192.5–193.5 °C; $[\alpha]^{21}_D$ –25.7° (*c* 1.18, EtOH) [lit.[4c] $[\alpha]^{21}_D$ –25.5° (*c* 1.01, EtOH)]; IR (KBr) 3340, 2980, 2800, 2535 (w), 2495 (w), 2395 (w), 1580, 1508, 1458, 1395, 1376, 1274, 1245, 1158, 1105, 1078, 1030, 1018, 994, 960, 911, 797, 776, 739 cm^{-1}; NMR (D_2O) δ 8.07 (m, 1 H), 7.70–7.75 (m, 1 H), 7.26–7.42 (m, 4 H), 6.77 (d, *J* = 7.5 Hz, 1 H), 4.18–4.27 (m, 1 H), 4.08 (dd, *J* = 4, 10.5 Hz, 1 H), 4.01 (dd, *J* = 5, 10.5 Hz, 1 H), 3.28 (quintet, *J* = 6.6 Hz, 1 H), 3.15 (dd, *J* = 4, 13 Hz, 1 H), 3.08 (dd, *J* = 8.5, 13 Hz, 1 H), 1.15 (d, *J* = 6.6 Hz, 3 H), 1. 14 (d, *J* = 6.5 Hz, 3 H).[9b] Anal. Calcd for $C_{16}H_{22}ClNO_2$: C, 64.96; H, 7.50; Cl, 11.99; N, 4.74. Found: C, 64.91; H, 7.50; Cl, 12.27; N, 4.75. A small amount of the (2*S*)-propranolol hydrochloride was treated with base (1 N NaOH–CH_2Cl_2) to regenerate the free amine, which was then protected as the benzylamine (1 equiv of BnBr, aqueous K_2CO_3–THF, reflux, 20 h). ^1H NMR analysis of the Mosher ester ((+)-MTPACl,[11] 4-DMAP, Et_3N, CH_2Cl_2) showed only one diastereomer.

Preparation of (2*S*)-Glycidyl Tosylate (4). An oven-dried 4-L three-necked flask equipped with a mechanical stirrer, low-temperature thermometer, Claisen adapter, nitrogen inlet, and rubber septum was charged with activated 3-Å powdered sieves (35 g) and 1.9 L of dichloromethane. D-(–)-Diisopropyl tartrate (14.0 g, 0.06 mol) was added via cannula as a solution in 15 mL of CH_2Cl_2, washing with an additional 10 mL of CH_2Cl_2. Allyl alcohol (68.0 mL, 58.1 g, 1.0 mol) was then added, the mixture cooled to –5 °C under nitrogen, and Ti(O-*i*-Pr)$_4$ (15.0 mL, 14.3 g, 0.05 mol) added via syringe. After the mixture was stirred for 30 min, precooled (ice bath) cumene hydroperoxide (80%, 350 mL, ca. 2 mol) was added via cannula over a period of 1 h with an internal temperature maintained at ≤–2 °C. The reaction mixture was stirred vigorously under nitrogen at –5 to 0 °C for 6 h. After the mixture was cooled to –20 °C, trimethyl phosphite was added very slowly via cannula, with the temperature not allowed to rise above –10 °C and the reduction of hydroperoxide carefully monitored [TLC in 40% EtOAc/hexane; tetramethylphenylenediamine spray indicator (1.5 g in 128:25:1 mL MeOH/H_2O/HOAc); ca. 141 mL (148.9 g, 1.2 mol) of $P(OMe)_3$ were required for complete reduction; further excess should be avoided]. The reaction is quite exothermic and addition took 1 h. Triethylamine (175 mL, 127 g, 1.26 mol) was then added, followed by addition of *p*-toluenesulfonyl chloride (200.4 g, 1.05 mol) as a solution in 250 mL of dichloromethane. The flask was stoppered and transferred to a freezer at –20 °C.

