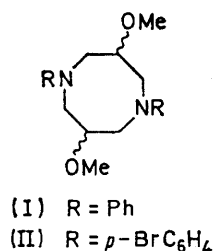


## Rearrangement of the Dihydrobromide of Octahydro-3,7-dimethoxy-1,5-diphenyl-1,5-diazocine

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The dihydrobromide of octahydro-3,7-dimethoxy-1,5-diphenyl-1,5-diazocine (I) reacts with dimethyl sulphoxide at room temperature to give exclusively 1,5-bis-(*p*-bromophenyl)octahydro-3,7-dimethoxy-1,5-diazocine (II).

THE rearrangement of the dihydrobromide of octahydro-3,7-dimethoxy-1,5-diphenyl-1,5-diazocine (I) into the bis-(*p*-bromophenyl)diazocine (II) in dimethyl sulphoxide



at room temperature can be followed by <sup>1</sup>H n.m.r. spectroscopy (see the Figure). Immediately after

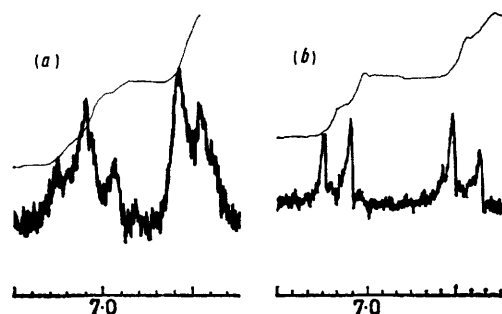


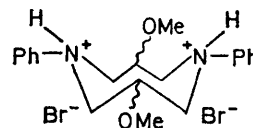
FIGURE N.m.r. spectra of the dihydrobromide of octahydro-3,7-dimethoxy-1,5-diphenyl-1,5-diazocine (I) in dimethyl sulphoxide at room temperature; (a) aromatic-proton absorption immediately after dissolution of dihydrobromide in solvent; (b) same absorption after 8 h

dissolution of the dihydrobromide, the aromatic region of the spectrum appeared as a typical anilinium complex multiplet. This signal slowly changed and after 8 h appeared as the AA'BB' pattern of an unsymmetrical *p*-disubstituted benzene.<sup>1</sup> When the rearrangement was complete (n.m.r.), the bis-(*p*-bromophenyl) compound (II) was precipitated by addition of water, and identified by analysis and spectroscopy. Bromination of the free base (I) with HBr-dimethyl sulphoxide<sup>2</sup> also gave the dibromide (II). Under these conditions, the brominating agent appears to be the bromonium ion (*cf.* ref. 2).

The rearrangement appears to be highly specific. Neither *N,N*-dimethylaniline hydrobromide nor *N*-phenylpiperidine hydrobromide rearrange in dimethyl sulphoxide even at elevated temperatures. Thus the diazocine (I) is only weakly basic. In order to in-

<sup>1</sup> N. S. Bhacca, L. F. Johnson, and J. N. Schoolery, 'N.M.R. Spectra Catalog,' vol. 1, Varian Associates, Palo Alto, California, 1962, Spectrum no. 123.

vestigate this weak basicity, the dihydrobromide from the diazocine (I) was studied by variable-temperature mass spectrometry. Peaks were observed at *m/e* 80 and 82 (HBr<sup>+</sup>) (at proper intensities for the isotopic abundance of bromide). As the temperature was raised from 0 to 80° the intensity of the peaks increased, but decreased slowly above 80° until all the HBr was removed at 100°. The m.p. of the dihydrobromide varies with the rate of heating and HBr is lost on gentle heating. If the dihydrobromide existed in a twist crown conformation (III), dipole-dipole repulsion would be expected to be severe and would be minimized by the loss of hydrogen bromide. This would explain the weak basicity.



Bromination in the rearrangement of the dihydrobromide occurs solely at the *para*-position and is the first example of such a rearrangement. No evidence for the formation of the bis-(*p*-bromophenyl) compound (II) was found after attempted bromination of the diphenyl-diazocine (I) directly in ether with bromine alone or in the presence of an iron catalyst, which only resulted in the formation of unidentified compounds. Although the absolute configurations of the diazocines (I) and (II) and the dihydrobromide of (I) are not known, they are assumed to have the *cis* configuration.<sup>3</sup> The diazocines are present in one stereoisomeric form.

### EXPERIMENTAL

I.r. spectra were obtained with a Perkin-Elmer model 700 spectrometer. N.m.r. spectra were recorded with a Varian A 60A spectrometer with tetramethylsilane as internal standard. Mass spectra were recorded with a Varian CH-5 instrument at 0–90 °C, 10<sup>-7</sup> Torr, and 70 eV.

