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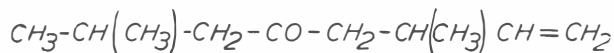
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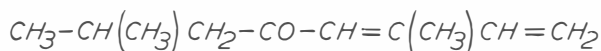
THE ULTRA-VIOLET ABSORPTION SPECTRA OF TAGETONE AND RELATED KETONES.

By T. G. H. JONES, D.Sc., A.A.C.I., and F. N. LAHEY, D.Sc., A.A.C.I.

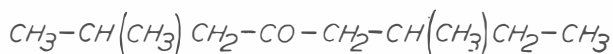
The chemistry of the two aliphatic ketones occurring in the essential oil from *Tagetes glandulifera* has been studied previously by one of us (T.G.H.J. in conjunction with F. B. Smith)^{1 2 3}. One of these ketones was shown to be 2: 6-dimethyl- Δ^7 -octen-4-one (1) and the other, tagetone, was considered to be represented by the formula (2).



1



2



3

Although the $\alpha\beta$ -unsaturated character of tagetone was confirmed by its chemical reactions, it was decided to examine it spectrographically in order to supply additional confirmation and also to place on record the absorption curve of this type of substance. The results of spectrographic analysis of tagetone and related ketones form the subject of this paper.

The absorption curve for tagetone (fig. 1) exhibits two bands, one of high intensity with a maximum at λ_{max} . 269m μ , ϵ_{max} . 20000, and the other of low intensity with a maximum at λ_{max} . 344m μ , ϵ_{max} . 105. From the work of Morton, Hassan and Calloway⁴ it is clear that the band of low intensity is due to the carbonyl group influenced by the conjugated double bonds and the band of high intensity is associated with the conjugated double bonds under the influence of the carbonyl group.

Many $\alpha\beta$ -unsaturated ketones have already been spectrographically examined. Cooke and Macbeth⁵ examined a number of $\alpha\beta$ -unsaturated cyclic ketones and compared their absorption curves with those of the corresponding saturated compounds. They found that the two maxima always shown by $\alpha\beta$ -unsaturated cyclic ketones are located between fairly narrow limits viz. 312-319 m μ for the low intensity maximum and 226-235.5m μ for the high intensity maximum.

More recently Woodward⁶ has examined a large number of $\alpha\beta$ -unsaturated ketones and narrowed down the limits between which the maxima of the intense bands of these ketones fall according to the number of substituent groups on the two carbon atoms separated by the double bond of the chromophoric group. Evans and Gillam⁷ have confirmed Woodward's generalisation and also observed that substituents in the β position have a greater bathochromic effect than those in the α position.

The absorption curve of tagetone (fig. 1) clearly resembles that of phorone which is recorded by Morton, Hassan and Calloway⁴ as showing two maxima, λ_{max} . 263m μ , ϵ_{max} . 20000 and λ_{max} . 357 m μ , ϵ_{max} . 100. Phorone, unlike tagetone, has the carbonyl group situated between the two double bonds. A substance more comparable

with tagetone in structure is crotonylidene-acetone (4). This substance gives an absorption curve very similar to that of tagetone. Its maxima occur at λ_{\max} . 273 $m\mu$, ϵ_{\max} . 16800 and λ_{\max} . 340 $m\mu$, ϵ_{\max} . 123. If Woodward's rule can be extended to doubly unsaturated conjugated ketones then it is to be expected that tagetone and crotonylidene-acetone will give principal absorption maxima within 5 $m\mu$ of one another as each has only one substituent group, on the α carbon in tagetone and on the δ carbon in crotonylidene-acetone. By analogy with simple $\alpha\beta$ -unsaturated ketones the δ substituent would be expected to have a greater bathochromic effect than the α substituent. (See Evans and Gillam⁷). This is realised in practice; crotonylidene-acetone giving a maximum at 273 $m\mu$ and tagetone at 269 $m\mu$.

