

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*-(4-DIMETHYLAMINOBENZYLIDENE) ANILINE (I) IN ETHER

I used (mmol)	Solvent (ml)	Lamp <sup>b)</sup> (W)	Time (hr)	Products (%) <sup>a,1)</sup>		
				I <sup>e)</sup>	IV <sup>f)</sup>	V <sup>g)</sup>
9.15	400	H 400 <sup>c)</sup>	42	67	20	25
8.62	200	L 160 <sup>c)</sup>	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 <sup>a)</sup>	H 100 <sup>c)</sup>	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<sup>-1</sup> above the ground state and its long lifetime suggests that the triplet state is abundant in  $\pi,\pi^*$  or intramolecular charge transfer electronic configuration.<sup>12)</sup>

### Experimental

*N*-(4-Dimethylaminobenzylidene)aniline (I) was prepared according to literature.<sup>13)</sup>

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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