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PHOTOCHEMICAL AND THERMAL INTERCONVERSIONS OF THREE DIMERS OF 2,4,5-TRIPHENYLIMIDAZOLYL (LOPHYL)

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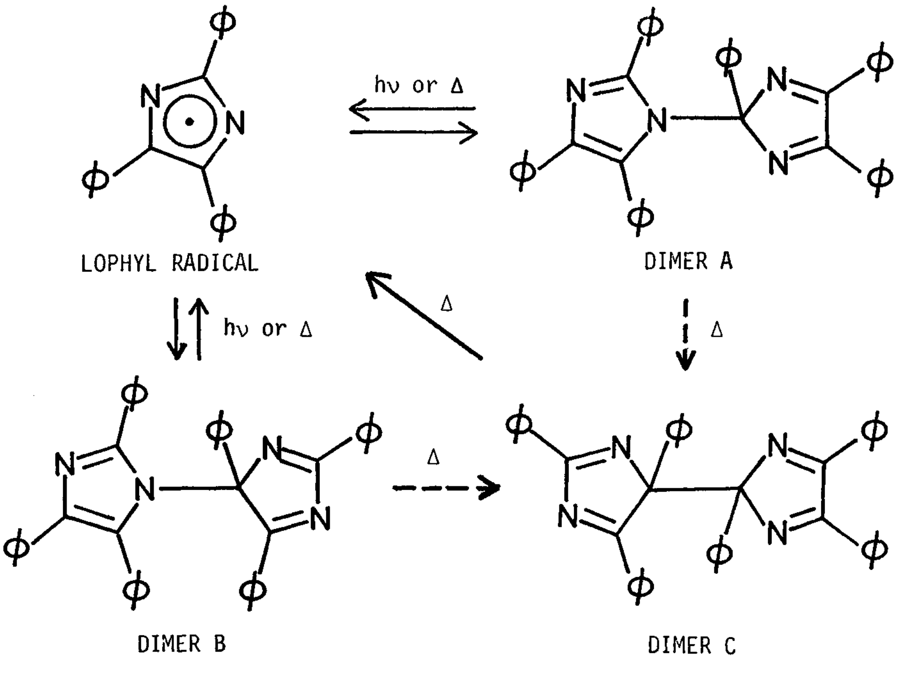
Two photochromic lophyl dimers, A and B, are interconverted by uv irradiation, while these two dimers and thermochromic dimer C can be equilibrated in benzene at 100°C. Compositions at equilibrium using the corresponding three dimers of 2-(p-tolyl)-4,5-diphenylimidazolyl are A:B = 96:4 and A:B:C = 14:18:68, respectively.

In relation to chemiluminescence of lophine,[1,2] Hayashi and Maeda[3] prepared two isomeric lophyl dimers by oxidation of lophine with ferricyanide; one is a piezochromic dimer that is very unstable compound existing only in a solid state and is converted to another photochromic dimer (dimer A) by crystallization from



benzene. Besides these two dimers we could prepare further two new dimers;[4] one (dimer B) is photochromic and another (dimer C) is thermochromic.

Photochromic dimers, A and B, could be converted each other by uv irradiation in benzene at room temperature, while dimer C was not affected by light. Instead, heating at 100°C in benzene, each of these three dimers gave a mixture of the three. The photochemical and the thermal interconversions were quantitatively measured using the corresponding three dimers of 2-(p-tolyl)-4,5-diphenylimidazolyl by monitoring pmr signals of their methyl groups[4] (Figs. 1 and 2) since pmr spectra of the parent lophyl dimers were too complicated to be analyzed.[4] Interestingly, the compositions of the three dimers (Table 1) are quite different between photochemical and thermal equilibrations. The intermediate of the photochemical interconversions is undoubtedly the common lophyl radical;[5] the photolysis of dimer B is faster than that of dimer A.[6] Indeed dark color due to lophyl radicals produced in the reaction. The lophyl radical however, must not be the precursor of dimer C,for dimer C is not produced photochemically; a possible mechanism of formation of dimer C from dimers A and/or B is the thermal [1,5]sigmatropic rearrangement.

TABLE 1. Compositions of the three dimers at equilibrium in C_6D_6 (34 mg/0.6 ml)

Starting material	Condition	Dimer A	Dimer B	Dimer C
Dimer A or B	High-pressure Hg lamp at room temp.	96%	4%	0%
Dimer A, B or C	In the dark at 100°C	14%	18%	68%

Since dimer C has uv spectrum similar to those of dimers A and B (Fig. 3), non-photochromism of dimer C must not be due to the absence of uv light absorption. It is of interest to note that photochromic dimers, A and B, have a central C-N (sp^3-sp^2) bond to be cleaved, whereas non-photochromic dimer C has a central C-C (sp^3-sp^3) bond. In the former case uv irradiation excites the aromatic imidazole ring, the energy of which is directly transmitted to the central C-N bond to be dissociated. No such excitation can be expected for the dimer C.

