cyanogen in 35 ml of ethyl acetate was prepared in the usual manner in the dark at 0°. To this cold solution was added 7.2 mmol of I in 20 ml of ethyl acetate over at 15-min period. At this point tlc indicated that no thiol remained. The appropriate thioether (7.2 mmol) was dissolved in 25 ml of ethyl acetate and added in one portion to the reaction mixture. The solution was stirred in the dark for 2 hr at 0°, allowed to warm to room temperature, and stirred for an additional period of time (3-33 hr depending on the reaction progress as demonstrated by tlc). After reaction was complete the solution was diluted to 200 ml with ethyl acetate and washed with 5% sodium bicarbonate solution, water, and saturated brine. The organic extract was dried and evaporated *in vacuo*, and the residue was triturated with hexane to remove the trityl thiocyanate. The resulting powder was purified by recrystallization or chromatography followed by recrystallization. The reported yields (Table I) are based on the amount of purified product.

B. Acidic Solvents.—To a cold, stirred solution containing 9 mmol of thiocyanogen in 35 ml of ethyl acetate was added 7.2 mmol of I in 20 ml of trifluoroacetic acid (TFA). After 10 min, 7.2 mmol of the appropriate thio ether in 15 ml of TFA was added and the mixture was stirred at 0° for 3 hr and at room temperature for 5-12 hr. The reaction mixture was poured into 1200 ml of cold 5% sodium bicarbonate and the mixture was extracted with ethyl acetate. The organic layer was washed, dried, and evaporated *in vacuo*. Trituration with hexane afforded a powder which was purified by recrystallization.

Registry No.—IIIb, 23465-05-6; IIIc, 23465-06-7; IIId, 23465-07-8; IIIe, 23465-08-9; IIIf, 23465-09-0; IIIg, 23435-44-1; IIIh, 23435-45-2; IIIi, 23435-46-3; IIIj, 23435-47-4; IIIk, 23465-10-3; IVa, 23465-11-4; IVb, 23435-52-1; IVc, 23435-53-2; IVd, 23435-54-3; IVe, 23435-55-4; IVf, 23465-12-5; IVg, 23500-37-0; IVh, 23435-56-5; IVi, 23500-38-1; IVj, 23435-57-6; IVk, 23435-58-7; VI, 23435-48-5; VII, 23435-49-6; VII (HCl), 23435-50-9; IX, 23435-51-0.

Acknowledgment.—The authors are grateful to Mrs. Mary W. Pendergraft for the polarimetry measurements. Valuable discussions with Mr. E. B. Williams, Jr., concerning the effect of histidine residues on the thiocyanogen reaction are gratefully acknowledged.

The Photodimerization of Substituted Stilbenes

HENRI ULRICH, DURVASULA V. RAO, F. A. STUBER, AND A. A. R. SAYIGH

The Upjohn Company, Donald S. Gilmore Research Laboratories, North Haven, Connecticut 06473

Received June 6, 1969

Stilbenes with electron-donating groups on either of the aromatic moieties undergo rapid photodimerization. With dissimilar phenyl groups, two photodimers are obtained, and their structures have been elucidated by nmr and mass spectral studies. The extent of dimerization was measured by gel-permeation chromatography and a singlet mechanism is proposed for the photodimerization process.

The photochemistry of stilbene is well known and the three photochemical reactions are *cis–trans* isomerization, cyclization, and dimerization. Although the dimerization of stilbene has been discovered at the beginning of this century by Ciamician and Silber,[1] it is the least understood of the three reactions. Shechter and coworkers[2] have isolated two photodimers from *trans*-stilbene (27% conversion upon irradiation for 2 months) and their structures were assigned on the basis of nmr data. In our study directed toward the use of stilbene derivatives for photocross-linking of polymers,[3] we noticed considerable enhancement of dimerization if electron-donating groups are attached to the aryl groups.[4] The quantum yield of dimerization of **5** was found to be *ca.* 0.06. In Table I the previously unreported stilbene derivatives used in this study are listed. The photodimerization was conducted on the mono- and bismethyl carbamates of the mono- and diisocyanates in order to approximate the bonding generated in polymer systems. As ultraviolet sources a 100- and a 450-W mercury lamp have been used and benzene, ethyl acetate, and tetrahydrofuran were the solvents employed in the photodimerization experiments. The quantitative determination of dimerization was achieved using gel permeation chromatography (gpc) and the monomer was used for calibration. The dimer yields were verified by column chromatography, which also allowed separation of the isomeric photodimers.

The gpc method is accurate, nondestructive (room temperature assay), and convenient, *i.e.*, the reaction mixture can be directly injected into the chromatograph. For example, the rate of photodimerization can be followed, and a first-order rate law is observed in the photodimerization of **5** (10% concentration) up to *ca.* 70% conversion. The results of the photodimerization experiments are listed in Table II.

