

The Formation of a Stable *o*-Semidine Rearrangement Intermediate

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Summary: Treatment of 5,6,11,12-tetrahydrodibenzo-*[b,f]*[1,2]diazocine with dilute acids affords a spiro-1,2,3,4-tetrahydroquinoline derivative which represents the first isolated stable *o*-semidine rearrangement intermediate.

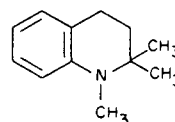
Sir:

In the course of studies directed towards the preparation of the potentially aromatic 1,2-dihydro-1,2-diazocines (1,2), we had occasion to prepare the dibenzodiazocine derivative **1**; pmr (deuteriochloroform): H-1,2,3,8,9,10 (m)  $\tau$  2.80-3.30; H-4,7 (d. of d.)  $\tau$  3.78; H-11,12 (s)  $\tau$  6.84; H-5,6 (s)  $\tau$  4.68. This compound, when treated with methanolic hydrogenchloride at 0° for a few minutes, affords, on basification, an isomeric substance (**2**) (m.p. 125-127°; *Anal. Calcd.* for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>: C, 79.96; H, 6.71; N, 13.32; Found: C, 79.93; H, 6.80; N, 13.54; MW 210 (mass spectrum); theoretical 210 (when the sample is recrystallized from deuterium oxide-acetone, the mass spectrometric molecular weight is increased by two mass units); pmr (deuteriochloroform): 2 sets of four H multiplets:  $\tau$  2.90-3.50;  $\tau$  3.60-4.10; 2 H multiplet  $\tau$  7.10-7.50; 1 H singlet (exchangeable)  $\tau$  6.00). The pmr spectrum clearly shows the lack of symmetry and the presence of only four aromatic protons in isomer **2**. Catalytic reduction of compound **2** (Pd/C, room temperature, atm. press., methanol solution) affords an unstable tetrahydro derivative **3** (C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>-from mass spectral data), which is readily hydrolyzed by aqueous hydrochloric acid to compound **4** (m.p. 78-79°; *Anal. Calcd.* for C<sub>14</sub>H<sub>17</sub>NO: C, 78.10; H, 7.99; N, 6.72, MW 215 (mass spec.) Found: C, 77.97; H, 8.12; N, 6.99; Theoretical 215; (potassium bromide): cm<sup>-1</sup> 1685 (C=O), 3300 (N-H), 1725-1900 (*o*-disubstituted phenyl pattern), 740 (*o*-disubstituted phenyl); loss of m/e 28 in mass spectrum; pmr (deuteriochloroform): 4H(m)  $\tau$  2.92-3.52; 1H (s., exchangeable)  $\tau$  5.50; 12H(m)  $\tau$  7.00-8.60).

The ketone **4** is readily reduced, by means of a Wolff-Kisner reduction, to the spiro tetrahydroquinoline derivative **5** (pmr (deuteriochloroform)) 4H, A<sub>2</sub>B<sub>2</sub>  $\tau$  7.28, 8.28, J<sub>AB</sub> = 6 Hz; 4H (arom. m.),  $\tau$  3.10-3.50; B·CH<sub>3</sub>HI, m.p. 168-169. *Anal. Calcd.* for C<sub>15</sub>H<sub>11</sub>N: C, 52.64; H, 6.19; N, 14.01; Found: C, 52.53; H, 6.34; N, 13.90; n.w.

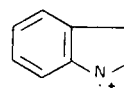
free base **201** (mass spectrometric), (theoretical 201).

The structure proof of this compound rests, in addition to these analytical data, upon a comparison of its pmr spectrum with that of the closely related 1,2,2-trimethyl-1,2,3,4-tetrahydroquinoline (**6**) (**3**) (pmr (deuteriochloroform) 4H, A<sub>2</sub>B<sub>2</sub>  $\tau$  7.30, 8.35, J<sub>AB</sub> = 6 Hz; 4H (arom., m.),  $\tau$  3.08-3.53).



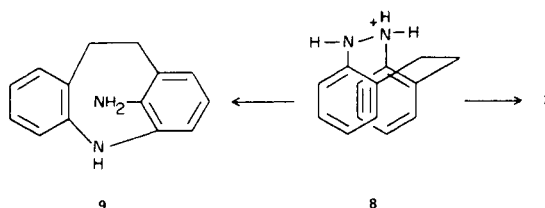
6

The common mass spectral pattern resulting from the generation of ion **7** from both, compounds **5** and **6** (m/e 117 (7-H) 91 (7-HCN); 90 (7-H<sub>2</sub>CN); 71 (7-C<sub>2</sub>H<sub>3</sub>N)), completes the structure proof for compound **5**.

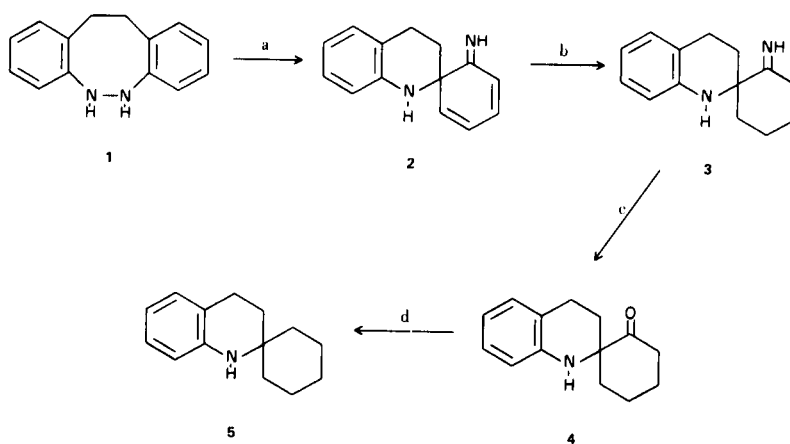


7

While the tetrahydrodiazocine **1** can approach the structure proposed for the transition state in the benzidine, *p*-semidine and *o*-semidine rearrangements (**4**), it cannot, because of the alkyl linkage, undergo the former two reactions. The *o*-semidine rearrangement of the protonated compound **8** could, in principle, occur to either side of the carbon atom bearing the nitrogen atom. If bond formation occurred to the non-alkylated *ortho*-carbon atom, the resulting product would be the highly strained unlikely compound **9**. On the other hand, if bond formation occurs to the alkylated carbon atom, the observed product **2** will be obtained.



SCHEME I



- a) HCl  
 b) H<sub>2</sub>/Pd/C  
 c) HCl, H<sub>2</sub>O  
 d) NH<sub>2</sub>NH<sub>2</sub>, H(OCH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>H

## REFERENCES

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 (2) W. W. Paudler and A. G. Zeiler, *J. Org. Chem.*, 34, 3237 (1969).  
 (3) H. Booth, *J. Chem. Soc.*, 1841 (1964).  
 (4) D. V. Banthrope and M. O'Sullivan, *J. Chem. Soc. (B)*, 627 (1969) and references therein.