After 10 h the reaction mixture was allowed to warm gradually to room temperature and then filtered through a pad of Celite, with additional dichloromethane washing. The resultant yellow solution was washed with 10% tartaric acid, followed by saturated brine, dried ($MgSO_4$), and concentrated to afford an oil, from which volatile components (e.g., cumene, 2-phenyl-2-propanol, $P(OMe)_3$, $OP(OMe)_3$, etc.) were removed under high vacuum (ca. 0.5 mm) at 65 °C on a rotary evaporator equipped with a dry ice condenser. The residue was filtered through a short pad of silica gel (ca. 1 g per g of crude oil), by eluting with dichloromethane under nitrogen pressure. Concentration gave a lemon yellow oil (193.5 g), which was dissolved in ca. 175 mL of warm Et_2O and crystallized by addition of petroleum ether and cooling, seeding with pure material.[12] The resulting off-white solid was recrystallized twice (Et_2O–petroleum ether), by seeding each time with pure material. (2*S*)-Glycidyl tosylate[13] was obtained as large white prisms (91.7 g, 40%); mp 46–48.5 °C: $[\alpha]^{25}_D$ +17.5° (*c* 2.13, $CHCl_3$); 94% ee;[14,15] IR (KBr) 3075, 3000, 2935, 1598, 1362, 1195, 1180, 965, 915, 815, 775, 666, 558 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.81 (d, *J* = 8 Hz, 2 H), 7.36 (d, *J* = 8 Hz, 2 H), 4.26 (dd, *J* = 3, 11.4 Hz, 1 H), 3.95 (dd, *J* = 6.0, 11.4 Hz, 1 H), 3.16–3.23 (m, 1 H), 2.82 (t, *J* = 5 Hz, 1 H), 2.60 (dd, *J* = 3, 5 Hz, 1 H), 2.46 (s, 3 H). Anal. Calcd for $C_{10}H_{12}O_4S$: C, 52.62; H, 5.30. Found: C, 52.75; H, 5.29.

Preparation of (2*S*)-Propranolol from (2*S*)-Glycidyl Tosylate. In a 250-mL round-bottomed flask equipped with a rubber septum was suspended sodium hydride (oil free, 1.15 g, 0.048 mol) in DMF (40 mL, Mallinkrodt, used as received but stored over 3-Å sieves) at room temperature under a nitrogen atmosphere. 1-Naphthol (6.06 g, 0.042 mol) was added via cannula as a solution in DMF (20 mL) to produce a foamy green sludge. After 15–30 min, a solution of (2*S*)-glycidyl tosylate (94% ee, from above, 9.138 g, 0.040 mol) in DMF (20 mL) was added via cannula. A clear green-brown solution resulted.

After 4 h the reaction was judged to be complete by TLC (40% EtOAc/hexane). Isopropylamine (34 mL, 0.4 mol) and water (3.4 mL, 0.19 mol) were added, the septum was replaced with a cold water condenser, and the reaction was heated to reflux (bath temperature was about 90 °C). The reaction was followed by TLC (50% CH_2Cl_2/hexane). After 4 h the heat was removed, the reaction mixture diluted with water (100 mL) and extracted with ether (3 × 100 mL). The combined organic extracts were washed with 1 N NaOH and saturated brine, dried over Na_2SO_4, and concentrated under reduced pressure. Overnight drying in vacuo afforded a yellow solid (9.75 g).

This solid was dissolved in ether (100 mL), treated with gaseous HCl and the resulting white solid (10.62 g) collected by suction filtration. Recrystallization from methanol–ether afforded 7.11 g (60%) of (2*S*)-(–)-propranolol hydrochloride as white crystals, mp 192–193.5 °C, $[\alpha]^{21}_D$ –25.7° (*c* 1.23, EtOH). Anal. Calcd for $C_{16}H_{22}ClNO_2$: C, 64.96; H, 7.50; N, 4.74. Found: C, 64.76; H, 7.61; N, 4.66. Slightly off-white crystals (1.5 g) were obtained as a second crop. Recrystallization afforded an additional 1.18 g (10%) of (2*S*)-(–)-propranolol hydrochloride, mp 191.5–194 °C, $[\alpha]^{21}_D$ –26° (*c* 0.94, EtOH).

