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Irradiations of 4-vinylpyridine and of 2-vinylpyridine in either *t*-butyl alcohol or benzene, with benzophenone, yielded a single photodimer, which, on the basis of the nmr and mass spectral data, was assigned the *trans*-head-to-head structure (I). Upon irradiation in either *t*-butyl alcohol or benzene, in the presence of benzophenone, 2-vinylquinoline gave a single photodimer whose structure and stereochemistry were also determined from the nmr and mass spectral evidence as (V). Irradiation of 2-vinylquinoline in benzene, in the absence of benzophenone, also gave rise to the same photodimer, but, when *t*-butyl alcohol or methanol was used as a solvent, no dimer formation was observed.

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Although the photocyclodimerizations of styrenes (1), stilbenes (2), and styrylpyridines (3), with or without a sensitizer, have received some attention, the dimerizations of their related compounds such as vinylpyridines and vinylquinoline, have not yet been reported in the literature. In connection with our studies (4) on the photochemistry of heterocyclic compounds and the evaluation of the pharmacological activities of their photoproducts, we have been interested in the photocyclodimerizations of 4-vinylpyridine, 2-vinylpyridine, and 2-vinylquinoline and the determination of the structures and stereochemistry of their products.

The irradiation of 4-vinylpyridine with a 450 W medium pressure mercury lamp through a Pyrex filter in the presence of benzophenone as a sensitizer in either *t*-butyl alcohol or benzene yielded only one and the same dimer (A), which was identified as a crystalline oxalate. In either case, in the absence of the sensitizer dimers

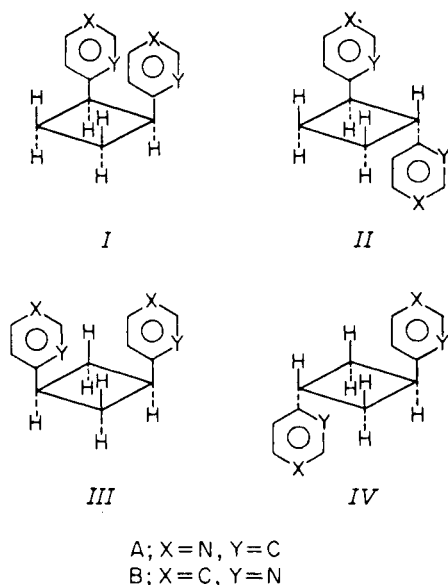
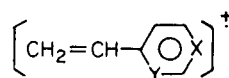
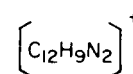


Fig. 1



m/e 105 ion *a* by
 symmetrical splitting



m/e 181 ion *b* by
 asymmetrical splitting with
 the loss of a hydrogen atom

Fig. 2

were not obtained.

On irradiation in either *t*-butyl alcohol or benzene in the presence of benzophenone under the same conditions as above, 2-vinylpyridine also yielded a single dimer (B), which was characterized as a crystalline picrate.

For the structures of these photodimers (A) and (B), the following four types of stereoisomers (I, II, III, and IV) were conceivable.

The mass spectra of the dimers (A) and (B) have proved to be of diagnostic value in distinguishing the head-to-head isomers (I) and (II) from the head-to-tail isomers (III) and (IV). It has been reported (5) that in the case of the isomers (I) and (II), two ways of ring opening pathways, that is, both symmetrical and asymmetrical ruptures of the cyclobutyl ring system, are possible upon electron-impact, whereas only the symmetrical splitting results in the case of the isomers (III) and (IV). Thus, the head-to-head isomers (I) and (II) would produce both the ions *a* (*m/e* 105) and *b* (*m/e* 181), but the head-to-tail isomers (III) and (IV) would only give rise to the ion *a* (*m/e* 105). In fact, in the mass spectra of the dimers (A) and (B), both ions *a* [X = N, Y = C in the case of (A); X = C, Y = N in the case of (B)] and *b* were observed in the abundance ratio of 4:1 and 3:1, respectively. Therefore, the dimers must have either the *cis*-head-to-head structure (I) [X = N, Y = C in the case of (A) and X = C, Y = N in the case of (B)] or the *trans*-head-to-head structure (II) [X = N, Y = C in the case of (A) and X = C, Y = N in the case of (B)]. Further differentiation between the structures (I) and (II) was made on the basis of the nmr evidence. According to the references (6) so far reported, because of the current effects of the aromatic rings, the aromatic

