentanone was surprising. The study of models shows, however, that only in this case would the phenyl group be forced to take the position toward the carbonyl oxygen. The shift of absorption may therefore be an effect of *cis–trans* isomerism. Without the methyl group, the phenyl group has more room away from the carbonyl oxygen. More evidence would certainly be needed to establish this point. The methyl group seems not in any way to inhibit the complete coplanarity of the conjugated system in these molecules.

The effect of change of solvent from alcohol to hexane is the usual one for this high-intensity band, a shift of about 70 Å.[2] to shorter wave lengths. In the curves for IV, V, VI and VII is shown the further effect of hexane in changing the "step-out" in the longer wave length region into a definite low-intensity maximum. This effect agrees with Ramart-Lucas and Hoch's[19] observation that alcohol shifts the low-intensity C=O band toward the violet and the high-intensity C=C—C=O band toward the red, resulting in a mere step-out for the former in alcohol solution instead of the definite maximum in hexane.

It will be noted that the cyclopentanone compounds III, IV, V, VIII, XI, XII and XIV all have analogous cyclohexanone compounds, VI, XV, VII, IX, XIII, XII and X. I and II are conspicuously without analogs. This emphasizes the fact, known at least since 1912,[20] that cyclopentanones and cyclohexanones react very differently with aliphatic ketones. Under the same conditions which give I with cyclopentanone and acetone, cyclohexanone and acetone form cyclohexylidene acetone.[20] Even this compound is unstable and forms an equilibrium mixture with the isomeric cyclohexenyl acetone.[21] The double bond exocyclic to a 6-atom ring is unstable by 3.5 kcal. with respect to the corresponding endocyclic compound.[22] The reason for an analog for IV is that pulegone is a naturally occurring compound! It must be emphasized in this connection that VI and VII must be prepared with great care, in order to keep the double bond exocyclic to the 6-atom ring. Reese[7] was the first to isolate the 2-cyclohexylidene cyclohexanone as a pure compound in 1942, a white crystalline solid, m. p. 57°. Before that time and even after 1942 reports of its preparation described the product as an oil boiling at 142–145° at 15 mm. (or at corresponding boiling points at various other low pressures).[23] It was the absorption spectrum of this liquid product that was reported by Evans and Gillam[24] with the comment that the low intensity of the absorption maximum indicated contamination by an unconjugated isomer. Unless kept *in vacuo*, the solid rearranges to the liquid, as would be expected from the foregoing discussion. To confirm the identity of the crystals as the conjugated α,β-unsaturated ketone, and the liquid as the unconjugated β,γ-unsaturated ketone, Reese[7] measured the molecular refractivities of both. The absorption spectra of these compounds VI and VII reported here confirm Reese's conclusions.

The benzal derivatives of cyclohexanone have the exocyclic double bond stabilized by conjugation with the aromatic ring.

In conclusion, α,β-unsaturated cyclopentanones have not been as widely investigated as the corresponding cyclohexanones. It is therefore not possible as yet to formulate for them rules such as Woodward's.[2] The following statements, however, can be made with a fair degree of confidence concerning cyclopentanones with an α,β-exocyclic double bond.

1. Their absorption is shifted farther to the red than that of the corresponding cyclohexanones, in constrast to cyclopentenones with endocyclic double bonds, whose absorption is shifted to the blue from that of the corresponding cyclohexanones.
2. Alkyl radicals on the ring carbon alpha to the exocyclic double bond cause a red shift which is unnoticeable in the cyclohexanones.
3. The exocyclic double bond is more stable and more completely conjugated with the carbonyl group than in the cyclohexanones.
4. The shifts toward the red caused by extension of conjugation by the phenyl radical are about 50 Å. greater than in the corresponding cyclohexanones.

Work is in progress in this Laboratory to determine the further effect on absorption of α,β-exocyclic double bonds on cyclic ketones already containing α,β-endocyclic double bonds.

Summary

1. The absorption spectra of seven α,β-unsaturated cyclopentanones and four α,β-unsaturated cyclohexanones are recorded in curves and a table.

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[19] Ramart-Lucas and Hoch, *Bull. soc. chim.*, [5] **2**, 327 (1935).

[20] Wallach, *Ann.*, **394**, 362 (1912).

[21] Kon and Linstead, *J. Chem. Soc.*, 1269 (1929).

[22] Hückel, "Theor. Grundlagen der org. Chem.," 2nd ed. Akad. Verlag., Leipzig, 1934, p. 72.

[23] Mannich, *Ber.*, **40**, 157 (1907); Wallach, *Ann.*, **381**, 97 (1911); Garland and Reid, THIS JOURNAL, **47**, 2333 (1925); Hurd, Greengard and Roe, *ibid.*, **61**, 3359 (1939); Wayne and Adkins, *ibid.*, **62**, 3401 (1940); Price, Knell and West, *ibid.*, **65**, 2469 (1943); Gault, Daltroff and Eck-Tridon, *Bull. soc. chim.*, **12**, 952 (1945).

