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# PHOTOCHEMICAL CYCLISATION OF N-(DIBENZYLAMINOMETHYL)PHTHALIMIDE

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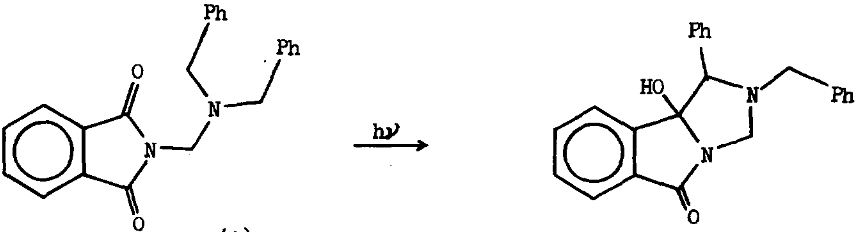
The photochemistry of N-substituted phthalimides has been the subject of several recent reports.[1] The carbonyl group can take part in intermolecular or intramolecular hydrogen abstraction processes, and the intramolecular reaction may lead to cyclisation. One group has shown[2] that irradiation of three Mannich bases of phthalimide gives cyclised products in yields of 13 - 35%. We now report that N-(dibenzylaminomethyl)phthalimide (1) gives rise to a product with a new imidazolidine ring and that the reaction probably occurs from a $(\pi,\pi^*)$ excited state of the imide by way of an initial electron transfer process.



(1)

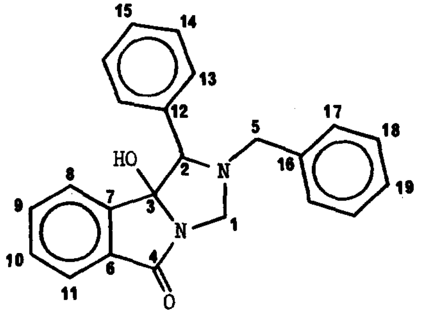
(2)

The substituted imide (1) was prepared by reaction of phthalimide, formaldehyde and dibenzylamine. On irradiation (Hanovia medium-pressure mercury arc, Pyrex filter) in benzene, acetone or acetonitrile, 2-benzyl-9b-hydroxy-1-phenyl-2,3,5,9b-tetrahydro-1H-imidazo-[4,3-a]isoindol-5-one (2) was obtained in yields up to 40% after purification. Found: C,77.5 ; H,5.68 ; N,7.68% ; $C_{23}H_{20}N_2O_2$ requires: C,77.5 ; H,5.66 ; N,7.86%. M.p. 176-7 °C. $\bar{\nu}$ (Nujol): 3350 (broad, O-H), 1675 (C=O) $cm^{-1}$. $\delta$ ($CDCl_3$) : 3.23 and 3.96 (two doublets, J ~ 13 Hz, 2H, N-C$\underline{H}_2$-Ph) ; 3.46 (singlet, 1H, -C$\underline{H}$Ph-) ;

3.6 (very broad, 1H, disappears on addition of $D_2O$, O$\underline{H}$); 4.05 and 4.42 (two doublets, J~6 Hz, 2H, N-C$\underline{H}_2$-N); 6.9 - 7.8 (multiplet, including strong 7.28 singlet, ~14H, aromatic C$\underline{H}$). The structure was amply confirmed by the carbon-13 n.m.r. spectrum (Table 1), in which all of the non-aromatic carbon signals can be readily assigned (1 - 5 on the arbitrary numbering scheme used here).

Table 1 Carbon-13 n.m.r. spectrum of (2)

| Carbon atom | $\delta$/ppm | |
|---|---|---|
| 1 | 64.8 | t |
| 2 | 73.8 | d |
| 3 | 94.0 | s |
| 4 | 171.1 | s |
| 5 | 56.5 | t |
| 6 | 131.9 | s |
| 7 | 145.4 | s |
| 8 or 11 | 123.4 | s |
| 9 | 132.9 | d |
| 11 or 8 | 124.2 | s |
| 12 or 16 | 134.5 | s |
| 16 or 12 | 137.0 | s |
| 10 and 13-15 and 17-19 | 127.3 - 130.1 | |



Our interest in this photoreaction is in its mechanistic aspects as well as its synthetic potential. In the hydrogen-abstraction reactions of aromatic carbonyl compounds where the process is fast and efficient, the reactive excited state is usually the $(n,\pi^*)$ triplet state. The introduction of electron-donor groups adjacent to the site of reaction in the side-chain (e.g. in $ArCOCH_2CH_2CH_2NR_2$) allows an electron-transfer/proton-transfer mechanism to operate in place of the hydrogen-atom abstraction mechanism,[3] and this permits reaction to be fast and efficient irrespective of the electronic nature of the lowest excited states. Norrish type 2 reaction for aromatic esters[4] ($ArCO\text{-}OCH_2CH_2X$) and amides[5] ($ArCO\text{-}NHCH_2CH_2X$), which have lowest $(\pi,\pi^*)$ excited states, is very inefficient unless there are electron-donor substituents ($X = NR_2$ or SMe) to make the electron-transfer mechanism feasible.