protons undergo an upfield shift in the *cis*-isomers (I), whereas they suffer a downfield shift in the *trans*-isomers (II). In the nmr spectrum in deuteriochloroform of the photodimer (A) from 4-vinylpyridine, the protons at C-2, 6, 2', and 6', and those at C-3, 5, 3', and 5', on the pyridine rings, absorb at δ 9.16 (4H, doublet, $J = 6$ Hz) and δ 7.66 (4H, doublet, $J = 6$ Hz), respectively. These protons are deshielded relative to those corresponding ring protons in, for example, 4-ethylpyridine [δ 8.91 (2H, m, 2,6-H) and δ 7.35 (2H, d, $J = 6$ Hz, 3,5-H)]. Thus, the dimer (A) must have the *trans*-head-to-head structure [$X = N$, $Y = C$ in (II)]. In the photodimer (B) from 2-vinylpyridine, the aromatic protons on the pyridine rings appear at δ 9.20 (2H, m, 6,6'-H) and δ 7.46-8.26 (6H, m, 3,4,5,3',4',5'-H), which are also rather shifted downfield relative to those corresponding ring protons [δ 8.90 (1H, m, 6-H) and δ 7.15-7.99 (3H, m, 3,4,5-H)] in 2-ethylpyridine. These nmr data also made it possible to assign the *trans*-head-to-head structure [$X = C$, $Y = N$ in (II)] to the dimer (B).

On irradiation in the presence of benzophenone in either *t*-butyl alcohol or benzene under the same conditions as above, 2-vinylquinoline yielded a single dimer which was characterized as a crystalline picrate. In the absence of benzophenone, the same photodimer was also obtained when benzene was used as a solvent, but no dimer formation was observed when *t*-butyl alcohol or methanol was used as a solvent. The structure and stereochemistry of the dimer was also determined by combining the mass and nmr data. The mass spectrum favors head-to-head structures rather than the head-to-tail alternatives since it gave both fragment ions at m/e 155 ($C_{11}H_9N^+$) and m/e 281 ($C_{20}H_{13}N_2^+$) (via a symmetrical and an asymmetrical rupture of the cyclobutane ring, respectively) in the abundance ratio of 6:1. In the nmr spectrum in deuteriochloroform, the aromatic protons on the quinoline rings absorb at δ 7.14-8.56 as a complex multiplet, which are shifted downfield relative to those corresponding ring protons in, for example, 2-methylquinoline [δ 7.14-8.17 (6H, complex m)]. From these nmr data, the photodimer from 2-vinylquinoline was also assigned the *trans*-head-to-head structure (V).

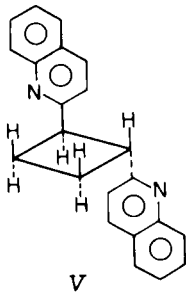


Fig. 3

Since the photodimerizations of 4-vinylpyridine and 2-vinylpyridine did not occur in the absence of benzophenone, they probably involve triplet energy transfer from benzophenone to 4-vinylpyridine and 2-vinylpyridine. The dimers (A) and (B) may be formed by the reaction of the lowest triplet states of 4-vinylpyridine and 2-vinylpyridine thus produced with their respective ground state molecules. It is interesting to note that the photodimerization of 2-vinylquinoline in benzene gave rise to the same dimer under either direct or sensitized irradiation. Under direct excitation, 2-vinylquinoline singlets may cross over to its lowest excited triplet state. The 2-vinylquinoline triplet thus produced reacts in the same manner as that produced by triplet energy transfer from benzophenone, and the dimer may be formed by the reaction of the triplet and ground states of 2-vinylquinoline. In a polar solvent such as *t*-butyl alcohol or methanol, no photodimer was formed in the absence of benzophenone, and this is probably because excited polar 2-vinylquinoline singlets may be deactivated in this solvent medium by self-quenching by the interaction with its ground state molecule.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Nmr spectra were obtained on a Varian A-60 instrument and chemical shifts are reported in parts per million downfield from internal TMS (δ scale). Abbreviations s = singlet, d = doublet, and m = multiplet. Mass spectra were recorded on a Du Pont 21-492B spectrometer at 70 eV using a direct inlet system. 4-Vinylpyridine and 2-vinylpyridine were purchased from Aldrich Chemical Company and 2-vinylquinoline from Eastman Kodak Company. All irradiations were carried out in a vessel into which a quartz immersion well containing a Pyrex filter sleeve and a Hanovia 450W medium pressure mercury lamp was fitted. The double-walled immersion well containing the light source was cooled at 15° and the solution was irradiated while nitrogen was bubbled through the solution before and during the irradiation. Microanalyses were made by A. Bernhardt Microanalytical Laboratory, 5521, Elbach über Engelskirchen, West Germany.

Irradiation of 4-Vinylpyridine with Benzophenone.

1) In *t*-Butyl Alcohol.

Freshly distilled 4-vinylpyridine (2 ml.) in anhydrous *t*-butyl alcohol (200 ml.) was irradiated with benzophenone (2 g.). The formation of the product was monitored by the thin layer chromatography, and only a single dimer was formed. After 17 hours, the solvent was evaporated in vacuo and the residue was chromatographed over Merck standardized alumina, activity II-III. Elution with benzene-chloroform (the amount of chloroform in benzene up to 30%) yielded a dimer (0.10 g.) as an oil; nmr (deuteriochloroform): 2.50 (4H, m, CH_2-CH_2), 3.86 (2H, m, $CH-CH$), 7.66 (4H, d, 3,5-H and 3',5'-H on the pyridine rings), and 9.16 (4H, d, 2,6-H and 2',6'-H on the pyridine rings); mass spectrum, m/e (relative intensity): 210 (M^+) (60), 181 (b) (25), 105 (a) (100), 78 ($C_5H_4N^+$) (32), and 51 ($C_4H_3^+$) (37). It formed a crystalline oxalate, m.p. 187-189° (from methanol-ether).

Anal. Calcd. for $C_{14}H_{14}N_2 \cdot 2C_2H_2O_4$: C, 55.38; H, 4.65; O, 32.79; N, 7.18. Found: C, 55.64; H, 4.63; O, 31.89; N, 7.10.

2) In Benzene.

Freshly distilled 4-vinylpyridine (2 ml.) in dry benzene (200 ml.) was irradiated in the presence of benzophenone (2 g.) for 17 hours. The thin layer chromatography indicated the formation of a dimer. Work-up of the product in the same manner as described above yielded a dimer (0.08 g.), which was shown to be identical with the dimer obtained in (1).

Irradiation of 4-Vinylpyridine without Benzophenone.

In *t*-Butyl Alcohol and in Benzene.

Freshly distilled 4-vinylpyridine (2 ml.) was irradiated in the absence of benzophenone under the same conditions as above. However, no dimer formation was observed on the thin layer chromatogram.

Irradiation of 2-Vinylpyridine with Benzophenone.

1) In *t*-Butyl Alcohol.

Freshly distilled 2-vinylpyridine (2 ml.) in anhydrous *t*-butyl alcohol (200 ml.) was irradiated in the presence of benzophenone (2 g.) for 17 hours. The thin layer chromatography indicated the formation of a single dimer. After removal of the solvent, the product was chromatographed over Merck standardized alumina, activity II-III. Elution with benzene-chloroform (the amount of chloroform in benzene up to 50%) yielded a dimer as an oil (0.45 g.). It formed a crystalline picrate, m.p. 208-210° (from acetone-ether).

Anal. Calcd. for $C_{14}H_{14}N_2 \cdot 2C_6H_3O_7N_3$: C, 46.71; H, 16.77; O, 33.53; N, 2.99. Found: C, 46.84; H, 16.53; O, 33.85; N, 2.91.

The liberation of the dimer from its picrate was effected as follows. The above picrate was dissolved in a small amount of acetone and passed through a column containing Merck standardized alumina, activity II-III, in benzene. Elution with benzene-chloroform yielded a dimer; nmr (deuteriochloroform): 2.56 (4H, m, CH_2-CH_2), 4.26 (2H, m, $CH-CH$), 7.46-8.26 (6H, m, 3,3'-H, 4,4'-H, and 5,5'-H on the pyridine rings), and 9.20 (2H, m, 6,6'-H on the pyridine rings); mass spectrum, m/e (relative intensity): 210 (M^+) (83), 181 (*b*) (30), 105 (*a*) (100), 78 ($C_5H_4N^+$) (67), and 51 ($C_4H_3^+$) (64).

2) In Benzene.

Freshly distilled 2-vinylpyridine (2 ml.) in dry benzene (200 ml.) was irradiated in the presence of benzophenone (2 g.) for 17 hours. The formation of a dimer was observed on the thin layer chromatogram. After work-up of the product in the same manner as above, a dimer (0.48 g.) was obtained as an oil. It gave a picrate which was shown to be identical with the picrate obtained in (1).