The results obtained in the photodimerization experiments (irradiation for 4 hr in ethyl acetate) show that electronic effects as well as steric effects are operative. For example, electron-donating groups, such as OCH_3, $NHCOCH_3$, and $NHCOOCH_3$, enhance dimerization (compare *trans*-stilbene with **14**, **2**, **3**, and **5**). The steric effects are also quite pronounced, as shown by the comparison of **15** (4,4′ substituted) with **9** (2,4′ substituted) and **12** (2,2′ substituted). Comparable yields were obtained using benzene, ethyl acetate, and tetrahydrofuran. However, highly polar solvents, such as N,N-dimethylformamide, lower the extent of dimerization. For example, irradiation of **5** in DMF for 4 hr, using a 450-W source, gave 68% photodimerization, while in tetrahydrofuran, under similar conditions, 91.3% dimerization was obtained. The extent of dimerization was not affected when the reaction was conducted in a nitrogen atmosphere.

No *cis*-stilbene or phenanthrene could be isolated, suggesting that, at the concentrations studied, only photodimerization is the major pathway. The extent of dimerization decreases with dilution (see compound **5** in Table II), meaning that at higher dilution isomeri-

---

[1] G. Ciamician and P. Silber, *Chem. Ber.*, **35**, 3128 (1902).

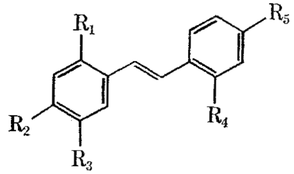
[2] H. Shechter, W. J. Link, and G. V. D. Tiers, *J. Amer. Chem. Soc.*, **85**, 1601 (1963).

[3] F. A. Stuber, H. Ulrich, D. V. Rao, and A. A. R. Sayigh, *J. Appl. Polym. Sci.*, **13**, 2247 (1969).

[4] This phenomenon appears to be general because we observed a similar effect in the photodimerization of coumarins and cinnamates: D. V. Rao, F. A. Stuber, H. Ulrich, and A. A. R. Sayigh, in press.

TABLE I

STILBENE DERIVATIVES[a]



Compd	R_1	R_2	R_3	R_4	R_5	Yield, %	Mp, °C	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
1[b]	CH_3O	H	H	H	NH_2	72	68–70	$C_{15}H_{15}NO$	79.97	6.71	6.22	79.89	6.67	6.28
2[c]	CH_3O	H	H	H	$NHCOOCH_3$	93	131–132	$C_{17}H_{17}NO_3$	72.06	6.05	4.94	72.22	6.17	5.02
3[d]	H	CH_3O	H	H	$NHCOOCH_3$	93	190–191	$C_{17}H_{17}NO_3$	72.06	6.05	4.94	71.90	6.14	4.83
4[e]	CH_3O	H	CH_3O	H	NH_2	99	91–92	$C_{16}H_{17}NO_2$	75.27	6.71	5.49	75.28	6.64	5.52
5	CH_3O	H	CH_3O	H	$NHCOOCH_3$	99	130–132	$C_{18}H_{19}NO_4$	68.99	6.11	4.47	68.96	6.33	4.57
6	H	H	H	NH_2	NH_2	86	105–107	$C_{14}H_{14}N_2$	79.96	6.71	13.32	79.78	6.76	13.28
7[f]	H	H	H	$NHCOOCH_3$	$NHCOOCH_3$	72	180–181	$C_{18}H_{18}N_2O_4$	66.24	5.56	8.58	66.32	5.77	8.73
8	H	CH_3O	H	NH_2	NH_2	100	153–155	$C_{15}H_{16}N_2O$			11.66			11.69
9[g]	H	CH_3O	H	$NHCOOCH_3$	$NHCOOCH_3$	57	207–208	$C_{19}H_{20}N_2O_5$	64.03	5.66	7.86	64.20	5.69	7.96
10	CH_3O	H	CH_3O	NO_2	NO_2	48	175–177	$C_{16}H_{14}N_2O_6$	58.18	4.27	8.48	58.31	4.16	8.33
11[h]	CH_3O	H	CH_3O	$NHCOCH_3$	$NHCOCH_3$		256–258	$C_{20}H_{22}N_2O_4$	67.78	6.25	7.91	67.72	6.45	7.82
12[g]	CH_3O	H	CH_3O	$NHCOOCH_3$	$NHCOOCH_3$	90	193–194.5	$C_{20}H_{22}N_2O_6$	62.16	5.74	7.25	62.16	5.72	7.30