In the light of this, we attempted first to identify the lowest energy singlet and triplet states of compound (1). This phthalimide exhibits weak fluorescence (de-gassed solution in ethanol):

$$\lambda_{max.} = 322 \text{ nm} \quad ; \quad \tau = 3.8 \text{ ns} \quad ; \quad \Phi = 0.010$$

The fluorescence shows strong concentration quenching and a very small Stokes' shift, which are properties typical of emission from $(\pi,\pi^*)$ singlet states. However, although the absorption spectrum shows an intense band which is related to this fluorescence, there is also a weak shoulder extending to longer wavelengths (beyond 350 nm). If this shoulder is caused by $n \rightarrow \pi^*$ absorption, fluorescence is occurring from a singlet state other than the lowest. This is unusual, though not without precedent, but it means that we cannot make a definite assignment of the electronic nature of the lowest energy singlet state. A recent spectral survey[6] which included unsubstituted phthalimide led to a similar conclusion, namely that there is no clear evidence for $n \rightarrow \pi^*$ absorption in the ultraviolet spectrum of phthalimide.

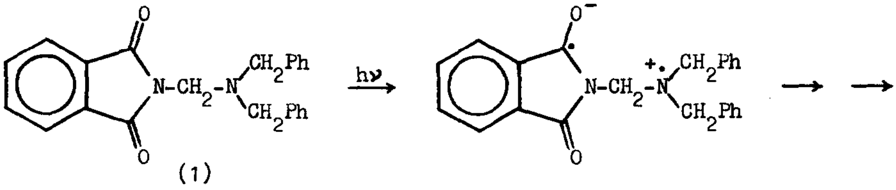
The phthalimide (1) phosphoresces at 77 K (see Table 2).

Table 2 Phosphorescence data for (1)

| solvent | lifetime / s | 0-0 band / nm | polarisation / % out-of-plane |
|---|---|---|---|
| ethanol | 1.03 | 410 | ~ 70 |
| methylcyclohexane | 0.53 | 414 | ~ 40 |
| bromocyclohexane | 0.17 | 418 | - |

The emitting state in ethanol can be confidently assigned as a $(\pi,\pi^*)$ triplet - there is little vibrational fine structure in the spectrum, the lifetime is long and is reduced considerably when a change is made to a heavy-atom solvent, and the polarisation is mainly out-of-plane.[7] The shorter lifetime and 'mixed' polarisation in hydrocarbon solvent suggest that the $(n,\pi^*)$ triplet state is quite close to the $(\pi,\pi^*)$ triplet in energy. The less polar solvent has the effect of lowering the $(n,\pi^*)$ excited state energy and so bringing the two triplets even closer together in energy.

The lowest excited states are therefore probably $(\pi,\pi^*)$ in nature (with the proviso mentioned above concerning the possibility of a non-emitting $(n,\pi^*)$ singlet), and on the basis of analogy with other aromatic carbonyl compounds the first step in the mechanism may be electron transfer rather than hydrogen abstraction:



(2)

Two further pieces of evidence support this postulate. First, the phosphorescence lifetime of the dibenzylaminomethyl compound (1) is very close to that of the related N-(dimethylaminomethyl)- and N-(di-n-propylaminomethyl)-phthalimides (0.97 s and 0.99 s respectively in ethanol at 77 K, compared with 1.03 s for (1) ). This indicates that the strength of the C-H bond at the site of reaction does not affect the triplet lifetime, at least at 77 K; hydrogen abstraction is therefore unlikely to be a major reaction pathway for the triplet state. Similar considerations hold for the singlet (fluorescence) lifetimes (3.8 ns for (1), 3.7 ns for the dimethylaminomethyl compound, and 3.7 ns for the di-n-propylaminomethyl compound). Secondly, the presence of a triplet quencher (penta-1,3-diene, 1.3 mol $l^{-1}$) does not significantly affect the rate of formation of the photoproduct. If a triplet state is reacting, then its lifetime must be less than $10^{-10}$ s, which is very short indeed if hydrogen abstraction is a major reaction route. It therefore seems best to postulate that the primary step is electron transfer.

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## References

1 Y.Sato, H.Nakai, T.Mizoguchi, Y.Hatanaka and Y.Kanaoka, J.Amer.Chem.Soc., 1976, 98, 2349, and references therein; Y.Kanaoka, K.Sakai, R.Murata and Y.Hatanaka, Heterocycles, 1975, 3, 719; H.J.Roth and G.Hundeshagen, Arch.Pharm., 1976, 309, 58.

2 H.J.Roth and D.Schwarz, Arch.Pharm., 1975, 308, 631.

3 P.J.Wagner and D.A.Ersfeld, J.Amer.Chem.Soc., 1976, 98, 4515, and references therein.

4 J.D.Coyle and D.H.Kingston, Tetrahedron Letters, 1975, 1021; J.Chem.Soc.Perkin II, 1976, 1475.

5 J.D.Coyle and D.H.Kingston, Tetrahedron Letters, 1976, 4525.

6 V.Galasso and G.C.Pappalardo, J.Chem.Soc.Perkin II, 1976, 574.

7 R.S.Becker, 'Theory and Interpretation of Fluorescence and Phosphorescence', Wiley, 1969, p.156; for comments on the criteria, see E.T.Harrigan and N.Hirota, Mol.Phys., 1976, 31, 681.