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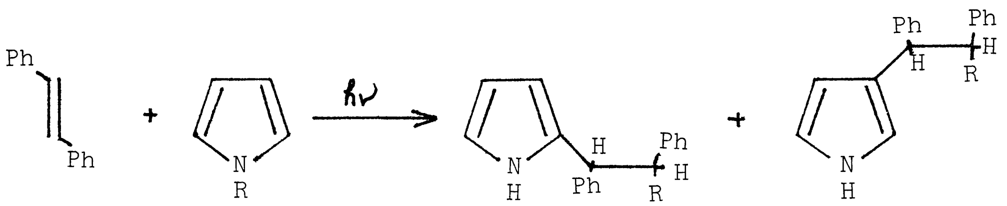
THE PHOTOADDITION OF STILBENE TO PYRROLE

Tadatoshi KUBOTA and Hiroshi SAKURAI
The Institute of Scientific and Industrial Research, Osaka University,
Suita, Osaka, Japan

Irradiation of trans-stilbene in pyrrole gave 2-(1,2-diphenylethyl)-pyrrole I and 3-(1,2-diphenylethyl)pyrrole II. It is suggested that this reaction proceeds via an exciplex.

Stilbene is known to react photochemically with 2,3-dihydropyran,[1)] 2-methyl-4,5-dihydrofuran,[2)] or tetramethylethylene[3)] to give cyclobutane derivatives and with phenyl isocyanate to give a β-lactam.[4)] We wish to report on the photoaddition of stilbene to pyrrole.

trans-Stilbene (0.8 g) in pyrrole (20 g) was irradiated in a Pyrex tube for 3 days with a 350 W high-pressure mercury lamp. Chromatography on silica gel gave oily products I (44 %) and II (10 %). Elemental analyses and the mass spectra (M^+ 247) indicated that these products are 1:1 adducts of stilbene and pyrrole. Compounds I and II had an infrared absorption at 3440 cm^{-1}(NH). The NMR spectrum of I showed two doublets of doublets at τ6.84 (2H, methylene protons, J 9 Hz 13 Hz 6 Hz 13 Hz), a doublet of doublets at 6.02 (1H, a methine proton, J 6 Hz 9 Hz), a triplet at 4.12 (2H, β-protons of pyrrole, J 2.1 Hz), a quartet at 3.74 (1H, an α-proton of pyrrole, J 2.1 Hz) and a multiplet for the aromatic protons and NH proton at 2.7 – 3.3 (11H).



I R = H

I′ R = D

II R = H

II′ R = D

The NMR spectrum of II showed two doublets at τ6.86 (2H, methylene protons, J 7 Hz 8 Hz), a doublet of doublets at 6.00 (1H, a methine proton, J 7 Hz 8 Hz), multiplets at 4.13 (1H, a β-proton of pyrrole), at 3.79 and 3.59 (2H, α-protons of pyrrole) and at 3.0 (10H, aromatic protons), and a broad signal at 2.5 (1H, NH). The IR and NMR spectra obtained from these products were identical to those obtained from those produced on reaction of pyrrylmagnesium bromide with 1,2-diphenylethyl chloride.[5] On the basis of these data, products I and II were identified as 2-(1,2-diphenylethyl)-pyrrole and 3-(1,2-diphenylethyl)pyrrole, respectively. Irradiation of stilbene in pyrrole-1-d gave products I′ and II′; this shows that N-proton plays an important role in this reaction.[6]

This reaction was not sensitized by Michler's ketone which sensitized the trans to cis isomerization of trans-stilbene. Furthermore, the fluorescence of trans-stilbene was efficiently quenched by pyrrole ($k_q\tau$ = 3.6 l/mol in cyclohexane). These results suggest that the addition involves singlet-excited trans-stilbene.