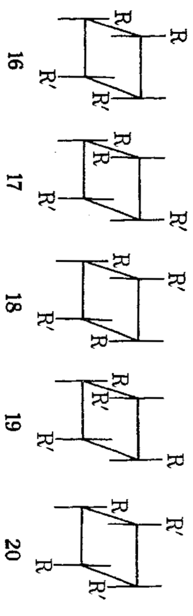
[a] The acetyl derivatives were obtained from the corresponding amines and acetic anhydride and the methyl carbamates were prepared by refluxing the corresponding isocyanates in excess MeOH. [b] Acetyl derivative, mp 135–137°. [c] The isocyanate was obtained as a liquid according to the general method. [d] Isocyanate, mp 163–166°. [e] Acetyl derivative, mp 172–173°. [f] Diisocyanate, mp 95–98°. [g] The diisocyanate was obtained as a liquid according to the general method. [h] The diamine was obtained as a light brown liquid according to the general method.

zation and cyclization compete with photodimerization. In the present investigation we have not examined this aspect of photochemistry.

The isolated stilbene photodimers are listed in Table III, and all compounds show the absence of the infrared band at 952–971 cm^{-1} which corresponds to the out-of-plane deformation of the olefinic CH bond in stilbenes. The mass spectra of the photodimers obtained from **5** show a molecular ion at *m/e* 626, which is in agreement with the dimer structure. Separation of both dimers derived from compounds **2**, **3**, and **5** could be accomplished by column chromatography. The high-melting photodimers (type B) gave a broad signal in their nmr spectra for the cyclobutane protons at δ 4.30–4.45 ppm. In contrast, the low-melting photodimers (type A), derived from **2** and **5**, show two symmetric multiplets centered at δ 4.30 and 4.33 ppm and 4.60 and 4.70 ppm, respectively. In the case of **3** both types of dimers gave a broad signal for the cyclobutane protons at δ 4.32.

The symmetric signals obtained for the four-ring protons correspond to an AA′BB′-type spectrum. Among the eleven possible isomers, six contain a symmetry element, but two isomers with all the substituents on the same side of the cyclobutane ring are unlikely for steric reasons; the remaining configurations are depicted in Chart I. Earlier studies by Shechter[2]

CHART I



16 17 18 19 20

on unsubstituted stilbenes showed that the two dimers formed had the structures indicated in Chart I. The dissimilar substituents attached to the aryl moieties in our investigation complicate the structural assignment because of the possibility of formation of head-to-head and head-to-tail dimers. The formation of a dimer with structure **20** seems quite improbable, since isomerization of the *trans* to the *cis* monomer would have to occur during the reaction.

In order to determine the fine structure of the multiplets in case of the photodimers of **5**, 100-MHz nmr spectra were recorded. Theoretical spectra were calculated for each of the five configurations using coupling constants derived from similar substituted cyclobutanes described in the literature, *e.g.*, $^3J_{cis}$ = 10 Hz, $^3J_{trans}$ = 6.5 Hz, $^4J_{cis}$ = 0.6 Hz, $^4J_{trans}$ = −1.5 Hz, and $\nu_A\nu_B$ = 31 Hz.[5,6] Comparison of the observed spectrum and the calculated transitions indicates that **16** (Chart I and Figure 1) is the most probable structure for the low-melting dimer. However, the lack of fine structure in the case of the high-melting dimer prevents differentiation between structures **17** and **19**.

The fragmentation pattern in the mass spectrum should allow further differentiation, because in the case of **16** and **17** three stilbene ion fragments, [RCH=CHR]·+, [RCH=CHR′]·+, and [R′CH=CHR′]·+,

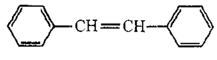
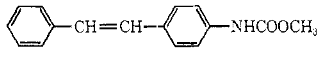
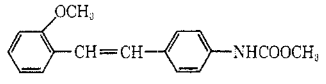
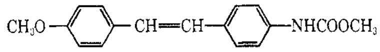
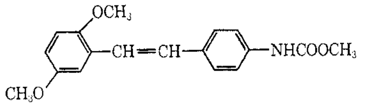
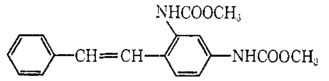
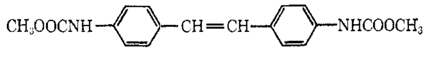
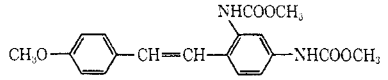
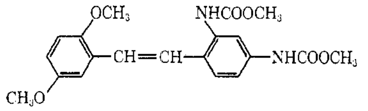
---

(5) C. H. Krauch, S. Farid, and G. O. Schenck, *Chem. Ber.*, **99**, 625 (1966).

(6) R. Steinmetz, W. Hartman, and G. O. Schenck, *ibid.*, **98**, 3854 (1965).

