

discussion will be offered in papers being submitted to the Chemical Society.

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Jan. 27.

¹ Hughes and Taher, *J. Chem. Soc.*, 956 (1940).

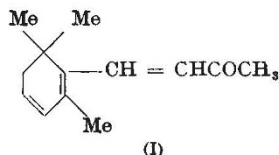
² Cooper, Hughes and Ingold, *J. Chem. Soc.*, 925 (1940).

³ Dostrovsky and Hughes, *J. Chem. Soc.*, 166 (1946).

⁴ Dostrovsky, Hughes and Ingold, *J. Chem. Soc.*, 191 (1946).

Synthesis of Dehydro- β -ionone

THE elegant brominating reagent, N-bromosuccinimide, has been employed by Karrer¹ to prepare bisdehydrolycopenes from the acyclic carotenoid, lycopene. It has now been shown that the cyclic compound β -ionone reacts in a facile manner with this reagent, giving a bromo-derivative which on dehydrobromination with diethylaniline yields dehydro- β -ionone (I), b.p. 75° at 1 mm. mercury pressure, n_D^{25} 1.5497. The absorption spectrum exhibited maxima at 2210 Å. and 3380 Å. ($\epsilon = 7,000$ and 9,000 respectively). The product was characterized by the formation of a semicarbazone (m.p. 144–146°) and a 2:4-dinitrophenylhydrazone (m.p. 150–151°).



The synthetic potentialities of dehydro- β -ionone for the preparation of dehydro-compounds of the vitamin A type are now under investigation in these laboratories. The synthesis of dehydrovitamin A₁ by the above approach would be of considerable interest, since this structure is one that has been suggested² as representing vitamin A₂.

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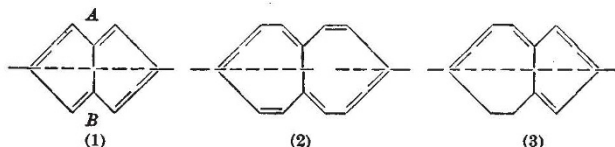
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¹ Karrer, P., and Rutschmann, J., *Helv. Chim. Acta*, 28, 793 (1945).

² Gray, E. LeB., and Cawley, J. D., *J. Biol. Chem.*, 134, 397 (1940).

The Non-Benzenoid Aromatic Hydrocarbon Pentalene

IT is an interesting fact that neither pentalene (1), nor heptalene (2), nor any derivatives of them have been definitely reported as being synthesized¹ or found to occur naturally. Azulene (3) is, on the other hand, a substance which can be made by the established procedures of organic chemistry and it is known in Nature.



When a study is made of these molecules by the valence-bond method first developed by Hückel², pentalene and heptalene prove to be different in one respect from azulene, and from other common hydrocarbons: the wave functions describing the most stable state of their π -electrons are antisymmetrical with respect to the axis indicated in the diagrams. In contrast, the π -electron wave functions of azulene, of all hydrocarbons built up from six-membered rings and of other common hydrocarbons, have the full molecular symmetry in their ground-states. An example of a possible exception to this statement is provided by acenaphthylene, which is being investigated. It is not obvious, however, whether this difference between the known hydrocarbons and the unknown pentalene and heptalene is connected with the difficulty of obtaining these latter structures.



In an earlier paper, Coulson and Rushbrooke³ have examined these molecules by the molecular orbital approximation. In that method, all molecules with an even number of π -electrons are described as having symmetrical ground-states, so that the distinction of symmetry does not emerge. Coulson and Rushbrooke did, however, find that the molecular orbital method encounters a difficulty in dealing with these molecules, but the same difficulty arises with the known molecule azulene as with the other two.

Details of energies, bond orders, etc., are being reported elsewhere, especially for pentalene. According to the calculations, this molecule should possess considerable resonance stabilization (c. 40 kcal.), and it has been confirmed in the calculations that the triplet state lies above the lowest singlet, so that the unsymmetric state discussed above is, in fact, the lowest of all the states. A calculation of bond orders by the method of Penney⁴ gives the unusual result that the central bond (A—B in formula 1) has a small negative bond order, expressing the fact that the π -electrons exert a considerable repulsion across that bond; the large resonance energy, however, confirms that the overall effect of π -electron interaction, when all the resonance possibilities are considered, is strongly stabilizing.

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¹ Horn, Nunn and Rapson, *Nature*, 160, 830 (1947).

² Hückel, *Z. Phys.*, 70, 204 (1931).

³ Coulson and Rushbrooke, *Proc. Camb. Phil. Soc.*, 36, 193 (1940).

⁴ Penney, *Proc. Roy. Soc., A*, 158, 306 (1937).

Xanthotoxin from the Fruits of *Ammi majus* L.

Fahmy and Abushady¹ have isolated from the fruits of *Ammi majus* L. a crystalline product to which they gave the name 'ammoidin'. We wish to express our gratitude to them for supplying us with this material and for allowing us to determine its constitution. We have found that the substance does not contain active hydrogen or an acetyl group², but it contains one methoxyl grouping. Analysis of ammoidin gave the formula C₁₂H₈O₄, and after degradation we found that it possesses the constitution: