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

By LARRY J. KRICKA, MARTYN C. LAMBERT, and ANTHONY LEDWITH*
(*Donnan Laboratories, University of Liverpool, Liverpool* L69 3BX)

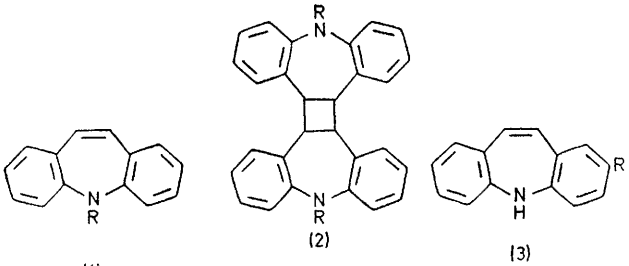
Summary Unsensitised and benzophenone-sensitised irradiation of *N*-acyl, -aroyl, and -ethoxycarbonyl derivatives of 5*H*-dibenz[*b*,*f*]azepine (**1**) (iminostilbene) gives good yields of cyclobutane dimers (**2**); the parent compound and its *N*-alkyl derivatives are photochemically inactive, whereas 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 γ-dialkylaminopropyl substituent at the 5-position have pharmacological activity.[1] 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 (**1i**). 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**).[2]

Benzophenone-sensitised irradiation (Hanovia Reading Reactor; Pyrex) of a degassed acetone or benzene solution of *N*-acetyliminostilbene (**1b**)† *in vacuo* gave the dimer (**2a**) (77% after 5 min; quantum yield Φ 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_2) had a retarding effect on the photodimerisation suggesting triplet-state intermediates. Michler's ketone (E_T 61·0 kcal mol^{-1}), but not fluorenone (E_T = 53·3 kcal mol^{-1}), 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^{-1}.



(1) (2) (3)

a; R = H
b; R = COMe
c; R = COEt
d; R = $COCH_2Cl$
e; R = COPh
f; R = Et
g; R = CO_2Et
h; R = tosyl
i; R = NO

a; R = COMe
b; R = COEt
c; R = $COCH_2Cl$
d; R = COPh
e; R = CO_2Et

a; R = tosyl
b; R = NO_2

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.[3]

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 ($\lambda_{max.}$ 365 nm), which gives rise to yellow colouration,[4] is (presumably) n–π^* 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°, ν(NH) 3350 cm^{-1}. This product was isolated by column chromatography (neutral Al_2O_3; 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.[5]

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.[6]

We thank the S.R.C. for a Research Studentship to M.C.L. and a Research Assistantship to L.J.K.

(*Received*, 22*nd February* 1973; *Com.* 247.)

[1] F. Hafliger and V. Burckhardt in 'Psychopharmacological Agents,' Academic Press, New York, 1964, vol. 4-1, p. 35.
[2] M. R. Bendall, J. B. Bremner, and J. F. W. Fay, *Austral. J. Chem.*, 1972, **25**, 2451.
[3] D. Seebach in 'Methoden Der Organischen Chemie (Houben-Weyl),' Georg Thieme Verlag, Stuttgart, 4/4, 1971.
[4] R. W. Schmid, *Helv. Chim. Acta*, 1962, **45**, 1982.
[5] D. Bellus, *Adv. Photochem.*, 1971, **8**, 109.
[6] L. A. Paquette and J. H. Barrett, *J. Amer. Chem. Soc.*, 1966, **88**, 1718.