TABLE II

PHOTODIMERIZATION OF STILBENE METHYL CARBAMATES[a]

Structure of monomer	Compd	Concn, %	Extent of dimerization, %[b]
		10	11
	**14**	10	27
	**2**	10	51
	**3**	10	66
	**5**	10 3 1	74[c,d] 42 25
	**7**	10 3[e]	10 6
	**15**	3[e]	45
	**9**	10 3[d]	35 22
	**12**	10	22

[a] The experiments were conducted using ethyl acetate as the solvent, a 100-W mercury lamp as the light source, and an exposure time of 4 hr. [b] Determined by gel-permeation chromatography. Two photodimers were generally obtained, except with **9** and **15** which yielded only one photodimer. [c] The same yield was obtained in benzene. [d] The extent of dimerization of the N-acetyl derivative of the amine precursor of **5** was found to be 75%, using 10% concentration. [e] Tetrahydrofuran was used as solvent.

TABLE III

STILBENE PHOTODIMERS

Starting stilbene	Dimer	Mp, °C	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found % C	Found % H	Found % N
2	A	102–105	$C_{34}H_{34}N_2O_6$	72.06	6.05	4.94	71.64	5.87	5.09
	B	219–221					72.16	6.07	4.75
3	A	116–118	$C_{34}H_{34}N_2O_6$	72.06	6.05	4.94	71.92	6.13	4.95
	B	220–222					71.90	6.04	4.83
5	A	103–105	$C_{36}H_{38}N_2O_8$	68.99	6.11	4.47	68.97	6.17	4.69
	B	223–224					68.72	6.21	4.49
15		194–195	$C_{36}H_{36}N_4O_8$	66.24	5.56	8.58	66.28	5.62	8.44
9		142–145	$C_{38}H_{40}N_4O_{10}$	64.03	5.66	7.86	63.79	5.28	7.50

are expected, whereas **18** and **19** could only produce [RCH=CHR′]·$^+$; the intensity of the fragment ions cannot be predicted *a priori*.

In the mass spectrum of the type A dimer of **5**, the main fragmentation sequence is formation of the monomer ion at *m/e* 313 followed by the loss of methanol leading to the base peak at *m/e* 281. Although the abundance of the ion at *m/e* 300 corresponding to a [R′CH=CHR′]·$^+$ [R′ = 2,5-$(CH_3O)_2C_6H_4$] fragment ion is only 3.3%, there is strong evidence from the nmr study that this dimer has structure **16**. Another peak of low intensity (0.5%) at *m/e* 262 corresponding to a fragment derived from [RCH=CHR]·$^+$(R = 4-$CH_3OOCNHC_6H_4$) by the loss of two CH_3OH supports the proposed structure.

The pattern of fragmentation in the case of the type B dimer is very similar to that of the A dimer, since the favored process leads to the formation of the monomer ion at *m/e* 313. However, the peak at *m/e* 300 is of very low intensity and represents mainly the +2 isotope peak of *m/e* 298; the peak at *m/e* 298 corresponding to the loss of CH_3 from the *m/e* 313 ion. The absence of a fragment ion at *m/e* 300 suggests that all-*trans* dimer has structure **19**, because ring fragmentation gives only rise to the formation of [RCH=CHR′]·$^+$ fragments.

In order to understand the nature of the excited state from which dimerization occurs, several experiments were conducted. Irradiation of a benzene solution of **5** (0.016 *M*) with light of 366 nm in the presence of Michler's ketone (97% of incident light being absorbed by the ketone) produced no appreciable dimerization. In contrast, 67% dimerization occurred upon direct irradiation of **5** under similar conditions. This experiment suggests that either the triplet energy of **5** is greater than that of Michler's ketone (E_t = 61 kcal/mol[7]) and hence not favorable for energy transfer or that the dimerization occurs from an excited singlet

---

(7) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1967, p 131.

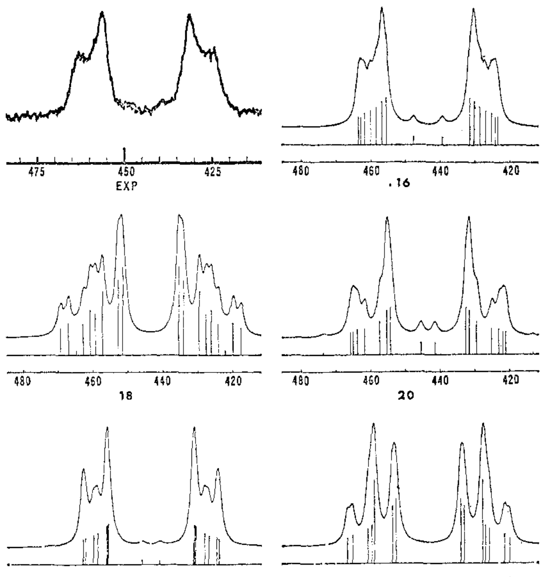


Figure 1.—Observed and calculated 100-MHz spectral bands for the protons in the four-membered ring of the low-melting dimer of **5**.