[24] Evans and Gillam, *J. Chem. Soc.*, 816 (1941).

2. The results are discussed in an attempt to formulate generalizations for cyclopentanones analogous to those formulated for cyclohexanones by Woodward.[2]

3. The most important of such generalizations is that the conjugated *exo*-cyclic double bond in the cyclopentanones shifts the absorption maximum to the red from that of the corresponding cyclohexanones and in contrast to the shift to the blue of the conjugated *endo*-cyclic double bond in the cyclopentenones.

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[CONTRIBUTION FROM THE BALLISTIC RESEARCH LABORATORIES, ABERDEEN PROVING GROUND]

The Explosion of Nitrous Oxide–Hydrogen Mixtures

BY CHARLES P. FENIMORE AND JOHN R. KELSO

This paper presents explosive limits for the nitrous oxide–hydrogen system. When combined with Melville's[1] interpretation of his slow reaction data between these gases, the explosive data strongly indicate the presence of the radical HO_2 in the reacting system. Although a detailed reaction mechanism cannot be based on these findings, it is of some interest that the processes forming HO_2 occur at temperatures 200° or more higher in this system than they previously have been known to occur in other reaction systems.[2]

Since Melville encountered explosions in his studies of the slow reaction but did not observe reproducible limits, it is necessary to state at the outset that reproducible limits can be readily obtained. To do so, the gases must be oxygen-free, however, and their entry into the reaction vessel must be rapid. The second requirement is necessary presumably so that not much molecular oxygen can be formed by the thermal decomposition of nitrous oxide before the pressure builds up to the explosion limit. Hence, the second requirement is only a restatement of the first, that the gases must be oxygen free.

Experimental

Hydrogen and nitrous oxide, freed from oxygen by treatment with aqueous alkaline pyrogallol and dried, were mixed in a previously evacuated vessel in the desired proportions. Proportions were estimated by an attached mercury manometer. The mixing vessel communicated to the reaction vessel through a stopcock of 2-mm. bore. The reaction vessel was heated in an electric resistance furnace and fitted with two chromel alumel thermocouples whose readings did not differ by more than 1°. Adequate temperature constancy could be maintained through a Sorensen voltage regulator and variable transformers with only occasional manual control. Two cylindrical quartz reaction vessels 30 cm. long were used; one measured 0.9 cm. inside diameter, the other 2.5 cm. These two vessels were new and manufactured at the same time and place, and presumably possessed similar surfaces. In addition, runs were made in a cylindrical vycor vessel of 1.5 cm. inside diameter. The findings obtained in the vycor vessel showed the same features as those in quartz up to 830° and are not reported in detail.

After the mixing vessel had been filled at a pressure such that the pressure would rise to the desired value in the previously evacuated reaction vessel when the gas was partitioned between them, the stopcock was opened rapidly. An explosion ensued immediately or not at all. No perceptible induction period was ever noted. Explosions were indicated by a sharp click and a bright flash of light which propagated back through the stopcock into the mixing vessel. The color of the light was dependent on temperature and composition. Explosions at low temperatures or of compositions rich in hydrogen appeared reddish; those at higher temperatures or of mixtures rich in nitrous oxide yellowish or white. At 800° only compositions containing over 50% hydrogen appeared at all reddish.

At a given temperature and gas composition, observations were repeated at varying pressures until the lower pressure limit was bracketed within 1–2 mm. The measurements were taken over a fairly extended period of time and frequent returns to limits measured weeks or months before proved the values, at temperatures $\leqslant 830°$, reproducible to 3–5 mm. The results obtained in vycor between 900 and 980° were less reproducible ($\simeq \pm 10$ mm.).

Results and Discussion

In Figs. 1 and 2, the lower limiting explosion pressure for nitrous oxide–hydrogen mixtures is plotted as a function of temperature and gas composition for vessels of two different sizes. The decimal point serves a double purpose in these contour maps. In addition to pointing off tenths of a cm. of a pressure determination, each point places the temperature and composition at which that determination was made. At temperatures below 720° in the small vessel (or 670° in the larger one) the explosion pressure was too high to observe in a quartz and glass apparatus. For the same reason, the minimum explosion pressure escaped capture in either vessel above 820°. In a vycor vessel of 1.5-cm. inside diameter, very similar results

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[1] Melville, *Proc. Roy. Soc.* (London), **142A**, 524 (1933); **146A**, 737, 760 (1934).

[2] For a discussion and for references, see Minkoff, *Faraday Soc. Discussions*, **2**, 151 (1947).