

## Photochemical Cyclodimerisation and Rearrangement of 5*H*-Dibenz[*b,f*]azepine Derivatives

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*Summary* Unsensitised and benzophenone-sensitised irradiation of *N*-acyl, -aroyl, and -ethoxycarbonyl derivatives of 5*H*-dibenz[*b,f*]azepine (**1**) (iminostilbene) gives good yields of cyclobutane dimers (**2**); the parent compound and its *N*-alkyl derivatives are photochemically inactive, whereas the *N*-tosyl compound undergoes photo-Fries rearrangement.

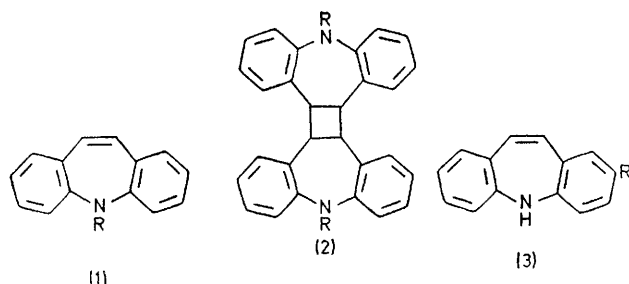
THE 5*H*-dibenz[*b,f*]azepine ring system (**1**) (iminostilbene) and its 10,11-dihydro analogue (iminobibenzyl) have received considerable attention in recent years, since derivatives bearing a  $\gamma$ -dialkylaminopropyl substituent at the 5-position have pharmacological activity.<sup>1</sup> However much of the fundamental chemistry of these ring systems remains unexplored. Descriptions of the photochemistry of 5*H*-

dibenz[*b,f*]azepines are limited to the parent compound (**1a**) and to 5-nitrosodibenz[*b,f*]azepine (**11**). Both materials were found to be photostable in the presence of argon but irradiation of the latter material in the presence of oxygen gave 2-nitrodibenz[*b,f*]azepine (**3b**).<sup>2</sup>

Benzophenone-sensitised irradiation (Hanovia Reading Reactor; Pyrex) of a degassed acetone or benzene solution of *N*-acetylaminostilbene (**1b**)† *in vacuo* gave the dimer (**2a**) (77% after 5 min; quantum yield  $\Phi$  0.27), m.p. 342—345° ( $M^+$  at  $m/e$  470). The unsensitised dimerisation was much less efficient (36% after 1 h). In both cases the presence of dissolved air (O<sub>2</sub>) had a retarding effect on the photodimerisation suggesting triplet-state intermediates. Michler's ketone ( $E_T$  61.0 kcal mol<sup>-1</sup>), but not fluorenone ( $E_T$  = 53.3 kcal mol<sup>-1</sup>), was found to sensitise the dimerisa-

† All new compounds had satisfactory elemental analyses and spectra.

tion in acetone or benzene indicating that  $E_T$  for (**1b**) lies in the region 53.3—61.0 kcal mol<sup>-1</sup>.



- |                             |                             |                        |
|-----------------------------|-----------------------------|------------------------|
| a; R = H                    | a; R = COMe                 | a; R = tosyl           |
| b; R = COMe                 | b; R = COEt                 | b; R = NO <sub>2</sub> |
| c; R = COEt                 | c; R = COCH <sub>2</sub> Cl |                        |
| d; R = COCH <sub>2</sub> Cl | d; R = COPh                 |                        |
| e; R = COPh                 | e; R = CO <sub>2</sub> Et   |                        |
| f; R = Et                   |                             |                        |
| g; R = CO <sub>2</sub> Et   |                             |                        |
| h; R = tosyl                |                             |                        |
| i; R = NO                   |                             |                        |

Similarly, sensitised irradiation of *N*-propionyl- (**1c**), *N*-chloroacetyl- (**1d**), *N*-benzoyl- (**1e**), and *N*-ethoxycarbonyl-iminostilbene (**1g**) afforded the dimers (**2b**), m.p. 323—325°, (**2c**), m.p. 317—320°, (**2d**), m.p. 300—304°, and (**2e**), m.p. 325—327°, respectively. Only one type of dimer could be isolated from each substrate and this, taken with

the presumed intermediacy of triplet state reactants, leads to an assumption of a thermodynamically stable *trans*-configuration for the cyclodimers.<sup>3</sup>

Sensitised and unsensitised photolyses of the parent (**1a**) and *N*-alkyl substituted [*e.g.* (**1f**)] iminostilbenes gave only unchanged starting materials. It is significant that in these compounds, the lowest energy transition ( $\lambda_{\text{max}}$ . 365 nm), which gives rise to yellow colouration,<sup>4</sup> is (presumably)  $n-\pi^*$  in character. The derivatives which photodimerised (**1b—e,g**) carry substituents which lower the energy of the non-bonding electron pair on nitrogen, as evidenced by u.v. spectra and absence of colour, and show photoreactivity similar to that of *cis*-stilbene analogues.

It should be noted however, that sensitised and unsensitised irradiation of 5-tosyliminostilbene (**1h**) afforded, in low conversion, 2-tosyliminostilbene (**3a**), m.p. 230—231°,  $\nu(\text{NH})$  3350 cm<sup>-1</sup>. This product was isolated by column chromatography (neutral Al<sub>2</sub>O<sub>3</sub>; benzene-methanol 9:1 v/v) and the position occupied by the tosyl group is assumed by analogy with the related photo-Fries rearrangement of sulpho-anilides, shown to yield exclusively *para*-tosylanilines.<sup>5</sup>

The intermolecular [2 + 2] photodimerisation of 5-acyliminostilbenes is in contrast to derivatives of the 1*H*-azepine ring system which undergo internal [2 + 2] photodimerisation to produce the isomeric 2-azabicyclo[3,2,0]-hepta-3,6-diene ring system.<sup>6</sup>

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