*Octahydro-3,7-dihydroxy-1,5-diphenyl-1,5-diazocine*.— This was prepared by a modification, described elsewhere,<sup>3</sup> of the method of Gaertner.<sup>4</sup>

*Octahydro-3,7-dimethoxy-1,5-diphenyl-1,5-diazocine* (I).— To a solution of octahydro-3,7-dihydroxy-1,5-diphenyl-1,5-diazocine (10.0 g, 0.034 mol) in toluene (75 ml) was added sodium hydroxide (4.5 g, 0.094 mol). The mixture was stirred at room temperature for 1 h and then heated under reflux for 2 h. After cooling to room temperature, methyl iodide (15 ml, 0.24 mol) was added to the solution. After heating under reflux for a further 4 h and being cooled to

<sup>2</sup> T. L. Fletcher, *Quart. Reports Sulphur Chem.*, 1968, **3**, 107.

<sup>3</sup> D. A. Nelson, J. J. Worman, and B. Keen, *J. Org. Chem.*, 1971, **33**, 3361.

<sup>4</sup> V. R. Gaertner, personal communication.

room temperature, water (100 ml) was added to the mixture to dissolve the sodium iodide. The toluene layer was dried ( $K_2CO_3$ ) for 30 min, filtered, and evaporated *in vacuo*. The resulting solid was recrystallized from ethanol as white *platelets* (7.66 g; 63.4%), m.p. 173—175°,  $\nu_{max}$  (Nujol) 1600, 1500, 1090, 840, and 665  $cm^{-1}$ ,  $\delta$  ( $CDCl_3$ ) 6.5—7.1 (10H, m), 2.7—4.2 (10H, m), and 3.5 p.p.m. (6H, s), *m/e* (70 eV) 326 (20%), 295 (6), 268 (50), 120 (45), 105 (100), 91 (45), and 77 (60) (Found: C, 72.5; H, 8.2.  $C_{20}H_{26}N_2O_2$  requires C, 73.6; H, 8.0%).

*Octahydro-3,7-dimethoxy-1,5-diphenyl-1,5-diazocine Dihydrobromide*.—Octahydro-3,7-dimethoxy-1,5-diphenyl-1,5-diazocine (I) (1.0 g, 3.3 mmol) was dissolved in ether (170 ml). Anhydrous hydrogen bromide (prepared by the procedure described by Duncan<sup>5</sup>) was passed through the solution for 30 min. The resulting white *solid* was filtered off (0.35 g; 22%), m.p. varies with the rate of heating,  $\nu_{max}$  (Nujol) 2400, 1600, 1500, 1100, 760, and 690  $cm^{-1}$ ,  $\delta$  [ $(CD_3)_2SO$ ] 6.4—7.2 (12H, m varies with time), 3.2—4.0 (10H, m), and 3.5 p.p.m. (6H, s); for mass spectral data see Discussion section (Found: C, 48.8; H, 5.9.  $C_{20}H_{28}Br_2N_2O_2$  requires C, 49.2; H, 5.7%).

*1,5-Bis-(p-bromophenyl)octahydro-3,7-dimethoxy-1,5-diazocine (II)*.—*Method A*. To a solution of the diphenyl-diazocine (I) (1.0 g, 3.3 mmol) in dimethyl sulphoxide (25

ml) was added hydrobromic acid (48%; 2.5 ml) and the mixture was stirred at room temperature. After 30 min, the resulting white precipitate was filtered off and dried. Recrystallization from carbon tetrachloride yielded a white *solid* (1.49 g, 47%), m.p. 149—151°,  $\nu_{max}$  (Nujol) 1590, 1500, 1320, 1270, 1220, 1190, 1100, 960, 850, 800, and 785  $cm^{-1}$ ,  $\delta$  ( $CDCl_3$ ) 6.7 (8H, AA'BB'), 3.4 (6H, s), and 2.8—4.0 (10H, m) (Found: C, 48.3; H, 5.2.  $C_{20}H_{24}Br_2N_2O_2$  requires C, 49.6; H, 5.0%).

*Method B*. To octahydro-3,7-dimethoxy-1,5-diphenyl-1,5-diazocine dihydrobromide (0.20 g, 0.6 mmol) was added dimethyl sulphoxide (25 ml) and the solution was left until no further change took place in the aromatic-proton absorptions of the n.m.r. spectrum (*ca.* 8 h). Water was added to precipitate a white *solid* (0.29 g; 50%), m.p. 148—150° (from carbon tetrachloride), identical in all respects with the material prepared by Method A.

We thank Dr. D. A. Nelson (University of Wyoming) for discussions and for performing the mass spectrometric determinations.

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<sup>5</sup> D. R. Duncan in 'Inorganic Syntheses,' ed. H. S. Booth, McGraw-Hill, New York, vol. 1, 1939, p. 151.