

테트라메틸에틸렌에 대한 트랜스-1, 2-비스피라질에틸렌의 광첨가반응

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Photoaddition Reactions of *trans*-1, 2-Bispyrazylethylene to Tetramethylethylene

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요 약. 트랜스-1, 2-비스피라질에틸렌 (BPE)과 테트라메틸에틸렌 (TME)용액에 빛을 쏘아진 이에 대응한 탄화수소와는 달리 자유라디칼중간체를 거쳐 광첨가반응이 일어난다. 이 광첨가반응은 BPE의 $^1(n, \pi^*)$ 상태가 어느정도 자유라디칼 성격을 띄어 TME로 부터 알릴위치에 있는 수소원자를 탈취하여 일어난다. 주생성물을 대용 크로마토그래피와 진공분별승화법으로 분리하여 2, 3-디메틸-5, 6-비스피라질-2-헥센임을 밝혔다.

ABSTRACT. *trans*-1, 2-Bispyrazylethylene (BPE) undergoes photoaddition reaction to tetramethylethylene (TME) which appears to involve radical intermediates under conditions where the corresponding hydrocarbons are unreactive. This photoaddition reaction involves abstraction of an allylic hydrogen atom of TME by $^1(n, \pi^*)$ states of BPE having radical character. The major photoadduct is isolated by column chromatography and fractional vacuum sublimation and characterized to be 2, 3-dimethyl-5, 6-bispyrazyl-2-hexene.

INTRODUCTION

Studies on the photoreactivities of nitrogen heteroaromatic compounds have received much attention. Interest in these compounds has been aroused in part by theoretical studies and in part by the presence of these structures in biologically important systems. Potential analogies with aromatic hydrocarbons and oxygen and sulfur heteroaromatics suggest that useful and

interesting photoreactions will occur with the isoelectronic nitrogen heteroaromatics. The presence of nitrogen as a reactive site in the products of these reactions should be useful in further conversions. The rich array of (n, π^*) and (π, π^*) states in nitrogen heteroaromatics should provide a variety of interesting physical and chemical conversion processes. Therefore these compounds are attractive candidates for study since, to a first approximation, they con-

tain both the well defined stilbene energy levels plus (n, π^*) states. Though there are still problems concerning mechanistic details of the photochemistry of stilbene, the reactivity of singlet and triplet states of stilbene and many substituted stilbenes has been well characterized. Therefore, it should be possible to gain a great deal of information by evaluating the perturbations introduced by nitrogen substitution. For example, acridine⁴⁻⁶, quinoline^{7,8}, purine⁹, and 1,2-bispyridylethylene¹⁰ undergo photoaddition and photoreduction reactions which appear to involve radical intermediates under conditions where the corresponding hydrocarbons are unreactive. One possibility for explaining this behavior is the involvement of (n, π^*) states having radical character and some excitation localization on nitrogen. Synthesis and photochemistry of 1,2-bisprazylethylene (BPE), one of the nitrogen containing stilbene analogues, were reported previously¹¹⁻¹³. As with other nitrogen heteroaromatics, spectroscopic studies of BPE showed that $^1(n, \pi^*)$ state has about the same energy as $^1(\pi, \pi^*)$ state. In the present paper we report study on the photoaddition reaction of BPE to 2,3-dimethyl-2-butene (tetramethylethylene, TME). This study is a good model reaction to see whether major reaction is ($\pi 2s + \pi 2s$) concerted photocycloaddition reaction or noncyclic photoaddition reaction through a radical intermediate.

EXPERIMENTAL

Materials. *trans*-BPE was synthesized by the method reported¹¹. m.p. 191 °C. TME (Aldrich Chemical Co., Inc.) was used as received. Benzene was purified as reported earlier.

Spectra. Nuclear magnetic resonance spectra were measured on a Varian T-60A spectrometer operated at 60MHz. The spectra were calibrated using tetramethylsilane as an internal stan-

dard. Chemical shifts are reported as δ values. The mass spectra were recorded at 70 eV on a Hewlett Packard 5985 A GC/MS system. UV absorption spectra were recorded on a Cary Model 17 spectrophotometer. Infrared spectra were measured on a Perkin-Elmer Model 267 spectrophotometer. Elemental analysis were carried out by the Korea Institute of Science and Technology, Seoul, Korea.

Irradiation Procedures. *trans*-BPE (300 mg) and excess TME (10 mL) were dissolved in purified benzene. The solution was deoxygenated by bubbling nitrogen through the solution for 0.5 hr and irradiated in a Pyrex tube using a preparative Rayonet photochemical reactor (The Southern New England Ultraviolet Company) equipped with 350 nm fluorescent lamps for 10 hrs.

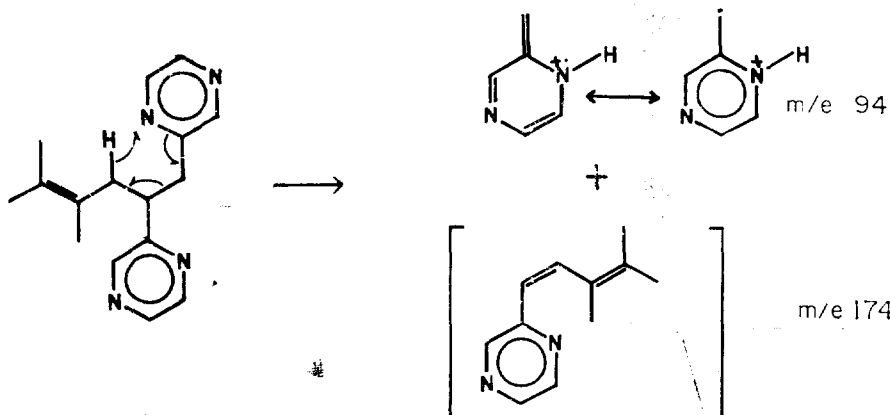
Isolation Procedures. The solvent was removed under reduced pressure. The concentrated reaction mixture was poured onto a 1.0 × 40 cm column packed with silica gel. The column was eluted with CCl_4 - Et_2O (3:2 v/v) mixed solvents. The photoaddition product was isolated by fractional vacuum sublimation of thus obtained reaction mixtures. At 30 °C, the three product mixtures were separated and at 45 °C, the major photoaddition product was obtained. Recrystallization of this product from petroleum ether yielded white needle crystals (25 %).

