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THE PHOTOADDITION OF STILBENE TO 1-METHYLPYRROLE.
THE EFFECT OF PROTIC SOLVENTS
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Irradiation of an acetic acid solution of trans-stilbene and l-methylpyrrole afforded l-methyl-2-(1,2-diphenylethyl)pyrrole (I), l-methyl-3-(1,2-diphenylethyl)pyrrole (II), and l,2-diphenylethyl acetate (III), though irradiation of stilbene in neat l-methylpyrrole gave complex mixtures.

In the preceding paper, we have reported that excited singlet stilbene reacts with pyrrole to give two 1:1 adducts and the NH proton of pyrrole plays an important role in this reaction.¹⁾ In this paper, we report on the photoreaction of stilbene and 1-methylpyrrole, which was greatly accelerated by the use of an acidic solvent (acetic acid).

Irradiation of trans-stilbene in l-methylpyrrole, followed by chromatography on silica gel, gave an unknown, labile material²⁾ and meso-1,2,3,4-tetraphenylbutane $(9 \%)^{3}$ as the major products. 1:1 Adducts such as the photo-adducts of stilbene and pyrrole were not formed in an appreciable amount.

The less reactivity of 1-methylpyrrole compared with pyrrole is consistent with the failure of aliphatic tertiary amines⁴⁾ and 1-methylpyrrole⁵⁾ to form adducts efficiently on irradiation with benzene. Since the photoaddition of benzene and tertiary amines is known to be accelerated in the presence of water,⁴⁾ we repeated the reaction of 1-methylpyrrole and stilbene in the presence of water. However, irradiation of a solution of trans-stilbene (0.8 g) and 1-methylpyrrole (10 g) in acetonitrile-water (3:1 v/v, 120 ml) merely gave meso-1,2,3,4-tetraphenylbutane (18 %)³⁾ as the main product.⁶⁾

The recent, interesting report⁷⁾ by Bryce-Smith and his co-workers of acid-catalyzed photochemical reactions led us to carry out the reaction in the presence of acetic acid. A solution of trans-stilbene (1 g) and 1-methylpyrrole (8 g) in acetic acid (120 ml) was irradiated for 19 hr. Chromatography on silica gel gave adducts I (24 %), II (10 %) and III (32 %), and 1,2,3,4-tetraphenylbutane (7 %).⁸⁾ Adduct III was identified as 1,2-diphenylethyl acetate by a comparison of its IR and NMR spectra with those of an authentic sample.⁹⁾ Compounds I and II were shown to be 1:1 adducts of stilbene and 1-methylpyrrole by elemental analyses and the mass spectra (M⁺ 261). The IR spectra of I and II showed no absorptions characteristic of NH. The NMR spectrum of I showed a singlet at δ 3.16 (3H, N-Me), two doublets of doublets at 3.2 (2H, methylene protons, J=9, 13, 5.5, and 13 Hz), a doublet of doublets at 3.99 (1H, a methine proton, J=9 and 5.5 Hz), triplets at 5.91 (1H, a β -proton of pyrrole, J=2.5 Hz) and at 6.32 (1H, an α -proton of pyrrole, J=2 Hz), and multiplets at δ .9.91 and 6.08 were assigned to β -protons

of pyrrole. The NMR spectrum of II showed two doublets at δ 3.17 (2H, methylene protons, J=6.2 and 8.5 Hz), a singlet at 3.49(3H, N-Me), a doublet of doublets at 4.01 (1H, a methine proton, J=6.2 and 8.5 Hz), triplets at 5.83 (1H, a β -proton of pyrrole, J=2 Hz) and 6.33 (1H, an α -proton of pyrrole, J=2 Hz), and multiplets at 6.14(1H, an α -proton of pyrrole) and 7.1 (10H, aromatic protons). These spectra were similar to those of the adducts of pyrrole and stilbene.¹⁾ Thus, adducts I and II were characterized as 1-methyl-2-(1,2-diphenylethyl)pyrrole and 1-methyl-3-(1,2-diphenylethyl)pyrrole, respectively.

The formation of these adducts was not sensitized by triphenylene which sensitized the trans to cis isomerization of trans-stilbene. Furthermore, the fluorescence of trans-stilbene was effectively quenched by 1-methylpyrrole and this fluorescence quenching was due to the exciplex formation.¹⁾ These results suggest that the addition involves singlet-excited trans-stilbene and probably the polarized exciplex. In a polar solvent such as acetonitrile-water, this exciplex is expected to dissociate into the solvated free radical ions.¹⁰⁾ The protonation of the stilbene radical anion followed by the coupling of the resulting radicals give 1,2,3,4-tetraphenylbutane. In the more efficient proton-donating solvent such as acetic acid, the stilbene part of this exciplex might be protonated and the combination of the resulting 1,2-diphenylethyl radical and 1-methylpyrrole radical cation, followed by deprotonation, might give adducts I and II.



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