Acknowledgment. We are grateful to the National Institutes of Health (GM28384) and to Eli Lilly and Company for financial support.

Registry No. **1**, 56715-19-6; **2**, 103728-77-4; **3**, 61249-00-1; **4**, 70987-78-9; (+)-MTPACl, 20445-33-4; (L)-(+)-$Me_2CHOCOCH(OH)CH(OH)CO_2CHMe_2$, 2217-15-4; $H_2C{=}CHCH_2OH$, 107-18-6; $Ti(OCHMe_2)_4$, 546-68-9; Me_2CHNH_2, 75-31-0; (D)-(–)-$Me_2CHOCOCH(OH)CH(OH)CO_2CHMe_2$, 62961-64-2; 4-$MeC_6H_4SO_2Cl$, 98-59-9; $C_6H_5CHMe_2$, 98-82-8; $MeC(OH)(C_6H_5)CH_3$, 617-94-7; BnBr, 100-39-0; (2*S*)-propranolol, 4199-09-1; (2*S*)-propranolol hydrochloride, 4199-10-4; 1-naphthol sodium salt, 3019-88-3; 1-naphthol, 90-15-3; (*S*)-1-((phenylmethyl)amino)-3-(1-naphthalenyloxy)-2-propanol, 103617-36-3.

(11) (+)-α-Methoxy-α-(trifluoromethyl)phenylacetyl chloride.

(12) In our experience, seeding greatly facilitates crystallization in this case. Seed crystals may be obtained by purifying a small portion of the crude oil by column chromatography (silica gel, EtOAc/hexane).

(13) This compound has previously been reported as the racemate: (a) Pierre, J.-L.; Arnaud, P. *Bull. Soc. Chim. Fr.* **1969**, 2868. (b) Chautemps, P.; Pierre, J.-L.; Arnaud, P. *C.R. Seances Acad. Sci., Ser. 3* **1968**, *266*, 622. (c) Nakabayashi, N.; Masuhara, E; Iwakura, Y. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 413. (d) Ichikawa, K. *Yuki Gosei Kagaku Kyokaishi* **1964**, *22*, 553.

(14) Enantiomeric excess was determined by Mosher ester analysis of the iodohydrin derived from glycidyl tosylate. See ref 2b for experimental details.

(15) *Note Added in Proof*: In a recent experiment, following the same procedure, material of 98% ee was obtained. We have also found that stirring during crystallization leads to higher chemical purity earlier in the recrystallization sequence.

Consequences of Hydrophobic Association in Photoreactions: Photodimerization of Stilbenes in Water

M. S. Syamala and V. Ramamurthy*

Department of Organic Chemistry, Indian Institute of Science, Bangalore-506 012, India

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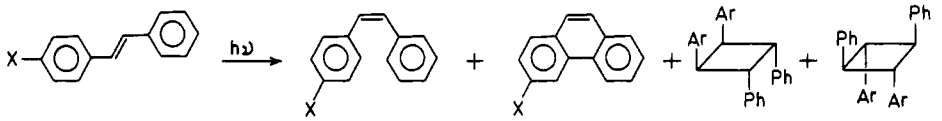
Hydrophobic interactions are of considerable importance in maintaining the structure of biological membranes, proteins, and nucleic acids. The same interaction is also responsible for the association of organic solutes in water, a well-substantiated phenomenon.[1] Such an association could play a significant role during cycloaddition reactions

(1) Duff, D. G.; Giles, C. H. In *Water—A Comprehensive Treatise*; Franks, F., Ed.; Plenum: New York, 1975; Vol. 4, p 175. Eagland, D. In *Water—A Comprehensive Treatise*; Franks, F., Ed.; Plenum: New York, 1975; Vol. 4, p 305.

