# Structure and Absorption Spectra. IV. Further Observations on α,β-Unsaturated Ketones

## By Robert Burns Woodward

In view of the significant effect of exocyclic linkages in determining the position of the band maxima in the absorption spectra of normal conjugated dienes,[1] it was of interest to investigate the possibility that a similar effect is operative in the case of α,β-unsaturated ketones, for which hitherto[2] only substitutive effects have been considered.[3]

In actual fact, considering ketones of substitution-type II (αβ or ββ substituted), for which the relevant data are available,[2] the average value of $\lambda_{max.}$ for those substances, as typified by mesityl oxide (I), in which the carbon–carbon double bond is not exocyclic, is 235 mμ, while for those with such a bond, e. g., Δ4-cholestene-3-one (II), $\lambda_{max.}$ has the average value 240 mμ.
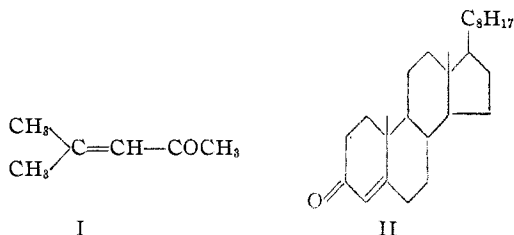


It seems clear that here also the positional effect is operative, and that the magnitude is very nearly the same as in the case of the dienes. It now becomes apparent that the effect of a single substituent ($\Delta\lambda_s$) is actually ca. 11 mμ, a value more in consonance with $\Delta\lambda_s$ in the diene series[1] than the value 15 mμ, deduced from the earlier work.[2]

It will be recognized that the new effect ($\Delta\lambda_{exo.}$) being small in comparison with $\Delta\lambda_s$, is not sufficient to affect the earlier substitution-type classification, at least as far as types I and II are concerned. On the other hand, the recognition of the new factor does permit the construction of a somewhat more precise system, and furthermore predicts a new sub-class in type III. This new group, which has as yet no ketonic members of known structure, will have average $\lambda_{max.}$ = ca. 247 mμ, and will comprise α,β,β-substituted carbonyl compounds *having no exocyclic carbon–carbon double bonds.*

In view of the fact that α,β-unsaturated aldehydes are spectrographically very similar[4] to the corresponding α,β-unsaturated ketones, β-cyclocitral (III), with $\lambda_{max.}$ = 245 mμ[5] (EtOH), may be considered as the first member of the new group. The ketone, m. p. 94°, obtained by the cyclization by means of formic acid of di-Δ1-
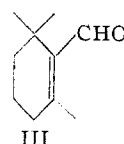


cyclohexenylacetylene[6] is undoubtedly a second member of the new sub-class. Although the gross structure of this ketone and of its congener,

### TABLE I

| Substitution | | | Most probable $\lambda_{max.}$ |
|---|---|---|---|
| α or β[a] | | | 225 mμ |
| αβ or ββ | i. | no exocyclic bond[b] | 235 |
| | ii. | one exocyclic bond | 240 |
| αββ | i. | no exocyclic bond | ca. 247 |
| | ii. | one exocyclic bond[c] | 252[d] |

[a] Even in the case of the monosubstituted ketones, the double bond can be exocyclic. All such substances, however, will be derivatives of o-methylenecyclohexanone, CH2=C—CO(CH2)3CH2. In view of the recent work of Mannich, *Ber.*, **74**, 554, 557, 565, 1007 (1941), and of Dimroth, Resin and Zetzsch, *ibid.*, **73**, 1399 (1940), it is unlikely that any member of this class would survive long enough to permit spectrographic determinations. [b] It should be emphasized that only the position of the *carbon–carbon* double bond is relevant in predicting the value of $\lambda_{max.}$ [c] It will be recognized that in the trisubstituted ketones, the carbon–carbon double bond may be *doubly exocyclic*, as in cyclohexylidenecyclohexanone, CH2(CH2)4C—=C—CO(CH2)3CH2. The most probable value of $\lambda_{max.}$ for this compound is consequently 257 mμ. [d] This value is for those ketones having only alkyl substituents. The value given previously[2] (254 mμ) was slightly higher as a result of the inclusion of ketones heavily substituted with bromine atoms, and should be used in conjunction with such compounds.

(1) Woodward, THIS JOURNAL, **64**, 72 (1942).

(2) Woodward, *ibid.*, **63**, 1123 (1941).

(3) Gillam, Lynas-Grey, Penfold and Simonsen, *J. Chem. Soc.*, 62 (1941), have recently suggested the possibility of such an effect, and indeed incorrectly attribute wholly to this cause the red shift in passing from piperitone to pulegone.

(4) *Cf.* Dimroth, *Angew. Chem.*, **52**, 552 (1939).

(5) Burawoy, *J. Chem. Soc.*, 23 (1941).