The fluorescence of trans-stilbene was also effectively quenched by N-methylpyrrole ($k_q\tau$ = 2.2 l/mol in cyclohexane) and a new emission increasing in intensity with increasing N-methylpyrrole concentration appeared at longer wavelengths, as shown in Figure.[7] This new emission was ascribed to an exciplex since the UV spectrum showed

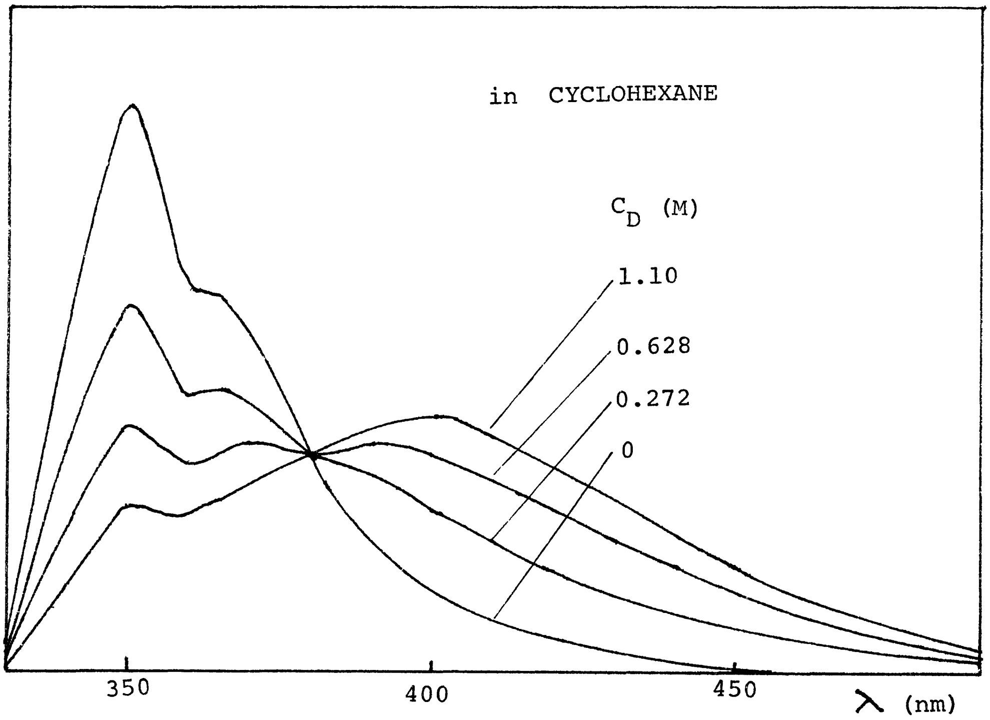
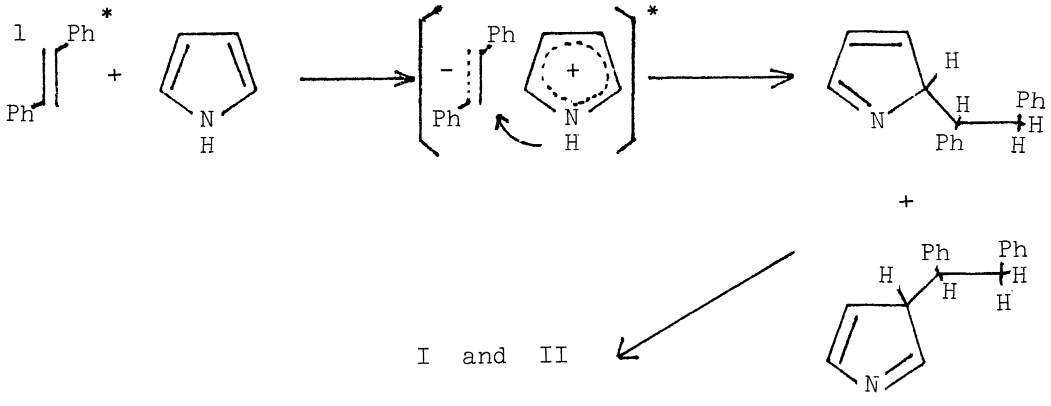