0022-3263/86/1951-3712$01.50/0

Scheme I. Photoreactions of Stilbene



1 X = H 3 X = CH_3
2 X = F 4 X = CN

Table I. Product Distribution upon Photolysis of Stilbenes[a,b]

substrate[c,d]	geometric isomer %		phenanthrene,[e] %	dimer,[h] %	
	cis[e]	trans[e]		A	B
p-fluorostilbene	7 (92)	53 (7)[e]	23 (1)[e]	8	7
p-methylstilbene	25 (88)	41 (9)	16 (3)	11	7
p-cyanostilbene	11 (80)	32 (18)	22 (2)	25	9
o-methoxystilbene	20 (91.5)	20 (8.5)	39	11	10
stilbene[f]	11 (84)	33 (12)	33 (4)	12	10
stilbene + LiCl (3 M)[f]	7	27	25	25	17
stilbene + guanidinium chloride (3 M)[f]	11	21	53	8	6
stilbene + β-cyclodextrin[f] (1:10)	29	71			
stilbene + SDS[f,g] [⟨S⟩ : 1]	36	26	33	3	2

[a] Analyzed by GC; error limit: ±2%. [b] Irradiated for 24 h with a 450-W medium-pressure mercury lamp. [c] Cis isomers used for irradiation. Trans isomers also gave a similar product distribution. [d] Saturated solutions ≃5 × 10^{-4} M. [e] Numbers within parentheses correspond to the values in benzene. Irradiation in benzene at such concentrations gave no dimer. [f] All solutions had identical concentrations (5.5 × 10^{-4} M) and matched OD: irradiated simulataneously in a merry-go-round style. [g] ⟨S⟩ = occupancy number. [h] For structural details see ref 15.

of organic molecules in aqueous medium. Indeed, Diels–Alder reactions are strikingly accelerated when water is the solvent.[2] Furthermore, significant selectivity in the product distribution (endo, exo) also resulted.[3] Although the potential role of "hydrophobic effect" in thermal reactions has attracted considerable attention in the last few years, curiously, however, the use of such an effect has not been reported for any typical photodimerization reactions of small molecules in aqueous solution except for cases which are fairly well soluble in water. The role of aggregates in concentrated aqueous solution during the photodimerization of thymine, uracil, and their derivatives has been demonstrated.[4] Our attention was drawn to the fact that many organic molecules tend to aggregate at concentrations even lower than 10^{-5} M. Clearly, the application of such a phenomenon could be of considerable interest to photochemists. Although the dimerization of stilbene has been known[5] since the beginning of this century it has eluded extensive investigation probably due to its poor efficiency. Typically, *trans*-stilbene in benzene (0.75 M) yields only 27% of dimer after two months of irradiation.[6] We report below that efficient dimerization can be obtained within 24 h of irradiation of stilbene at concentrations as low as ~10^{-6} M in water. This remarkable acceleration of the efficiency of dimerization is demonstrated to be due to the association of stilbene molecules in water.

Results and Discussion

We, promoted by the recent reports of efficient Diels–Alder reactions in water,[2,3] undertook an exploration into the use of ground-state aggregation in photodimerization reactions. In this context stilbenes (Scheme I) were chosen as substrates. The photochemistry of stilbene is well-known, and the three photochemical reactions it undergoes are geometric isomerization, cyclization, and dimerization. Of these, dimerization is the least efficient reaction and becomes active only above ~0.1 M in benzene.[7] Therefore, acceleration of such a reaction through external features appeared desirable.

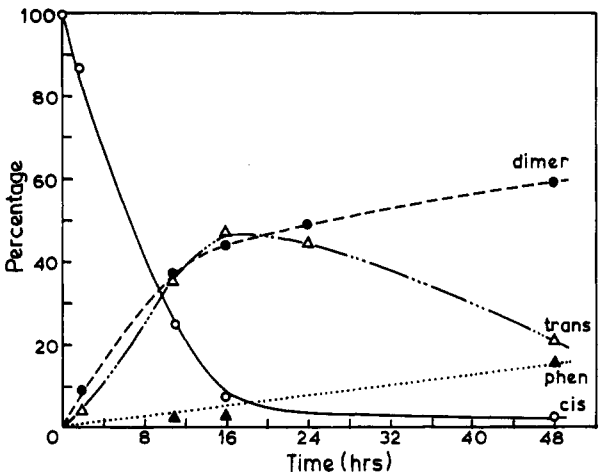


Figure 1. Plot of reaction mixture composition vs. irradiation time for *cis*-stilbene.

