Hemi-Dewar Biphenyl

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THE system (I) is of interest in that it represents a compound possessing two of the several renowned classical representations of a benzene nucleus incorporated as distinct entities within the same molecule. As one hundred years have now elapsed since the Kekulé structure for benzene was first proposed,¹ it is appropriate to report at this time the synthesis of this member of a family of several such possible systems.

Compound (I), which is referred to as hemi-Dewar biphenyl,² has now been prepared by decomposition of cyclobutadieneiron tricarbonyl (II) with ceric ammonium nitrate in the presence of phenylacetylene.⁴ In the course of the oxidative



spectrum. (Figure 1) The areas of the absorption bands centred at $\tau 2.80$, 3.43, 6.00, and 6.20 occur in the ratio 5:3:1:1 respectively; these are readily assigned in the order given, to the five aromatic, three olefinic, and the two non-equivalent allylic hydrogens expected for structure (I).



FIGURE 1. N.m.r. Spectrum of Hemi-Dewar Biphenyl.

decomposition of the complex a molecule of cyclobutadiene is transferred from (II) to phenylacetylene with the formation of hemi-Dewar biphenyl, (I). The product, which is purified by liquid chromatography over silica gel, is obtained as a colourless oil $(n_{p}^{26}, 1.5834)$.

The principal evidence for the assignment of structure (I) to the compound is seen in the n.m.r.

In addition the ultraviolet absorption spectrum of the material resembles that of styrene; also the infrared absorption spectrum shows a sharp absorption at 1555 cm.⁻¹ expected for a cyclobutene derivative.⁵ Finally, upon heating to 90° for several minutes the material is converted quantitatively into biphenyl.

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¹ A. Kekulé, Bull. Soc. chim. France, 1865, 1, 98.

² The prefix "Dewar" remains a very convenient term to indicate the bicyclo[2,2,0]hexadiene skeleton; it being clear that this system, because of its particular stereochemistry, is not the familiar Dewar canonical form used in valencebond parlance and due cognizance being taken of the intentions of Professor Dewar in introducing this structure to the literature (ref. 3).

³ see W. Baker, Chem. in Britain, 1965, 1, 191.

⁴ L. Watts, J. D. Fitzpatrick, and R. Pettit, J. Amer. Chem. Soc., 1965, 87, 3253.

⁵ K. B. Wiberg and B. J. Nist, J. Amer. Chem. Soc., 1961, 83, 1226.