cases. The discussion on keten itself by Hannay and Smyth¹, although using a slightly different terminology, utilizes essentially the same conception. 'Resonance', therefore, provides an acceptable qualitative explanation of the present and other² physical facts, together with the more outstanding of the chemical reactions of the class³.

A. A. HUKINS
R. J. W. LE FÈVRE

Chemistry Department,
University of Sydney.
July 18.

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Synthesis of 4-Methylsafranal

SAFRANAL (I) and its glycosidic precursor picrocrocin (the bitter principle of saffron)¹ have been shown by Kuhn, Moewus and Wendt² to play a remarkable part in controlling the sexual characteristics of the hermaphroditic green alga *Chlamydomonas eugametos* f. *synoica*. It was demonstrated that the glycoside acted as a gynotermone for the organism (that is, caused the cells to become female), the minimum quantity required being 10^6 molecules per cell. On the other hand, safranal (I) acted as a male termone (androtermone), the effect being observable at a far greater dilution, only 10 molecules per cell being required. The closely allied compound, 4-hydroxy- β -cyclocitral, was also observed to act as an androtermone³.

Safranal itself has been synthesized in very poor yield by the direct dehydrogenation of β -cyclocitral, the product being isolated as a semicarbazone of 85 per cent purity⁴. A further synthesis envisaged by Karrer and Ochsner⁵ has not proved successful.

In the course of an investigation of the Diels-Alder reaction between acetylenic aldehydes and conjugated dienes, the condensation between tetrolaldehyde and 1:1:3-trimethylbutadiene was studied. This yielded the cyclic aldehyde (II), which is readily converted to 2:4:6-trimethylbenzaldehyde; this latter was found to be the main product if the reaction be

carried out at higher temperatures. On treatment of (II) with a trace of sulphuric acid in methanol, a facile rearrangement occurred, and 4-methylsafranal (III), boiling point 80–85° (bath temp.)/0.2 mm. mercury (found: C, 80.6; H, 9.75; C₁₁H₁₆O requires C, 80.45; H, 9.8 per cent) was produced in good yield. The absorption spectrum exhibited a maximum at 3080 Å. ($\epsilon = 10,500$). The aldehyde was characterized by the formation of a semicarbazone (m.p. 157°) and a 2:4-dinitrophenylhydrazone (m.p. 195°).

In view of the biological work mentioned above, it is obviously of great interest to determine whether (III) acts as a termone; this would throw light on the specificity of the molecular architecture associated with this type of activity.

Full details will be published elsewhere. We wish to thank Sir Ian Heilbron, Prof. E. R. H. Jones and Dr. R. A. Raphael for their interest in this work. One of us (J. C. L.) thanks the Durham County Education Committee for a major university scholarship, and the other (F. S.) the Department of Scientific and Industrial Research for a senior award.

J. C. LUNT
F. SONDHEIMER

Department of Organic Chemistry,
Imperial College of Science and Technology,
London, S.W.7.
July 27.

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Reactivity of 4-Substituted Heterocyclic Nitrogen Compounds

FOR some considerable time we have been engaged in a study of the relative reactivities of derivatives of cinnoline, quinazoline and quinoxaline containing a series of identical substituents attached to C₄. Although the results of this work appeared to be clear-cut and to lead to certain clearly formulated conclusions, they were nevertheless equivocal in so far as they were essentially based on qualitative or semi-quantitative observations and not on kinetic measurements.

In a recent paper, Longuet-Higgins and Coulson¹ have calculated the electron densities for (among others) these three ring-systems. Calculations of this sort will be welcomed by organic chemists interested in the chemistry of nitrogenous heterocyclic compounds; and, correspondingly, the mathematical burden involved in making such predictions will be more readily undertaken if it is known that they are likely to be the subject of experimental test.

There is a very satisfactory degree of agreement, over a wide range of 4-substituted derivatives of these heterocyclic types, between the order of reactivity indicated by our experiments and that predicted by the calculations of Longuet-Higgins and Coulson. Details will be published elsewhere; but the position may be summarized by saying that the experimental evidence is concerned with (i) the relative order of basic strengths of derivatives of the three heterocyclic types²; (ii) the location of the basic centres of cinnoline and quinazoline derivatives^{3,4,5}; and (iii) the relative order of reactivity of derivatives carrying identical 4-substituents as