While a saturated solution of *cis*-stilbenes 1–4 could be obtained by stirring them in water for ~24 h, a solution of only ~10^{-6} M of *trans*-stilbenes could be obtained by this method. Photolysis solutions of trans isomers always contained suspended crystals. The formal concentrations of *cis*- and *trans*-stilbenes prepared by stirring them in water were ~10^{-4} and 10^{-6} M, respectively. Photolysis of 1–4 at these concentrations in benzene resulted only in geometric isomerization and cyclization to phenanthrene as shown in Table I. Even prolonged irradiation (3 days) did not give dimers, and this is consistent with the literature reports. A striking observation was made when

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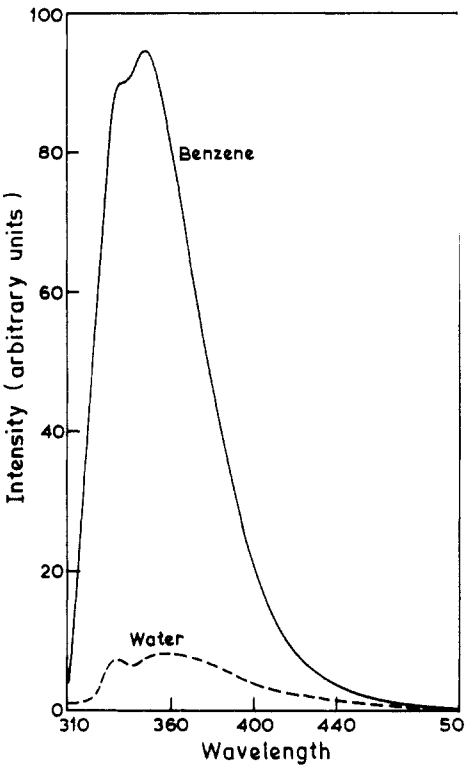

Figure 2. Fluorescence emission spectra of *trans*-stilbene solutions in benzene and water with matched optical density.

aqueous solutions of the stilbenes 1–4 were irradiated. Most remarkably, *trans*-stilbenes even at concentrations of $\sim 10^{-6}$ M gave rise to dimers within 2 h of photolysis. The results of photolyses of *cis* isomers of 1–4 in water are summarized in Table I. Efficient conversion to dimers was obtained within 24 h of photolysis. In all cases two dimers, identified to be the same ones formed during benzene irradiation at high concentrations, were formed along with the cyclization product. The dimer isomer ratio obtained in water is identical with that in benzene. The plot of reaction mixture composition vs. irradiation time shows that isomerization precedes dimerization in the case of *cis*-stilbene (Figure 1). Thus addition is presumed to occur only from the excited singlet state of *trans*-stilbene. No comparison of the relative quantum yield of dimerization with benzene could be made owing to the absence of dimerization in the latter. Fluorescence spectra of *trans*-stilbene in water and benzene, of matched optical density, are shown in Figure 2. As seen in the figure, fluorescence intensity of *trans*-stilbene in water is considerably reduced relative to benzene. This is possibly an indication of the presence of additional decay channels, namely, excimer formation and dimerization in water for the S_1 state.