state. The triplet energies of *trans*- and *cis*-stilbene are reported to be 50 and 57 kcal/mol, respectively.[8] Attempts to observe the phosphorescence emission of **5** at 77°K in EPA failed. However, **5** exhibits fluorescence with an emission maximum at 410 nm, and the 0–0 band was located at 378 nm, corresponding to a singlet energy of $E_s = 75.6$ kcal/mol. The extent of dimerization was not affected by the presence of air. In contrast to **5**, 2,5-dimethoxy-4′-nitro-*trans*-stilbene does not undergo photodimerization and exhibits only weak fluorescence (emission maximum at 510 nm, 0–0 band at 445 nm). This can be explained by the effect of the NO_2 group, which is known to enhance intersystem crossing.[9] In EPA at 77°K 2,5-dimethoxy-4′-nitro-*trans*-stilbene exhibits phosphorescence with a maximum at 495 nm and the blue edge at 440 nm.

The above data seem to preclude the involvement of an excited triplet state in the photodimerization of substituted stilbenes and therefore strongly suggest the intermediacy of an excited singlet state.

Experimental Section

Melting and boiling points are uncorrected. Analyses were by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and Galbraith Laboratories, Knoxville, Tenn. Ir spectra were determined using a Beckman IR-8 spectrophotometer. Uv spectra were recorded on a Cary-14 spectrophotometer. Fluorescence emission spectra were obtained on an Aminco-Bowman spectrofluorometer. Nmr spectra were obtained from samples in deuteriochloroform or deuterated dimethyl sulfoxide solutions with a Varian A-60 instrument using tetramethylsilane as the internal standard. Mass spectra were determined using a MS 12 mass spectrograph. Glpc chromatography was conducted using a Waters instrument and authentic monomers and dimers were used for calibration. Column chromatographic separations were conducted over silica gel (100–200 mesh supplied by Bio-Rad Laboratories, Richmond, Calif.).

Reagents and General Procedures.—Benzene and ethyl acetate were spectral grade solvents and were used without further purification. Tetrahydrofuran was purified by refluxing over $LiAlH_4$ followed by distillation. The following stilbene derivatives were prepared according to the literature: *trans*-4-isocyanatostilbene,[10] *trans*-2-methoxy-4′-nitrostilbene,[11] *trans*-4-methoxy-4′-aminostilbene,[11] *trans*-4-methoxy-2′,4′-dinitrostilbene,[12] *trans*-2,4-dinitrostilbene,[13] *trans*-4,4′-diisocyanatostilbene,[10] and *trans*-2,5-dimethoxy-4′-nitrostilbene.[14] The N-acetyl derivatives of the corresponding amines were obtained by treating the corresponding amines with acetic anhydride at room temperature. The methyl carbamates were obtained by refluxing the corresponding isocyanates with excess methanol.

***trans*-2,5-Dimethoxy-2′,4′-dinitrostilbene (10). General Procedure.**—The preparation of **10** exemplifies the procedure followed in the synthesis of the reported nitrostilbene derivatives. A mixture of 2,5-dimethoxybenzaldehyde (28.19 g, 0.168 mol) and 2,4-dinitrotoluene (27.0 g, 0.148 mol) in 200 ml of chlorobenzene containing 30 drops of piperidine was heated for 3 hr with azeotropic removal of water. Evaporation of the solvent under vacuum and addition of 200 ml of ethanol gave 17 g (35%) of **10**: mp 175–177° after recrystallization from ethyl acetate; ir ($CHCl_3$) 1342 (NO_2) and 966 cm^{-1} (olefinic CH).

***trans*-2,5-Dimethoxy-4′-aminostilbene (4). General Procedure.**—The preparation of **4** exemplifies the procedure followed in the reduction of the nitrostilbenes. To 6.0 g (0.023 mol) of *trans*-2,5-dimethoxy-4′-nitrostilbene[13] suspended in 250 ml of methanol 1.0 g of Raney nickel was added and the reaction mixture was hydrogenated using a Parr hydrogenator at 50 psi. After the uptake of the theoretical amount of hydrogen (5.5 lb), the reaction was stopped and filtration and evaporation yielded 5.3 g (99%) of **4**: mp 91–92° after recrystallization from 2-propanol; ir ($CHCl_3$) 3509, 3390 (NH_2), 1618 (C=C), and 966 cm^{-1} (olefinic CH); uv max (methanol) 345 nm (ϵ 2.10 × 10^4) and 220 (1.85 × 10^4); fluorescence emission λ_{max} (methanol) 415 nm; nmr ($CDCl_3$) δ 3.47 (s, 2, NH_2), 3.78 and 3.80 (2 s, 6, OCH_3), 7.0 and 7.28 (2 d, 2, $J = 16$ Hz, CH=CH), and 6.62–7.35 (m, 7).

