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Photochemistry of N-(4-Dimethylaminobenzylidene)aniline¹⁾

Hiroyuki Онта and Katsumi Токимаки

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113 (Received November 30, 1974)

Synopsis. Irradiation of N-(4-dimethylaminobenzylidene) aniline, contrary to an earlier report, does not give cis-4,4'-bis(dimethylamino) stilbene and azobenzene, however, its triplet state has, exceptionally as an acyclic imine, enogh lifetime at 77 K to exhibit phosphorescence.

Recently increaseing attention has been paid to photochemistry of carbon-nitrogen double bonds.2) For the irradiation of several imines in alcoholic solvents to give the reduced products, once the excited states of the imines were supposed to abstract hydrogen atoms from the solvents, but it is now accepted that carbonyl compounds present as impurities or as hydrolysis products are responsible for initiating the reaction on irradiation.³⁾ Cyclic imines, whose excited triplet states have longer lifetimes than the most acyclic imines, are still unreactive towards hydrogen atom abstraction probably on account of high π , π^* character of their triplet states.⁴⁾ Most imines are also photochemically unreactive in unimolecular cleavage except those carrying heteroatoms adjacent to carbon-nitrogen double bonds,5) azirines⁶⁾ and acyclic imines substituted with benzyl groups.7) The unreactive nature of the most imines in photochemical cleavage is attributable to the too short lifetimes of their excited states owing to their facile radiationless deactivation accompanid by syn-anti isomerization. Many carbonyl compounds in the n,π^* excited states and olefins in the π,π^* excited states are well known to undergo cycloaddition to unsaturated bonds.8) On the other hand, imines have not been reported to add to unsaturated compounds except the following cases. One exception is recent finding by Koch and Rodehorst on capability of cyclic imines with conjugated carbonyl groups for addition to vinyl ether.9) The other one, with which the present work concerns, is Searles and Clasen's report in 1965 that irradiation of N-(4-dimethylaminobenzylidene)aniline (I) in ether gave cis-4,4'-bis(dimethylamino)stilbene (II) and azobenzene (III) probably through cycloaddition between the imine to give diazetidine intermediate followed by its cleavage into the products. 10)

2 ArCH=NPh
$$\xrightarrow{h\nu}$$
 ArCH-NPh
(I) ArCH-NPh
 \longrightarrow cis-ArCH=CHAr + PhN=NPh
(II) (III)
(Ar: ρ -Me₂NC₆H₄)

Since most benzylideneanilines were known not to undergo this type of reaction, this report prompted us to explore the nature of the excited state of the imine (I) and the mechanism with which this excited state would be so reactive contrary to the most imines. This photochemical reaction was reinvestigated in several conditions as described below, but their results were not repro-

ducible in our experimental conditions. However, the triplet state of this imine was found to have enough long lifetime at 77 K to phosphoresce in contrast with the most acyclic imines.

Results and Discussion

The imine (I) was irradiated in ether and in methanol with a high or a low pressure mercury lamp. The results are summarized in the Table. It indicates that after the irradiation most of the imine was recovered and a part of the imine was converted into 4-dimethylaminobenzaldehyde (IV) and aniline (V) but the reported products, II and III, were not found among the products. Thus, irradiation of I in 0.02 M ether solution with a high pressure mercury lamp or in 0.04 M ether with a low pressure mercury lamp did not afford the reported products. Use of concentrated solution (0.16 M) which would favour the bimolecular cycloaddition still failed in giving the reported products. Irradiation was also undertaken at solid carbon dioxideethanol temperature, but the reported products were not produced. Replacement of solvent from ether to methanol gave no effect on the reaction. A control experiment showed that II was not consumed on irradiation with the imine in ether. Therefore, we are forced to conclude that, in our experimental conditions, the imine (I) does not lead to the products earlier reported, and the reported products seem to have arisen in an adventitious or a limited condition.

Formation of IV and V in the irradiation are supposed to be due to hydrolysis of the imine by trace amount of water eventually present. Since the solution of the imine, on being kept in the dark, did not afford the hydrolysis products, the observed hydrolysis appears to be promoted by the irradiation as was reported by Furey and Kan for unsubstituted benzyldeneaniline.¹¹⁾

$$ArCH=NPh + H_2O \xrightarrow{hr} ArCHO + PhNH_2$$

To our knowledge, acyclic imines have never been reported to phosphoresce. It is therefore remarkable to have found that I exhibited phosphorescence in EPA at 77 K with maxima at 435 and 455 nm with lifetime of 0.4 sec. However, it did not fluoresce at room temperature and at 77 K. A possibility that the observed phosphorescence would result from the triplet state of IV eventually present as an impurity or as hydrolysis product of the imine is ruled out, because IV showed phosphorescence with a maximum at 465 nm in EPA and the maximum of the phosphorescence excitation spectrum of I, 345 nm, or IV, 335 nm, corresponded nearly to the respective absorption maximum, 345 or 339 nm. So, it is evident that the observed phosphorescence originates from the triplet state of I. The above result indicates that the triplet state of the imine (I) lies 63

Table 1. Products from the irradiation of *N*-(4dimethylaminobemzylidene) aniline (i) in ether

I used (mmol)	Sovent (ml)	Lamp ^{b)} (W)	Time (hr)	Products (%) d,i)		
				I ^{e)}	$IV^{f)}$	$\sqrt{V_{g}}$
9.15	400	H 400°)	42	67	20	25
8.62	200	L 160 ^{c)}	42	80	13	15
4.72	30	H 100	60	ca. 80	h	h
3.48	30	H 100	40	ca. 80	h	h
7.77	400 ^{a)}	H 100 ^{c)}	68	ca. 80	h	h

a) methanol; b) H and L: a high or low pressure mercury lamp, respectively; c) immersion-type lamp; d) based on I used; e) recovered; f) 4-dimethylaminobenzaldehyde; g) aniline; h) present but not determined; i) IV and V were determined by vpc and I was isolated by column chromatography and weighed.

kcal mol⁻¹ above the ground state and its long lifetime suggests that the triplet state is abundant in π,π^* or intramolecular charge transfer electronic configuration.¹²⁾

Experimental

N-(4-Dimethylaminobenzylidene)aniline (I) was prepared according to literature. (I)

Irradiation was carried out for runs using 200-400 ml solution with a Riko immersion-type high or low pressure mercury lamp under nitrogen. For a concentrated ethereal solution of the imine in a Pyrex tube kept under argon atmosphere, external irradiation was done with a Riko high pressure mercury lamp. For a run at low temperature, the ethereal imine in a Pyrex tube under argon was kept in a solid carbon dioxide-ethanol in a Dewar vessel and irradiated with a high pressure lamp placed in the same bath. The irradiated mixture was analyzed by vpc with a Hitachi 063 gas chromatograph with a FID detector using a 2 m SE-30 column at 200 °C. 4-Dimethylaminobenzaldehyde (IV) and aniline (V) were determined with the use of nitrobenzene as an internal standard, however, cis-4,4'-bis(dimethylamino)stilbene (II) and azobenzene (III) were not detected. The mixture was concentrated under vacuum and the residue was chromatographed over well-washed silica gel to give the recovered imine together with IV and V.

The emission was measured with a Hitachi MPF 2A spectro-

fluorometer together with an attachment for phosphorescence observation.

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