Irradiation of 2-Vinylpyridine without Benzophenone.

In *t*-Butyl Alcohol and in Benzene.

Freshly distilled 2-vinylpyridine (2 ml.) was irradiated in the absence of benzophenone under the same conditions as above. No dimer was formed as checked by the thin layer chromatography.

1) In *t*-Butyl Alcohol.

Freshly distilled 2-vinylquinoline (0.5 g.) was irradiated in anhydrous *t*-butyl alcohol (70 ml.) with benzophenone (0.29 g.) for 17 hours. The thin layer chromatography indicated that only a single dimer was formed. The solvent was removed in vacuo and the residue was chromatographed over Merck standardized alumina, activity II-III. Elution with benzene yielded an oily fraction (54% yield) which, on the basis of the nmr and mass spectra, corresponded to a dimer. This fraction gave a crystalline

picrate, m.p. 246-248° (from acetone-ether).

Anal. Calcd. for $C_{22}H_{18}N_2 \cdot 2C_6H_3N_3O_7$: C, 53.13; H, 3.15; N, 14.58. Found: C, 53.31; H, 3.29; N, 14.43.

The above picrate was dissolved in a small amount of acetone, treated with 1% aqueous sodium hydroxide, and the liberated base was extracted with ether. After evaporation of the ether, the residue was dissolved in benzene and filtered on Merck standardized alumina, activity II-III. Elution with benzene yielded a pure dimer. All the spectroscopic data were taken on this sample; nmr (deuteriochloroform): 2.50 (4H, m, CH_2-CH_2), 4.40 (2H, m, $CH-CH$), and 7.14-8.56 (12H, m, aromatic protons); mass spectrum, m/e (relative intensity): 310 (M^+) (42), 281 ($C_{20}H_{13}N_2^+$) (16), 155 ($C_{11}H_9N^+$) (100), and 128 ($C_{10}H_8^+$) (15).

2) In Benzene.

Freshly distilled 2-vinylquinoline (0.65 g.) was irradiated in dry benzene (40 ml.) with benzophenone (0.76 g.) for 26 hours. The presence of a dimer was detected on the thin layer chromatogram. Work-up of the product in the same manner as above yielded a dimer (55% yield) as an oil. It gave a picrate which was shown to be identical with the picrate obtained in (1).

Irradiation of 2-Vinylquinoline without Benzophenone.

1) In Benzene.

Freshly distilled 2-vinylquinoline (0.27 g.) in dry benzene (80 ml.) was irradiated in the absence of benzophenone for 28 hours. The formation of a dimer was confirmed by the thin layer chromatography. After work-up of the product in the same manner as above, a dimer (55% yield) was obtained as an oil. It formed a picrate which was shown to be identical with the picrate obtained earlier.

2) In *t*-Butyl Alcohol and in Methanol.

The irradiations were carried out under the same conditions as above, but no dimer formation was observed on the thin layer chromatogram.

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- (5) S. Caccamese, G. Montaudo, and M. Przybylski, *Org. Mass Spectrom.*, **9**, 1114 (1974).
- (6) In the case of the *cis*-head-to-head isomers, diamagnetic

circulations of the ring currents, which are induced by their sandwich-like folded aromatic rings, cause shielding at the aromatic protons. In the case of the *trans*-head-to-head isomer, however, their aromatic protons experience deshielding because of the paramagnetic currents resulting from the antiparalleled orientation of the aromatic rings. For example, in the *cis*-head-to-head isomers from the dimerization of *p*-(*N,N*-dimethylamino)styrene, the aromatic protons of the benzene rings absorb at higher field

of δ 6.42-7.02 (8H, q), whereas in the *trans*-head-to-head isomer, they resonate at δ 6.68-7.25 (8H, q), which are shifted downfield relative to those corresponding aromatic protons [δ 6.50-7.10 (8H, q)] in *N,N*-dimethyl-*p*-toluidine [T. Asanuma, M. Yamamoto, and Y. Nishijima, *J. Chem. Soc., Chem. Commun.*, 56 (1975)]. For other similar references, see M. Yamamoto, T. Asanuma, and Y. Nishijima, *ibid.*, 53 (1975), and H. Nozaki, I. Otani, R. Noyori, and M. Kawanishi, *Tetrahedron*, **24**, 2183 (1968).