***trans*-2,5-Dimethoxy-4′-isocyanatostilbene. General Procedure.**—The preparation of *trans*-2,5-dimethoxy-4′-isocyanatostilbene demonstrates the method of phosgenation used in the preparation of the isocyanatostilbenes. In a four-necked flask, provided with a stirrer, thermometer, dewar condenser with Dry Ice, and an inlet tube was placed 200 ml of dry chlorobenzene. At 0–2°, 1800 ml (0.08 mol) of phosgene was added followed by the dropwise addition of **4** (10.0 g, 0.039 mol) in 75 ml of chlorobenzene, while the temperature was maintained at 1–4°. After the addition, the dewar condenser was removed, an Allihn condenser was attached and the solution was heated at 90–95° for 1.5 hr while a gentle stream of phosgene was added. After excess phosgene had been removed with N_2 (2 hr), the solvent was removed under vacuum on a hot-water bath and the yellow residue crystallized after addition of 200 ml of ligroin. Thus 10.1 g (91%) of *trans*-2,5-dimethoxy-4′-isocyanatostilbene, mp 69.5–70.5° after recrystallization from benzene–ligroin (1:9, v/v), was obtained: ir (CCl_4) 2247 (NCO) and 966 cm^{-1} (olefinic CH); uv max (*n*-hexane) 342 nm (ϵ 1.72 × 10^4), 296 (2.35 × 10^4), 231 (1.37 × 10^4), and 219 (1.69 × 10^4); fluorescence emission λ_{max} (*n*-hexane) 402 and 383 nm; nmr (CCl_4) δ 3.72 and 3.75 (2 s, 6, OCH_3) and 6.9 and 7.30 (2 d, 2, $J = 16$ Hz, CH=CH).

Methyl Carbamate (5).—An amount of 8.0 g of *trans*-2,5-dimethoxy-4′-isocyanatostilbene, dissolved in 100 ml of methanol, was refluxed for 3 hr. After cooling, 8.8 g (99%) of **5**, mp 130–132°, was obtained: ir ($CHCl_3$) 3425 (NH), 1724 (C=O), and 969 cm^{-1} (olefinic CH); uv max (methanol) 343 nm (ϵ 2.44 × 10^4), 301 (2.37 × 10^4), 233 (1.00 × 10^4), and 217 (0.90 × 10^4); fluorescence emission λ_{max} (CH_3OH) 410 nm; nmr (DMSO-d_6) δ 3.72, 3.78, and 3.81 (3 s, 9, OCH_3-2, OCH_3-5, $COOCH_3$), 7.24 and 7.30 (2 d, 2, $J = 17$ Hz, CH=CH), and 9.70 (s, 1, NH).

Irradiation of the Methyl Carbamate (5) Derived from *trans*-2,5-Dimethoxy-4′-isocyanatostilbene. A. Benzene.—A solution of 2.0 g of **5** in 20 ml of benzene was irradiated in a 250-ml quartz flask provided with a water-cooled condenser using a 100-W Hanovia utility model mercury lamp (Type SH, 616A) for a period of 21 hr. The flask was placed at a distance of 8–10 cm

---

[8] L. M. Stephenson and G. S. Hammonn, *Angew. Chem.*, **81**, 279 (1969).

[9] M. Kasha, *Discuss. Faraday Soc.*, **9**, 14 (1950).

[10] V. H. Bertsch, E. Ulsperger, and M. Bock, *J. Prakt. Chem.*, **11**, 225 (1960).

[11] P. Pfeiffer, *Chem. Ber.* **48**, 1793 (1915).

[12] P. Pfeiffer, *Ann. Chem.*, **411**, 132 (1916).

[13] J. Thiele and R. Escales, *Chem. Ber.*, **34**, 2843 (1901).

[14] H. Ulrich and A. A. R. Sayigh, *J. Org. Chem.*, **31**, 4148 (1966).

from the uv source. The precipitated solid material was filtered, washed with excess benzene, and dried to yield 0.5 g (25%) of photodimer B: mp 220–223° (recrystallization from acetone or ethyl acetate rasised the melting point to 223–224°); ir ($CHCl_3$) 3378 (NH) and 1701 cm^{-1} (C=O); nmr (DMSO-d_6) 3.55 and 3.64 (2 s, 18, OCH_3, $NHCOOCH_3$), 4.45 (m, 4, cyclobutane H), 6.64–7.28 (m, 14), and 9.40 (s, 2, $NHCOOCH_3$); mass spectrum (70 eV) *m/e* (rel intensity) 626 (*ca.* 0.01), 313 (27), 300 (0.15) 281 (100), and 238 (15.4).