Figure. Fluorescence spectra of trans-stilbene (0.00067 M) in cyclohexane at different concentrations (C_D) of N-methylpyrrole no evidence for a ground state complex.8) The new emission did not appear in acetonitrile solutions, though the fluorescence was also quenched by N-methylpyrrole. This behavior is consistent with exciplex emissions, which are observed in the system of aromatic hydrocarbons and aromatic amines.8)

Since N-benzylpyrrole is known to isomerize to 2- and 3-benzylpyrrole thermally9) and photochemically,10) the mechanism that N-(1,2-diphenylethyl)pyrrole, which was once formed, isomerizes photochemically to I and II might explain the deuterium distribution well. Compounds I and II are primary photoproducts since these increase linearly with time. Furthermore, the irradiation of N-(1,2-diphenylethyl)pyrrole, which constituted only 0.5 % of the total photoproducts according to glpc, in the presence of trans-stilbene hardly yielded the isomerized products, though under these conditions stilbene reacted with pyrrole rapidly to give the 2- and 3-substituted products. It is very unlikely that the N-substituted pyrrole isomerizes photochemically to I and II so rapidly, because most of light is absorbed by stilbene. Thus, products I and II do not seem to be formed via N-(1,2-diphenylethyl)pyrrole.

We suggest that this reaction proceeds via an exciplex of pyrrole and stilbene,11) though direct evidence is not obtained. In the case of fluorescence quenching of stilbene by pyrrole, a new emission was not observed,12) but it is reasonable to consider that this fluorescence quenching by pyrrole is also due to the exciplex formation. In this exciplex an electron has been transferred to stilbene.8) The N-proton made more acidic by the exciplex formation would be transferred to the negatively charged stilbene and the combination of the resulting radicals followed by isomerization might give the products. This mechanism can explain the behavior of deuterium and efficient fluorescence quenching of stilbene by pyrrole well.



References

1) H. M. Rosenberg, R. Rondeau, and P. Servé, J. Org. Chem., 34, 471 (1969).

2) H. M. Rosenberg and M. P. Servé, J. Org. Chem., 36, 3015 (1971).

3) O. L. Chapman and W. R. Adams, J. Amer. Chem. Soc., 90, 2333 (1968).

4) T. Kubota and H. Sakurai, Chem. Commun., 362 (1972).

5) A similar reaction that pyrrylmagnesium bromide reacts with benzyl bromide to give 2-benzylpyrrole has been reported ; C. F. Hobbs, C. K. McMillin, E. P. Papadopoulos, and C. A. VanderWerf, J. Amer. Chem. Soc., 84, 43 (1962).

6) The similar behavior of pyrrole has been reported ; J. J. McCullough, C. W. Huang, and W. S. Wu, Chem. Commun., 1368 (1970).

7) The new emission did not appear in the absence of trans-stilbene. Irradiation of stilbene in N-methylpyrrole also gave 1:1 adducts,whose structures are not determined conclusively, in a low yield. This reaction rate was three times as slow.

8) A. Weller, Pure Appl. Chem., 16, 115 (1968).

9) J. M. Patterson, L. T. Burka, and M. R. Boyd, J. Org. Chem., 33, 4033 (1968).

10) J. M. Patterson and L. T. Burka, Tetrahedron Lett., 2215 (1969).

11) Chapman proposed exciplex formation in the photoreaction of trans-stilbene with tetramethylethylene : O. L. Chapman and R. D. Lura, J. Amer. Chem. Soc., 92, 6352 (1970) ; J. Saltiel, J. T. D'Agostino, O. L. Chapman, and R. D. Lura, J. Amer. Chem. Soc., 93, 2804 (1971).

12) The similar behavior that exciplexes of electron donors having N-proton are not emissive at room temperature has been reported by Mataga et. al. They explain these results in terms of the efficient, radiationless transition. The effective reaction of stilbene with pyrrole may relate to the radiationless process. N. Mataga, T. Okada, and H. Oohari, Bull. Chem. Soc. Japan, 39, 2563 (1966).

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