(6) Marvel, *et al.*, THIS JOURNAL, **58**, 972 (1936); **59**, 2666 (1937); Linstead and Walpole, *J. Chem. Soc.*, 842, 850 (1939).

m. p. 39°, is not entirely certain,[7] the carbon skeleton of that part of the molecule containing the chromophoric group may be regarded as established. The observed values of $\lambda_{max.}$ are in excellent agreement with the assignment to the two ketones of the structures IV [$\lambda_{max.}$ (calcd.) = 247 m$\mu$] and V [$\lambda_{max.}$ (calcd.) = 240 m$\mu$].

The new position is summarized in Table I, which is an adaptation of Table V in the earlier communication.[2]

(7) Professor R. P. Linstead in private conversation has informed me that recent work has shown that the previous formulation of these substances as hydrophenanthrene derivatives is untenable, and has suggested, on the basis of the work of Levitz, Perlman and Bogert, *J. Org. Chem.*, **6**, 105 (1941), that the ketones are spirane derivatives.



m. p. 94°, 247 m$\mu$          m. p. 39°, 241 m$\mu$
IV                              V
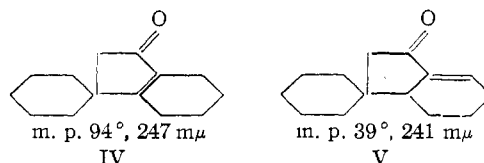
## Summary

The effect of exocyclic double bonds in determining the position of the band maxima for the intense band in the absorption spectra of $\alpha,\beta$-unsaturated ketones is demonstrated.

The recognition of the new effect permits certain refinements in the classification system previously proposed.

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[Contribution from the Sterling Chemistry Laboratory of Yale University]

# The Saponification of Acetylsalicylic Acid at 35°[1]

By Julian M. Sturtevant

LaMer and Greenspan[2] studied the rates of saponification of several acetylated hydroxy acids at 25° by titration of the remaining alkali, and found that the reactions were sufficiently cleancut to be susceptible to precise velocity measurements. Reactions of this type appeared to offer promising material for study by the calorimetric method developed by the author,[3] and some experiments were therefore performed with acetylsalicylic acid at 35°. The results of these experiments have shown, however, that it would be very difficult to get accurate heat data on these reactions, and it has therefore not been considered worthwhile to carry the measurements any further. The present paper reports the data obtained; even though significant thermal data were not obtained, the velocity constants observed in the range $\mu$ = 0.0032 to 0.021 follow the Brönsted theory better than would be expected from the work of LaMer and Greenspan at 25°.

## Experimental

Acetylsalicylic acid (of unknown source) was recrystallized four times from chloroform, once from dilute alcohol, and twice more from chloroform. Neutralization equivalent: observed 180.24, 179.97; calculated 180.15. The stock so-

dium hydroxide solution was prepared, analyzed, and handled by the methods described in an earlier communication.[4] The measurements were carried out in the apparatus described elsewhere.[3b]

In the calorimetric determination of reaction velocities it is impossible to obtain a value for the temperature at the start of the reaction, because of the heat of mixing of the reactants, or for the final temperature, because of calorimetric difficulties. It is therefore necessary to use some method of calculation which does not involve these two temperatures. The present reaction follows the second order law

$$kt = \frac{1}{A - B} \ln \frac{B(A - Y)}{A(B - Y)} \qquad (1)$$

where $A < B$ are the initial concentrations of sodium acetylsalicylate and sodium hydroxide, and $Y$ is the concentration of sodium salicylate at time $t$. Application of the method of calculation described in a previous paper[5] gives the following results

$$\frac{B}{A} = \frac{\alpha(\mu_3 - \mu_2) - (\mu_2 - \mu_1)}{(\mu_3 - \mu_2) - \alpha(\mu_2 - \mu_1)} \alpha^{(t + \Delta t)/\Delta t} \qquad (2)$$

$$\mu_\infty = \frac{\mu_3(\mu_2 - \mu_1) - \alpha\mu_1(\mu_3 - \mu_2)}{(\mu_2 - \mu_1) - \alpha(\mu_3 - \mu_2)} \qquad (3)$$

$$\mu_\infty - \mu_0 = \frac{A}{A - B}\left[\mu_\infty - \frac{\mu_1(\mu_3 - \mu_2) - \alpha\mu_3(\mu_2 - \mu_1)}{(\mu_3 - \mu_2) - \alpha(\mu_2 - \mu_1)}\right] \qquad (4)$$

$$k = \frac{1}{(A - B)\Delta t}\ln \alpha \qquad (5)$$

(1) Part of the material in this paper was presented before the Division of Physical and Inorganic Chemistry at the Atlantic City meeting of the American Chemical Society, September, 1941.

(2) LaMer and Greenspan, This Journal, **56**, 1492 (1934).

(3) (a) Sturtevant, *ibid.*, **59**, 1528 (1937); (b) *J. Phys. Chem.*, **45**, 127 (1941).

(4) Sturtevant, *ibid.*, **62**, 2276 (1940).

(5) Sturtevant, *ibid.*, **59**, 699 (1937).