The concentrated filtrate was chromatographed over silica gel and eluted with benzene, yielding 0.4 g (20%) of the starting material as evidenced by mixture melting point and ir comparison. Elution with benzene–ether (9:1 and 8:2, v/v) gave a light brown liquid material which upon trituration with ether–*n*-hexane yielded 0.7 g (35%) of photodimer A: mp 103–105° after recrystallization from chloroform–*n*-hexane; ir ($CHCl_3$) 3425 (NH) and 1724 cm^{-1} (C=O); nmr (DMSO-d_6) δ 3.52, 3.57, and 3.63 (3 s, 18, OCH_3, $NHCOOCH_3$), 4.33 and 4.65 (2 m, 4, cyclobutane H), 6.65–7.28 (m, 14), and 9.40 (s, 2, $NHCOOCH_3$); mass spectrum (70 eV) *m/e* (rel intensity) 626 (*ca.* 0.01), 313 (44), 300 (3.3), 281 (100), 262 (0.5), and 238 (15.5).

A quantitative determination of dimerization (by gpc) gave a value of 73.3% when a 10% solution of **5** was irradiated for 4 hr.

B. Ethyl Acetate.—Irradiation of a 10% solution of **5** in ethyl acetate for 4 hr yielded 74% photodimers as determined by gel-permeation chromatography.

C. Tetrahydrofuran.—A solution of 0.5 g of **5** in 5 ml of tetrahydrofuran was placed in a quartz test tube which was taped to the quartz probe (19434, supplied by Hanovia Lamp Division) containing a water-cooled immersion-type 450-W Hanovia mercury lamp (Type L, 679A). The entire system was controlled at 15–17° and the uv light was filtered through a Pyrex 7740 filter sleeve. After irradiation for 4 hr the photodimer content was determined by gpc to be 91.3%. Repeating the experiment under nitrogen gave a photodimer yield of 91.8%.

Irradiation of the Methyl Carbamate (2) Derived from *trans*-2-Methoxy-4′-isocyanatostilbene.—A solution of 2.0 g of **2** in 20 ml of benzene was irradiated for 4 hr using the 100-W Hanovia lamp as described above. On standing, 0.51 g (25.5%) of a crude photodimer, mp 89–92°, precipitated. Recrystallization from benzene and from chloroform–*n*-hexane gave photodimer A: mp 102–105°; ir ($CHCl_3$) 3425 (NH) and 1724 cm^{-1} (C=O); nmr (DMSO-d_6) δ 3.56 and 3.62 (2 s, 12, OCH_3 and $NHCOOCH_3$), 4.30 and 4.70 (2 m, 4, cyclobutane H), and 9.40 (s, 2, $NHCOOCH_3$).

The benzene filtrate was concentrated and chromatographed over silica gel (55 g) and the following fractions were obtained. Benzene gave 0.8 g (40%) of starting material. Benzene–ether (9:1 and 8:2, v/v) gave 0.45 g (22.5%) of photodimer B: mp 219–221° after recrystallization from benzene; ir ($CHCl_3$) 3425 (NH) and 1724 cm^{-1} (C=O); nmr (DMSO-d_6) δ 3.62 and 3.65 (2 s, 12, OCH_3 and $NHCOOCH_3$), 4.48 (m, 4, cyclobutane H), and 9.40 (s, 2, $NHCOOCH_3$).

A quantitative determination of photodimerization by gpc indicated a 51% yield of photodimers. In tetrahydrofuran, using the 450-W Hanovia lamp, a 75% yield of photodimers was realized.

Irradiation of the Methyl Carbamate (3) Derived from *trans*-4-Methoxy-4′-isocyanatostilbene.—A solution of 2.0 g of **3** in 20 ml of ethyl acetate was irradiated for 4 hr using the 100-W Hanovia lamp. The reaction mixture was evaporated, dissolved in benzene, and chromatographed over silica gel. Elution with benzene gave 0.3 g (15%) of starting material. Elution with benzene–diethyl ether (8:2, v/v) gave a mixture of photodimers from which 0.4 g (20%) of photodimer B, mp 220–222° after recrystallization from benzene, was precipitated with diethyl ether: ir (KBr) 3311 (NH) and 1695 cm^{-1} (C=O); nmr (DMSO-d_6) δ 3.62 (s, 12, OCH_3 and $NHCOOCH_3$), 4.32 (m, 4, cyclobutane H), and 9.36 (s, 2, $NHCOOCH_3$).

Concentration of the filtrate and addition of *n*-hexane precipitated 0.66 g (33%) of photodimer A: mp 116–118° after recrystallization from chloroform–*n*-hexane; ir ($CHCl_3$) 3425 (NH) and 1712 cm^{-1} (C=O); nmr (DMSO-d_6) δ 3.60 and 3.63 (2 s, 12, OCH_3 and $NHCOOCH_3$), 4.32 (m, 4, cyclobutane H), and 9.36 (s, 2, $NHCOOCH_3$).