The observed dramatic enhancement in the rate of dimerization indicates a mutual binding of stilbenes in water. This is also warranted by the reported lifetime of *trans*-stilbene in methyl cyclohexane (τ = 0.07 ns).[8] Assuming that such a short lifetime may hold good in water, even a diffusion-controlled reaction between an excited singlet stilbene and a ground-state melecule would be insufficiently competitive with singlet decay ($\Phi_{dimer}^{max} \leq 10^{-4}$ at 10^{-4} M). The obvious alternative is preassociation. Such a binding may not be due to formation of microcrystals of *trans*-stilbene as it has been reported that the packing geometry in the crystals of *trans*-stilbene is not suitable for dimerization.[9] Neither excimer emission nor dimerization occurs upon irradiation of crystalline *trans*-stilbene. Furthermore, irradiation of *trans*-stilbene crystals both dry and wetted with water did not yield any dimers even after a week. Therefore, in water either a multimolecular aggregation or a simple 1:1 packing is suggested. In order to assess the importance of association of stilbene molecules in water the following experiments were carried out. Lithium chloride and guanidinium chloride which are known to alter the water structure[10] were employed to increase and decrease the hydrophobic association, respectively. Further, β-cyclodextrin and sodium dodecyl sulfate (SDS) micelle were used to deaggregate the stilbene present in the aqueous phase. Results of irradiations conducted in presence of the above addends (under identical conditions and matched OD) are summarized in Table I. It is evident that lithium chloride enhances the dimerization and guanidinium chloride lowers the dimerization yield. Even more striking are the results obtained in the presence of cyclodextrin and SDS micelle. In the presence of these very little dimerization occurred, clearly pointing out that stilbene molecules need to be present in the aqueous phase for the photoreaction to occur. The size of the β-cyclodextrin cavity is too small to accommodate more than one molecule of stilbene. The occupancy number of stilbene in SDS micelle under our experimental conditions being less than one, both β-CD and SDS serve as hydrophobic pockets in aqueous solution, deaggregating the stilbenes and thus preventing their dimerization. Supporting the aggregation proposal is the results of UV absorption spectral measurements. A plot of optical density (at any wavelength between (220–300 nm) vs. concentration showed a nonlinear behavior for *cis*-stilbene (Figure 3).

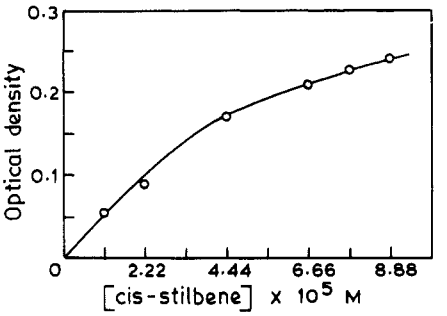

Figure 3. Beer's law plot for *cis*-stilbene.

Diels–Alder reactions investigated in water indicate that selectivity in the adduct isomers can be obtained. But no such selectivity was observed during the photodimerization of stilbene. This seems surprising, but one can only speculate that the geometry of the excimer is unchanged between benzene and water. Hydrophobic association can alter the course of a reaction through local concentration effect by aggregating the reacting molecules and/or by favoring a transition state with a smaller volume. Thus it emerges from the above presentation that the association of organic molecules in water can be profitably utilized for photochemical reactions.

Experimental Section

trans-Stilbene (Aldrich) was used as received. The trans isomers of *p*-methyl, *p*-fluoro, and *p*-cyanostilbenes were prepared by reported procedures.[11] In each case the corresponding cis isomer was obtained by standard photolysis method.[12]

(8) Birch, D. J. S.; Birks, J. B. *Chem. Phys. Lett.* **1976**, *38*, 432.

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(10) Von Hippel, P. H.; Schleich, T. *Acc. Chem. Res.* **1969**, *2*, 257.

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Preparation of Solutions for Photolysis and Spectral Studies. Dissolution of *trans*-stilbenes in water was generally difficult. A solution of 10^{-6} M (as checked by UV absorption) could be prepared by stirring *trans*-stilbene (20 mg) in 200 mL of water for 24 h. However, solutions of *cis*-stilbene having concentrations $\simeq 10^{-4}$ M were prepared by magnetically stirring 20 mg of *cis*-stilbene in 200 mL of water for 24 h. These solutions after bubbling with nitrogen for 30 min were used for photolysis.

