meta-Photocyclisation of Phenylalkylamines

By DEREK BRYCE-SMITH,* ANDREW GILBERT, and GARUNE KLUNKLIN
(*Department of Chemistry, The University, Whiteknights Park, Reading, Berkshire*)

Summary The phenylalkylamines (**2c** and **d**) undergo intramolecular *meta*-photocyclisation in methanol to give the isomers (**3c** and **d**) respectively, possibly *via* fluorescing intramolecular charge-transfer exciplexes.

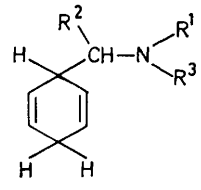
IT has previously been reported that tertiary amines undergo acid-catalysed 1,4-addition to benzene, giving cyclohexa-1,4-diene derivatives (**1**).[1] We now describe intramolecular analogues of this reaction.

Irradiation (254 nm; 20 °C; N_2) of a 0·01M-solution of 1-dimethylamino-3-phenylpropane (**2c**) in dry methanol gave slow conversion into two products. The major product† was isomeric with (**2c**) and was separated from the reaction mixture by preparative g.l.c. It has been assigned structure (**3c**), resulting from *meta*-cyclisation, on the basis of the following evidence. The u.v. spectrum showed λ_{max} (EtOH) 209 nm (ϵ 4045 cm^{-1} mol^{-1} l) with a shoulder at 260 nm (ϵ 250). The i.r. spectrum had major absorptions at 3000, 2950, 2920, 2840, 2780, 1640, 1460, and 705 cm^{-1}. Complete identification of the product as (**3c**) was afforded by its n.m.r. data and their comparison with those of the adducts from intermolecular addition of tertiary amines to benzene[1] [τ 4·26—4·62 (2H, ABq, J 11 Hz, 10- and 9-H), 4·66br (1H, s, 11-H), 7·0—7·55 (5H, m, 8-, 1-, and 6-H), 7·76 (5H, s with side peaks, *N*-Me and 2-H), 7·92 (2H, m, 4-H), and 8·20—8·60 (2H, m, 5-H)]. These results are inconsistent with the structures which could have resulted from *ortho*- or *para*-cyclisation.

In confirmation of the assigned structure, the product proved resistant to dehydrogenation (which would give an extremely strained product), although the intermolecular adducts (**1**) are readily aromatised.[1] Similarly, the mass spectrum showed a parent ion at M 163, but the $M-2$ peak was very small.

Irradiation of (**2d**) under similar conditions led to the slower formation of one product which was likewise assigned structure (**3d**) from its spectroscopic properties.

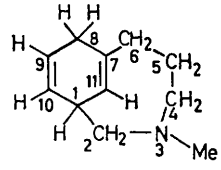
The present reactions may be contrasted with the photocyclisations of *N*-chloroacetyl derivatives of certain aromatic amines which result from C–Cl homolysis.[2]



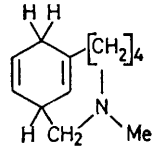
(1)

$Ph[CH_2]_nNMe_2$

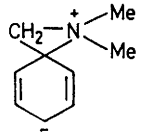
(2) a; $n = 1$
b; $n = 2$
c; $n = 3$
d; $n = 4$



(3c)



(3d)



(4)

Other workers have observed the formation of fluorescing intramolecular exciplexes from a series of diethyl-(1-naphthylalkyl)amines,[3,4] and the corresponding 9-anthryl derivatives.[4] Reactions typical of the hydrocarbon singlet

† The minor product had a molecular weight and mass spectral breakdown pattern consistent with an adduct of the starting material and methanol; its structure is under investigation.

states were thereby quenched,[4] but no cyclisation products were observed. We have carried out similar studies with compounds of type (**2**) where $n = 1$—**4**. Their u.v. absorption spectra are identical with those of the corresponding hydrocarbons $Ph[CH_2]_{n+1}Me$, so there is no appreciable ground state interaction between the phenyl group and the amino-function. The fluorescence spectra of the amines (**2b**—**d**) (n-hexane, 260 nm excitation) show maxima at 306, 330, and (double peak) 283 and 323 nm, respectively, and, except for the shorter wavelength emission of (**2d**), these contrast with the emission at 283 nm reported for all the corresponding hydrocarbons.[5] The emission in the 300—330 nm region is assigned to fluorescence from an intramolecular exciplex of charge-transfer character resulting from interaction of the singlet excited aromatic ring with the tertiary amine function. The lack of fluorescence from (**2a**) may be due to formation and subsequent ring opening of the zwitterion (**4**), as with the naphthalene derivative.[3]

Amine (**2c**) fluoresces more strongly than (**2d**), suggesting that its amine function interacts more effectively with the aromatic ring. It also cyclises the more readily, so the two processes may proceed from the same excited precursor, the cyclisation involving a mechanism analogous to that outlined for the intermolecular additions.[1]

Finally, these *meta*-cyclisations offer the prospect of a simple new approach to the synthesis of heterocyclic species related to the morphine alkaloids.

(*Received, 8th March* 1973; *Com.* 321.)

[1] D. Bryce-Smith, M. T. Clarke, A. Gilbert, G. Klunklin, and C. Manning, *Chem. Comm.*, 1971, 916.
[2] See for example, O. Yonemitsu, H. Nakai, Y. Kanaoka, I. L. Karle, and B. Witkop, *J. Amer. Chem. Soc.*, 1970, **92**, 5691 and references therein.
[3] E. A. Chandross and H. T. Thomas, *Chem. Phys. Letters*, 1971, **9**, 393.
[4] D. R. G. Brimage and R. S. Davidson, *Chem. Comm.*, 1971, 1385.