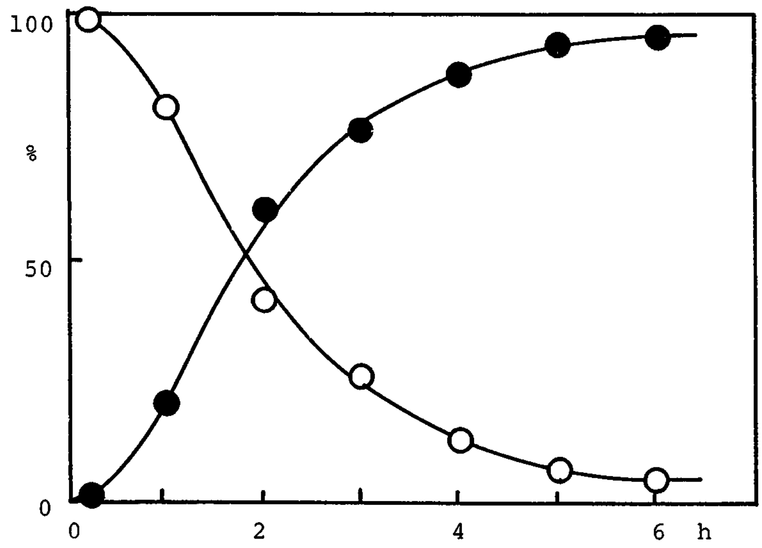


Fig. 1. Photochemical conversion of dimer B to dimer A with a high-pressure Hg lamp at room temp. in C_6D_6 (34 mg/0.6 ml): —●— Dimer A; —○— Dimer B

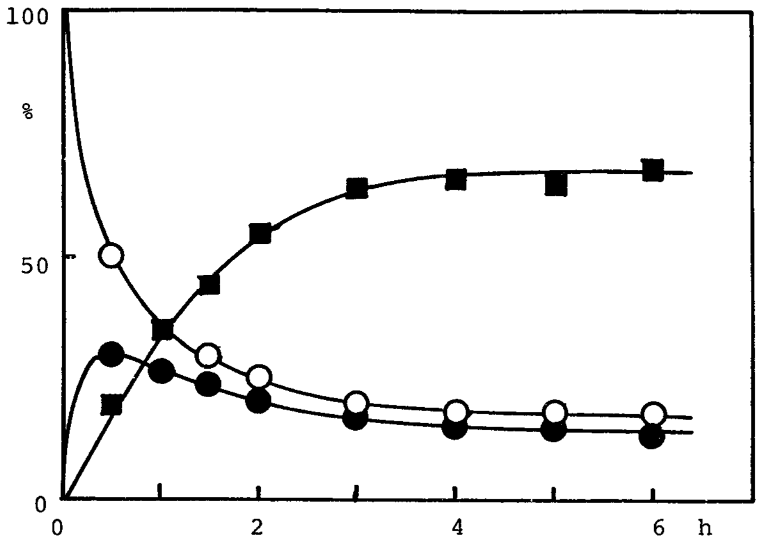


Fig. 2. Thermal conversion of dimer B to dimer A and C in the dark at 100°C in C_6D_6 (34 mg/0.6 ml): —●— Dimer A; —○— Dimer B; —■— Dimer C

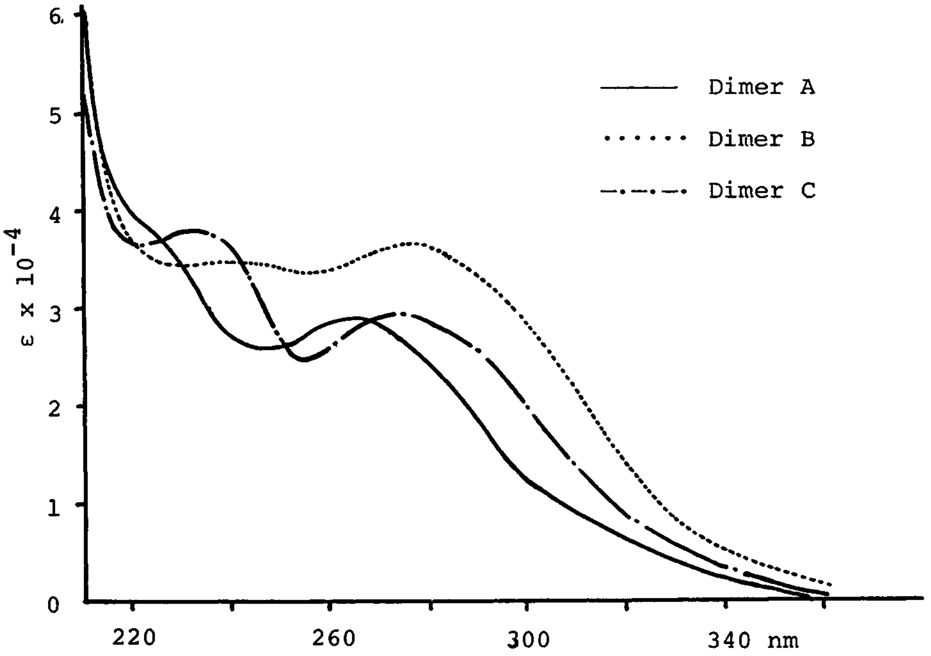


Fig. 3. Uv spectra of three dimers of 2-(p-tolyl)-4,5-diphenylimidazolyl in methanol

REFERENCES AND FOOTNOTE

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6. A large steric hindrance among the phenyl groups in dimer B is apparent from its pmr spectra; one of the phenyl groups shows restricted rotation in $CDCl_3$ even at room temp. about the C-C single bond between the phenyl and the imidazole ring.[4] This may be related to the photochemical instability of dimer B.

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