In order to check the possible association of stilbene molecules in water, absorption spectra were recorded (Shimadzu UV-180 spectrophotometer) for aqueous solutions of *cis*-stilbene in the concentration range $(1.1–8.8) \times 10^{-5}$ M. Solutions of these were prepared as follows. A stock solution (1–8 μL) of *cis*-stilbene in methanol (1.1×10^{-2} M) were added to 10-mL portions of water, and the solutions were stirred for 24 h. A plot of optical density vs. concentration indicated a deviation from Beer's law. No attempt was made to carryout such studies with stilbenes **2**–**4**.

β-Cyclodextrin complexes of stilbene **1**–**4** were prepared by the standard procedure.[13] A typical photolysis solution consisted of 20 mg of stilbene, 1.25 g of β-cyclodextrin, and 200 mL of water. An excess of cyclodextrin was required to fully complex the stilbene.

Miceller solutions (SDS) of stilbene under conditions where the occupancy number was less than one were prepared by stirring 10 mg of stilbene in 100 mL of water containing a gram of SDS. The stilbenes (cis and trans) went into aqueous solution rapidly in the presence of SDS.

Photolysis. Aqueous solutions of *trans*-stilbenes **1**–**4** (20 mg in 200 mL of water) were irradiated in Pyrex tubes with a 450-W medium-pressure mercury lamp. Except for a small amount which had gone into solution most of the *trans*-stilbenes were floating as microcrystals during irradiations. Aqueous solutions of *cis*-stilbenes **1**–**4** were also irradiated under similar conditions. Under the conditions these solutions were transparent. The products of photolyses were extracted with chloroform and analyzed by GC (Chemito: Model 3800; 8 ft × $^1/_8$ in. 5% SE-30 column; temperature 170–300 °C programmed at the rate of 10 deg/min). GC and H^1 NMR indicated that the product mixture consisted of *trans*- and *cis*-stilbenes, phenanthrene, and dimers. The absolute yield of the products were measured by using an internal standard, *trans*-2,5-dimethyl-4-methoxystilbene. The material balance was ≃80%, and no products other than the ones mentioned above were seen in GC and H^1 NMR (Brucker WH-270). The structure of the dimers were identified by comparison with authentic samples prepared by irradiating benzene solutions of **1**–**4** (1.0 M) according to the literature reports.[6,14] The two isomeric dimers obtained after purification by column chromatography (silica gel, hexane–chloroform) were identical with the ones obtained from aqueous solution irradiation.[15]

The progress of the photolysis in the case of *cis*-stilbene was monitored by GC. A 10^{-5} M solution of *cis*-stilbene in water was irradiated for 24 h as described above. A small aliquot of the solution was taken out every 30 min, extracted, and analyzed by GC. The results are shown in Figure 1.

In order to assess the importance of association of stilbene molecules in aqueous phase the following experiments were carried out. Five Pyrex tubes consisting of identical concentrations of *cis*-stilbene (10^{-5} M) in water with addends as mentioned below and matched optical densities were irradiated simultaneously with a 450-W medium-pressure mercury lamp in a merry-go-round style. These five Pyrex tubes contained the following solutions: (i) *cis*-stilbene, (ii) *cis*-stilbene and 3 M lithium chloride, (iii) *cis*-stilbene and 3 M guanidinium chloride, (iv) *cis*-stilbene and 1 g of β-cyclodextrin, and (v) *cis*-stilbene and 1 g of SDS. The products were extracted and analyzed by gc. Yields of the dimers are presented in Table I.

For the sake of comparison, benzene solutions of *trans*- and *cis*-stilbenes of **1**–**4** of the same concentration as employed for aqueous irradiation (matched OD), were irradiated by using a 450-W medium-pressure mercury lamp. GC and H^1 NMR analyses of the reaction mixtures indicated only geometric isomers and phenanthrene. No dimers were obtained.

