

## The Photo-induced Stereospecific Formation of 9-Ethyl-1,4a-dimethyl-4,4a-dihydrocarbazole from *N*-Ethyl-2,6-dimethyldiphenylamine and its Photoreactions

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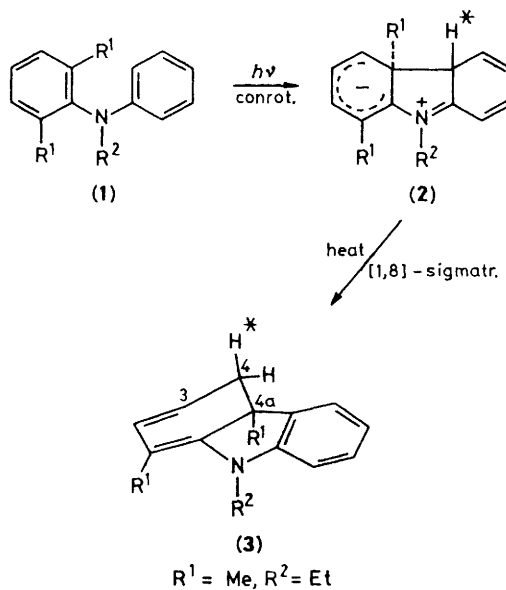
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The light-induced ring closure reaction of *N*-ethyl-2,6-dimethyldiphenylamine to 9-ethyl-1,4a-dimethyl-4,4a-dihydrocarbazole, (**3**), and the light-induced ring opening of (**3**) to give butadienylindoles was found to proceed stereospecifically and in accordance with the Woodward–Hoffmann rules.

*N*-Ethyl-2,6-dimethyldiphenylamine (**1**) is converted by light (Scheme 1) into 9-ethyl-1,4a-dimethyl-4,4a-dihydrocarbazole (**3**) via the zwitterionic, transient species (**2**) which absorbs strongly in the visible region ( $\lambda_{\text{max}}$  640 nm). By means of flash experiments it was shown<sup>1</sup> that a tunnel process contributes significantly to the hydrogen shift reaction (**2**)  $\rightarrow$  (**3**). In order to calculate quantum mechanical transmission probabilities of the tunnelling proton ( $\text{H}^*$  in Scheme 1) the width of the tunnel barrier had to be determined. Therefore, it was important to find out whether the rearrangement of (**2**) is regioselective and stereospecific.

Illumination experiments were carried out in methylcyclohexane–isopentane (1 : 3) under a nitrogen atmosphere at 173 K because the reaction step (**2**)  $\rightarrow$  (**3**) occurs at this temperature mainly by proton tunnelling.<sup>1</sup> The structure of the primary stable photoproduct (**3**) was deduced from the 270 MHz FT-n.m.r. spectra† in [<sup>2</sup>H<sub>6</sub>]DMSO. In order to facilitate the spectrum analysis [and to determine the magnitude of the isotope effect on the kinetics of the reaction (**2**)  $\rightarrow$  (**3**)] the deuteriated derivative *N*-ethyl-2',3',4',5',6'-pentadeuterio-2,6-dimethyldiphenylamine (**1<sub>D</sub>**) was also investigated.

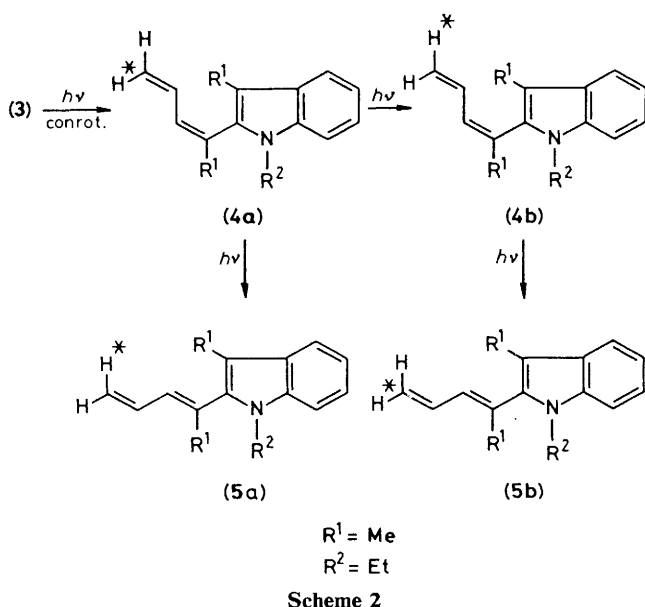
The results are as follows. (i), Only the proton  $\text{H}^*$  (cf. Scheme 1) shifts from the phenyl moiety of (**1**) via the transient (**2**) to the methyl-substituted ring of (**3**). In the case of (**1<sub>D</sub>**), which yields (**3<sub>D</sub>**), the proton  $\text{H}^*$  at C-4 of (**3**) ( $\delta$  2.25) is replaced by a deuterium and the signal at  $\delta$  2.25 is entirely missing.