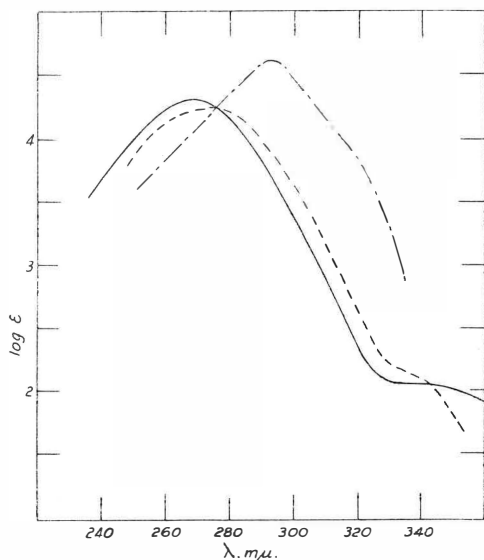


Fig. 1.

— tagetone.
 --- crotonylidene-acetone.
 - · - pseudo-ionone.

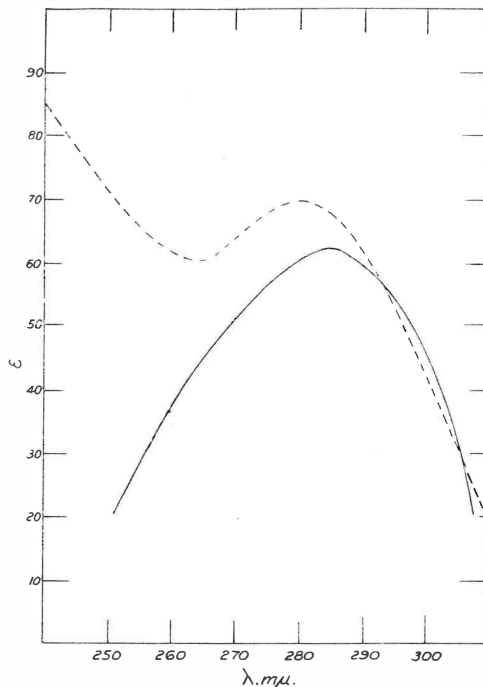
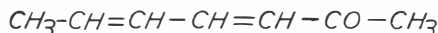


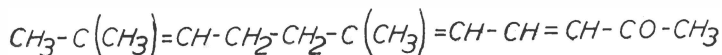
Fig. 2.

— 2,6-dimethyl-octan-4-one.
 --- 2,6-dimethyl- Δ^8 -octen-4-one.

Pseudo-ionone (5) belongs to the same class of substance as tagetone and crotonylidene-acetone having a doubly unsaturated conjugated ketone group in it. Its principal absorption band has a maximum well displaced towards the red end of the spectrum at λ_{\max} . 294 $m\mu$, ϵ_{\max} . 24500. This substance has two substituents in the δ position and if the extension of Woodward's rule holds, might be expected to give a maximum in the region $288 m\mu \pm 5 m\mu$ by comparison with crotonylidene-acetone at 273 $m\mu$. This is in good agreement with the observed maximum at 294 $m\mu$.



4



5

From the examples studied it would appear, then, that Woodward's rule can be satisfactorily extended to cover doubly unsaturated conjugated ketones. The case of phorone, however, with its maximum at $263m\mu$ appears worthy of comment. If the conjugation of one double bond with another through a carbonyl group as in phorone has the normal bathochromic effect then this effect combined with that of the four β substituents would be expected to result in a maximum even further towards the red than in the case of pseudo-ionone. Its position, however, at $263m\mu$ can be explained by the effect of the four β substituents alone if Woodward's rule can be extended to this class of substance. By this extension phorone should give a maximum at $268m\mu \pm 5m\mu$ which is in keeping with the value found. It would appear then that the second double bond when it is located on the opposite side of the carbonyl group to the other double bond exerts no bathochromic effect.

The unsaturated ketone 2 : 6-dimethyl- Δ^7 -octen-4-one (1) was also examined. The curve has a maximum at $\lambda_{\max.} 280 m\mu$, $\epsilon_{\max.} 70$ while another maximum is indicated somewhere in the far ultra-violet (fig. 2). This curve is very similar to that of the corresponding saturated ketone 2 : 6-dimethyl-octan-4-one (3) ($\lambda_{\max.} 285.5m\mu$, $\epsilon_{\max.} 60$) a result fully expected as the double bond is well insulated from the carbonyl group and so has little or no influence on the position and intensity of the band due to that group.

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