m.p 73 °C: NMR (CDCl_3) δ (ppm), 8.2~8.6 (6H, *m*), 3.9(1H, *m*), 3.3(2H, *m*), 2.5(2H, *d*) 1.6(6H, *s*), 1.4(3H, *s*). The mass spectrum, *m/e* (relative intensity), 268(M^+ , 10.0), 185(19.7), 175(100.0), 174(10.1), 94(69.6), 83(6.9).

Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{N}_4$: C, 71.9; H, 7.4; N, 21.0. Found: C, 71.6; H, 7.5; N, 20.9. The UV absorption spectrum shows $\lambda_{\text{max}}^{\text{EtOH}}$ at 267, 310nm.

RESULTS AND DISCUSSION

The structure of the major photoaddition product was determined to be 2,3-dimethyl-5,6-bispyrazyl-2-hexene, noncyclic addition product. This structure was established by the mass and nmr spectra and the bromination test for unsaturation. It is well known that N-heteroaromatics having an alkyl group of more than three carbon atoms in the 2-position can undergo rearrangement of a hydrogen atom of alkyl chain to the ring nitrogen^{7,14}. Therefore, the *m/e* 94 peak results from the McLafferty rearrangement of an allylic hydrogen atom to the ring nitrogen as shown below.



ground state TME giving an exciplex which demotes to the adduct with retention of the *trans*-stereochemistry^{16,17}. However, no singlet exciplex formation between BPE and TME is evident from the fluorescence quenching studies. Spectroscopic studies of BPE has shown that $^1(n, \pi^*)$ state has about the same energy as $^1(\pi, \pi^*)$ state and the extensive mixing of these two states obscures $n \rightarrow \pi^*$ band and shows weak fluorescence ($\Phi = 0.025$ at 77 °K) from $^1(\pi, \pi^*)$ compared to the strong fluorescence of *trans*-stilbene ($\Phi = 1.0$ at 77 °K).

In several nitrogen heteroaromatic compounds, rapid radiationless decay of initially formed ex-

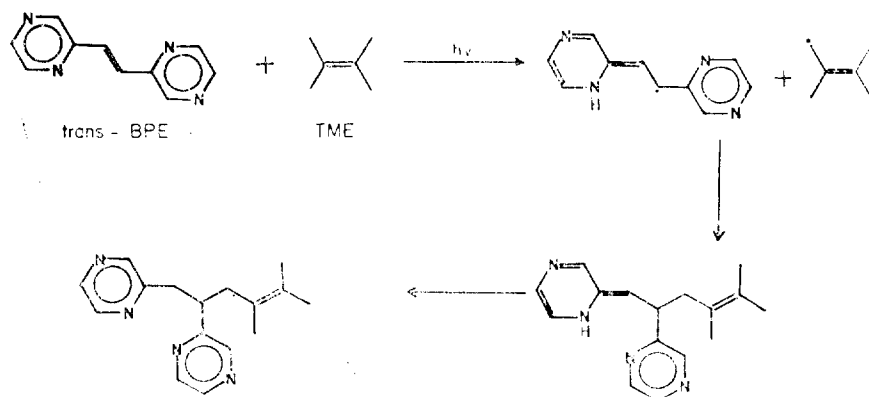
The IR spectrum does not show an olefinic stretching band near 1630 cm^{-1} indicating the symmetric environment of olefinic bond. The presence of double bond was proven by decoloration of bromine in CCl_4 . The UV absorption spectrum shows $\lambda_{\text{max}}^{\text{EtOH}}$ at 267 nm and 310 nm which are similar to those of methyl pyrazine ($\lambda_{\text{max}}^{\text{EtOH}}$ 262, 306nm). The NMR spectra are consistent with the structure.

Irradiation of either *trans*- or *cis*-stilbene, which has been the subject of extensive investigation, in TME undergoes a $(\pi 2s + \pi 2s)$ photocycloaddition in high yields¹⁵. The mechanism of this photocycloaddition involves reversible reaction of $^1(\pi, \pi^*)$ *trans*-stilbene with

cited singlet states evidently competes favorably with fluorescence, intersystem crossing, and chemical reactions¹⁸⁻²⁰. Therefore, the photoaddition reaction of BPE to TME is expected to be different from that of *trans*-stilbene and the failure of the exciplex formation between BPE and TME is no surprise because of the short lifetime of $^1(\pi, \pi^*)$ state of BPE compared to that of stilbene. Consequently no $(\pi 2s + \pi 2s)$ photocycloaddition reaction occurred between BPE and TME under the experimental conditions used and noncyclic photoaddition product was obtained instead. Evidently $^1(\pi, \pi^*)$ state of BPE rapidly undergoes internal conversion.

to lower $^1(n, \pi^*)$ state which has some radical character and this $^1(n, \pi^*)$ state abstracts an allylic hydrogen atom from TME just like in the

photoreduction of BPE. No such hydrogen abstraction was observed in stilbene photo-reactions.



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