Quantitative determination of photodimerization by gpc indicated a 66% yield of photodimers.

Irradiation of the Bismethylcarbamate (9) Derived from *trans*-4-Methoxy-2′,4′-diisocyanatostilbene.—A solution of 1.4 g of **9** in 14 ml of ethyl acetate was irradiated for 4 hr using the 100-W Hanovia lamp. Evaporation of the solvent and addition of benzene caused precipitation of 0.4 g (28%) of starting material. The benzene filtrate was chromatographed over silica gel, and elution with benzene–diethyl ether (8:2, v/v) afforded more starting material and an unknown by-product. Elution with diethyl ether gave 0.3 g (21.4%) of the photodimer: mp 142–145° after repeated crystallization from aqueous methanol (4:1, v/v); ir ($CHCl_3$) 3425 (NH) and 1718 cm^{-1} (C=O). Quantitative determination of photodimerization by gpc indicated a 35% yield of photodimer.

Irradiation of the Bismethylcarbamate (15) Derived from *trans*-4,4′-Diisocyanatostilbene.—A solution of 0.6 g of **15** in 20 ml of tetrahydrofuran was irradiated for 4 hr using the 100-W Hanovia lamp. The resulting solution was repeatedly chromatographed over silica gel, and elution with benzene–acetone (8:2, v/v) gave a low yield of a photodimer: mp 194–195° after recrystallization from ethyl acetate; ir (Nujol) 3311 (NH) and 1695 cm^{-1} (C=O). Quantitative determination of photodimerization by gpc indicated a 45% yield of photodimer.

Irradiation of 2,5-Dimethoxy-4′-nitro-*trans*-stilbene.—A solution of 3.0 g of the above compound in 30 ml of ethyl acetate was irradiated for 4 hr with unfiltered light from the 100-W light source. The solution contained no photodimers as evidenced by thin layer chromatography on an Eastman silica gel plate using benzene–ether (4:1, v/v).

Quantum Yield Determination.—A rotating turntable assembly (Merry-Go-Round Model MGR-500, supplied by the Southern New England Ultraviolet Co.) with a centrally located light source (450-W medium-pressure lamp, Type L, using Pyrex and Corning CS-7-39 filters to isolate 366-nm region) was used to obtain quantitative data. Benzophenone–benzhydrol actinometry[15] was used and the solutions were irradiated in quartz test tubes (13 mm) after thoroughly degassing with prepurified nitrogen. A quantum yield of 0.6 was obtained from the intercept. Using this value the output of the lamp was calculated to be 8.21×10^{16} quanta/sec. Simultaneously, a 5-ml benzene solution of **5** (0.03 *M*) was irradiated, and from the percentage dimerization (34.3%), the quantum yield was found to be *ca.* 0.057.

Irradiation of 5 in the Presence of Michler's Ketone.—Two quartz test tubes (13 mm) containing in each 5 ml of benzene solution of **5** and Michler's ketone in concentration of 0.016 and 0.126 *M*, respectively, were degassed with prepurified nitrogen, stoppered with a rubber septum, and irradiated for 4 hr in the system used for quantum-yield measurements. Simultaneously, two tubes containing in each 5 ml of benzene solution of **5** (0.016 *M*) were irradiated. The amount of dimer formation was measured by gpc, and in the former not more than 5% dimer was observed, whereas in the latter the dimerization occurred to the extent of 67%.

Emission Spectra of 5.—The fluorescence emission spectrum of **5** was determined in methanol at room temperature using an excitation wavelength of 350 nm. The emission maximum occurred at 410 nm and the 0–0 band was chosen at the point of crossing of the excitation and emission spectra which occurs at 378 nm. The phosphorescence emission at 77°K in EPA could not be detected.

Registry No.—**1**, 23435-25-8; **1** (acetyl derivative), 23435-26-9; **2**, 23465-04-5; **2** (dimer A), 23435-27-0; **3**, 23435-28-1; **3** (isocyanate), 23435-29-2; **3** (dimer A), 23435-30-5; **4**, 23435-31-6; **4** (acetyl derivative), 23435-32-7; **5**, 23435-33-8; **5** (isocyanate), 23435-34-9; **5** (dimer A), 23435-35-0; **6**, 23435-36-1; **7**, 23435-37-2; **7** (diisocyanate), 23435-38-3; **8**, 23435-39-4; **9**, 23435-40-7; **10**, 23435-41-8; **11**, 23435-42-9; **12**, 23435-43-0.

Acknowledgment—The authors wish to express their appreciation to B. V. Cheney, The Upjohn Co., Biochemical Research, Kalamazoo, Mich., for the 100-MHz nmr spectra and computer simulation. The invaluable assistance of F. P. Recchia and A. R. Marchant of our laboratories in obtaining the gpc results is greatly appreciated.

---

(15) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961).