Scheme 1

The signal of the second proton at C-4 ( $\delta$  2.48) appears in the spectrum of (**3**) and of (**3<sub>D</sub>**) with the same magnitude. The other four <sup>2</sup>H-atoms remain in the phenyl ring of (**3<sub>D</sub>**). (ii), Only a [1,8]-sigmatropic proton shift takes place. (A [1,4]-shift is also conceivable, but thermodynamically less favourable.<sup>1</sup>) (iii), The methyl group at the bridge of (**3**) (carbon atom C-4a) and the shifted proton  $\text{H}^*$  at C-4 are in a *trans*-configuration. This follows from the coupling constants, *J*, of the

† <sup>1</sup>H n.m.r. data for (**3**) measured in [<sup>2</sup>H<sub>6</sub>]dimethyl sulphoxide at 300 K:  $\delta$  1.00 (3H, s, 4a-CH<sub>3</sub>); 1.14 (3H, t, *J* 6.8 Hz, ethyl CH<sub>3</sub>), 1.94 (3H, s, 1-CH<sub>3</sub>), 2.25 (1H, dd,  $J_{3,4}^* 3$ ,  $J_{4,4a}^* 16.5$ , and  $J_{2,4}^* 3$  Hz, 4-H\*), 2.48 (1H, dd,  $J_{3,4} 6.5$  Hz, 4-H), 3.81 (2H, m, ethyl CH<sub>2</sub>), 5.30 (1H, m, 3-H), 5.78 (1H, dd,  $J_{2,3} 10$  Hz, 2-H), and 6.6–7.2 (4H, m, aromatic H).



geminal protons H and H\* at C-4 of (3) with the proton at C-3;  $J_{3,4}$  6.5 and  $J_{3,4}^* < 3$  Hz. Molecular models of (3) show that the conformation of these three protons is rigidly fixed. If the  $\text{CH}_3$ -group at C-4a and H\* are in a *trans*-relationship, the dihedral angles between the proton at C-3 and the protons H ( $\delta$  2.48) and H\* ( $\delta$  2.25) at C-4 are about 30 and 90°, respectively. The observed coupling constants are in agreement with the values predicted from the Karplus-Conroy curve for such angles. [In (3<sub>b</sub>) only the coupling  $J_{3,4}$  6.5 Hz is observed.]

The structure of the transient (2) could not be determined experimentally because of its short life time.<sup>1</sup> However, the Woodward-Hoffmann (WH) rules predict that in an electronically excited state the 1,5-electrocyclic ring closure reaction (1) → (2) takes place conrotatorily.<sup>2</sup> If this is the case the  $\text{CH}_3$ -group and the proton H\* at the bridge of (2) are in the *trans*-configuration and the (thermal) [1,8]-sigmatropic proton shift (2) → (3) is, in agreement with the WH rules, suprafacial.

The photoreactions of (3) and (3<sub>b</sub>) demonstrate the applicability of the WH rules to the entire reaction sequence. As in other cyclohexadiene systems (*e.g.* 1,2-dihydronaphthalenes<sup>3</sup> or ergosterol<sup>4</sup>) the ring opening reaction (3) → (4) (Scheme 2) is stereospecific. The WH rules predict a conrotatory ring opening for the light-induced reaction. If one avoids consecutive photoreactions as much as possible by photolysing only about 50% of (1), one observes the formation of (3) and of the stereoisomers 1-ethyl-3-methyl-2-(*cis*-1'-methylbuta-1',3'-dienyl)indole (4) and 1-ethyl-3-methyl-2-(*trans*-1'-methylbuta-1',3'-dienyl)indole (5) with the concentration ratio for (3):(4):(5) of 15:6:1.

Using (1<sub>b</sub>) one can distinguish between the n.m.r. spectra of the isomers (4a), (4b) and (5a), (5b) (*cf.* Scheme 2). Under the above conditions (50% conversion) the concentration ratio (4a):(4b) was at least 10:1 (n.m.r. detection limit). The concentration of (5) was too small to determine the concentration ratio (5a):(5b) accurately. Higher conversions of (1) or (1<sub>b</sub>) yield mainly (4) and (5) in a concentration ratio (4):(5) of 2:1 and very little (3).

The concentration ratios (4a):(4b) and (5a):(5b) are in this case 7:3. It is possible to separate (4) and (5) by means of gas chromatography. After separation of the deuteriated compounds the concentration ratios (4a):(4b) and (5a):(5b) are still 7:3. Illumination of the mixture (4a), (4b) leads to a photostationary state mixture of isomers with the concentration ratios for (4):(5) of 3:2 and for (4a):(4b) and (5a):(5b) of 1:1.

We conclude from these results that the first step of the ring opening reaction is indeed stereospecific, yielding exclusively (4a) as a result of a conrotatory reaction in accordance with the WH rules. The three other *cis-trans*-isomers are the products of consecutive photoreactions.

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