

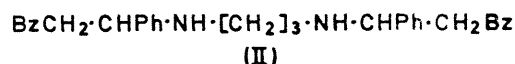
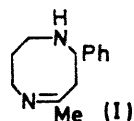
## Simple Formation of a Diazocine Ring

By KÁLMÁN HIDEG† and DOUGLAS LLOYD\*

(Department of Chemistry, Purdie Building, University of St. Andrews, St. Andrews, Fife)

**Summary** 1,3-Diaminopropane reacts with benzylideneacetone to give an eight-membered ring in high yield.

ETHYLENEDIAMINE reacts with arylideneacetones in cyclohexane-ether under reflux in the presence of potassium carbonate to form 14-membered rings.<sup>1</sup> In contrast, under the same conditions 1,3-diaminopropane reacts with benzylideneacetone to form a hexahydro-1,5-diazocine (I) and not a 16-membered ring. This is indicated by the molecular weight of the product (202·146282; C<sub>13</sub>H<sub>18</sub>N<sub>2</sub>



requires 202·146991). The n.m.r. spectrum is consistent with this structure, but would also be consistent with a tetra-azacyclohexadecadiene structure. Compound (I) is readily reduced by sodium borohydride to the corresponding octahydrodiazocine (Mol. wt. 204·162153; C<sub>13</sub>H<sub>20</sub>N<sub>2</sub> requires 204·162641).

Two points of note are (i) the high yield (90%) in which this eight-membered ring is formed without utilising any special techniques such as high dilution, and (ii) the completely different reaction path which is predominant in this case compared to that which predominates in the reaction using ethylenediamine, a difference which was unexpected in view of the normal greater difficulty of cyclisations leading to eight-membered rings than of those leading to seven-membered rings.

Like ethylenediamine,<sup>1</sup> 1,3-diaminopropane reacted with benzylideneacetophenone to form an uncyclised adduct (II) derived from one molecular equivalent of amine and two of ketone. The much lower reactivity of the carbonyl group in this case presumably enables the addition of the second primary amine group to a carbon-carbon double bond to compete successfully with ring closure.

Mesityl oxide, which reacted with ethylenediamine to form a tetrahydrodiazepine,<sup>2</sup> reacted with 1,3-diaminopropane to form a complex mixture of products (which is under further examination) including both a diazocine and a tetra-azacyclohexadecadiene derivative, the former predominating.

(Received, January 11th, 1971; Com. 044.)

† On leave from University of Pécs, Hungary.

<sup>1</sup> K. Hideg and D. Lloyd, *Chem. Comm.*, 1970, 929.

<sup>2</sup> I. Guareschi, *Atti R. Accad. Sci. Torino*, 1894, **29**, 694; L. K. Mushkolo and Z. I. Shokol, *Zhur. obshchei Khim.*, 1960, **30**, 1023; B.P. 1,108, 440/1966; (*Chem. Abs.*, 1968, **69**, 52034); J. Elguero, E. Gonzalez, and R. Jacquier, *Bull. Soc. chim. France*, 1969, 2054.