tion energies for nucleophilic substitutions, require position 1 to be the more reactive in this type of reaction. This anomaly is understandable if the self-atom polarizability[3], π, of position 1 is sufficiently greater than that of position 2. The polarizabilities have now been calculated and are compared with the π-electron densities and atomic polarization energies in Table 1. It must be concluded that the difference

Table 1. Self-atom polarizabilities

Position	$\pi(1/\beta)$	A'_n (k.cal.)	q
1	0·608	28·5	1·097
2	0·599	30·5	0·976

in polarizabilities is sufficient to cause the apparent discordance between A'_n and q, and so it is likely that fulvalene will prove to be the first example of a molecule in which the static charge distribution does not provide an adequate picture of the chemical reactivity.

The second unexpected result for fulvalene[1] is that the bond orders[4], p, and bond-localization energies[5], B', predict the opposite relative reactivities of bonds 2 : 3 and 9 : 10. From the classical bond diagram (I) and from the calculated mobile orders[2] it would be anticipated that the 9 : 10 bond is the more reactive. However, the bond-localization energy results[1] indicate that the 2 : 3 bond is the more reactive. Again these facts can be reconciled if the self-bond polarizability[3] of the 2 : 3 linkage is sufficiently greater than that of the 9 : 10 bond. Calculations of these polarizabilities indicate that this is so (Table 2).

Table 2. Self-bond polarizabilities

Bond	$\pi(1/\beta)$	B' (k.cal.)	p
2 : 3	0·509	21	0·448
9 : 10	0·191	29	0·390

Thus fulvalene is also likely to be unusual in that the classical bond diagram (I), or even the quantum mechanical static-bond orders, do not correctly reflect the reactivity for reactions such as ozonolysis.

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Enzymatic Oxidation of —CH₃ to —CHO

WE have previously shown[1] that peroxidase, together with hydrogen peroxide, will oxidize mesidine (I) to the purple crystalline compound 2 : 6-dimethylbenzoquinone-4-(2' : 4' : 6'-trimethyl) anil (V) in 95 per cent yield. When ferrous iron was substituted for the enzyme, the product was mainly ill-defined amorphous material. This enzymatic oxidation involves the elimination of a methyl group, and at the time we postulated the intermediate formation of 2 : 6-dimethylbenzoquinone (II) to explain the reaction. More recently we have shown[2] that the peroxidase system will oxidize 4-methoxy-2 : 6-dimethylaniline with the facile elimination of a methoxyl group (detected as methyl alcohol). p-Anisidine is also oxidized[3], with the elimination of a methoxyl group, to 2-amino-5-p-anisidinobenzoquinone-bis-p-anisylimine and tetra-p-methoxy azophenine.
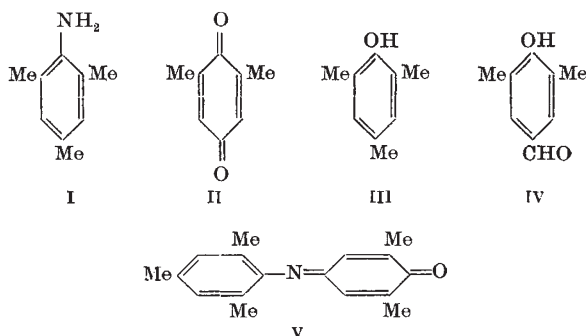
We have now investigated the peroxidase oxidation of mesitol (III), and have so far isolated two products in a pure condition, namely, 4-hydroxy-3 : 5-dimethyl-benzaldehyde (IV) and the quinone (II). Moreover, the aldehyde is oxidized by the further action of the peroxidase system to II.

It is believed that the oxidation of III to IV constitutes the first recorded peroxidase oxidation of a ·CH₃ group to a ·CHO group. Experiments with ferrous iron in place of the enzyme are in progress.

Experimental details and suggestions for the mechanism of the peroxidase oxidation will be published elsewhere later.

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A Colour Reaction Applicable to the Pyrethrins

HESTRIN[1] has described the analytical application of a reaction between carboxylic acid derivatives and hydroxylamine. The reaction product gives a coloured complex with ferric chloride in acid solution. This reaction takes place with the pyrethrins and their synthetic analogues, and coloured complexes are formed with ferric chloride.

The experimental procedure, which was very similar to that used by Hestrin, was as follows. 6 ml. of alkaline hydroxylamine reagent (3 ml. 2 M hydroxylamine hydrochloride solution and 3 ml. 3·5 N sodium hydroxide solution) was added to 3 ml. of an ethanolic solution of ester and the mixture allowed to stand for one minute or more. The solution was then acidified with 3 ml. of hydrochloric acid (1 vol. concentrated hydrochloric acid sp.gr. 1·18 + 2 vol. of water), and finally 3 ml. of ferric chloride solution (0·37 M in 0·1 N hydrochloric acid) was added. Absorption measurements were made with a 'Unicam' diffraction grating spectrophotometer (Model S.P.350). It is important that a blank should be carried out with the ethanol alone, to ensure the absence of impurities giving a coloured complex.

The absorption spectra of the complexes obtained from a mixture of the natural pyrethrins, purified by the nitromethane technique[2], and the synthetic pyrethrin analogue, the DL-cis-trans chrysanthemum monocarboxylic acid ester of 3-methyl-2-allyl-cyclo-penten-4-ol-1-one (see graph), are closely similar to that described by Hestrin[1].