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Registry No. (Z)-**1** (X = H), 645-49-8; (E)-**1** (X = H), 103-30-0; (Z)-**1** (X = OMe), 1898-14-2; (E)-**1** (X = OMe), 52805-92-2; (Z)-**2**, 1657-46-1; (E)-**2**, 718-25-2; (Z)-**3**, 1657-45-0; (E)-**3**, 1860-17-9; (Z)-**4**, 14064-68-7; (E)-**4**, 13041-79-7; Dimer A (Ar = *p*-C_6H_4F), 103563-99-1; Dimer A (Ar = *p*-C_6H_4Me), 103564-00-7; Dimer A (Ar = *p*-C_6H_4CN), 103564-01-8; Dimer A (Ar = *o*-C_6H_4OMe), 103564-02-9; Dimer A (Ar = Ph), 54515-63-8; Dimer B (Ar = *p*-C_6H_4F), 103564-03-0; Dimer B (Ar = *p*-C_6H_4Me), 103564-04-1; Dimer B (Ar = *p*-C_6H_4CN), 103564-05-2; Dimer B (Ar = *o*-C_6H_4OMe), 103564-06-3; Dimer B (Ar = Ph), 54515-64-9; SDS, 151-21-3; LiCl, 7447-41-8; phenanthrene (X = F), 440-40-4; phenanthrene (X = Me), 832-71-3; phenanthrene (X = CN), 21661-50-7; phenanthrene (X = OMe), 834-99-1; phenanthrene (X = H), 85-01-8; guanidinium chloride, 50-01-1; β-cyclodextrin, 7585-39-9.

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(15) Spectral details of the dimers are as follows. Dimer of stilbene: ^1H NMR ($CDCl_3$) [dimer A] δ 7.28–7.35 (m, 20 H), 4.45 (s, 4 H), [dimer B] δ 7.36 (m, 20 H), 3.66 (s, 4 H); mass spectrum, (70 eV) *m/e* 360, 180. Dimer of *p*-fluorostilbene: ^1H NMR ($CDCl_3$) [dimer A] δ 7.4–7.2 (m, 18 H), 4.58 (s, 4 H), [dimer B] δ 7.4–7.2 (m, 18 H), 3.78 (dd, 4 H); mass spectrum (70 eV) *m/e* 396, 216, 198, 180. Dimer of *p*-cyanostilbene: ^1H NMR n$CDCl_3$) [dimer A] δ 7.0–7.78 (m, 18 H), 4.58 (s, 4 H), [dimer B] δ 7.0–7.78 (m, 18 H), 3.88 (m, 4 H); mass spectrum, (70 eV), *m/e* 410, 230, 205, 180. Dimer of *p*-methylstilbene: ^1H NMR ($CDCl_3$) [dimer A] δ 7.1–7.88 (m, 18 H), 4.45 (s, 4 H), 1.88 (s, 6 H), [dimer B] δ 7.1–7.88 (m, 18 H), 3.68 (s, 4 H), 1.88 (s, 6 H); mass spectrum, (70 eV) *m/e* 388, 208, 194, 180.

Determination of Enantiomeric Purity of Tertiary Amines by ^1H NMR of α-Methoxy-α-(trifluoromethyl)phenylacetic Acid Complexes

Frank J. Villani, Jr.,* Michael J. Costanzo, Ruth R. Inners, Martin S. Mutter, and David E. McClure

Department of Chemical Research, McNeil Pharmaceutical, Spring House, Pennsylvania 19477-0776

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Over the last two decades, several new techniques have been developed for determination of the enantiomeric purity of chiral compounds. In general, these methods are independent of optical rotation and involve the formation of diastereomeric complexes or derivatives for analysis by NMR (^1H, ^{19}F, ^{13}C, ^{31}P)[1] or chromatography.[2] Despite

(1) NMR methods showing the wide utility are α-methoxy-α-(trifluoromethyl)phenylacetic acid derivatives,[3] chiral solvating agents,[4] chiral shift reagents,[5] and other acid derivatives of alcohols and amines.[6]

(2) Chromatographic methods have also employed MTPA and related derivatives[3,6] and the more recently developed chiral stationary phases for direct analysis of enantiomeric purities by HPLC.[7]

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