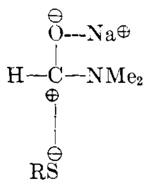

Figure 2

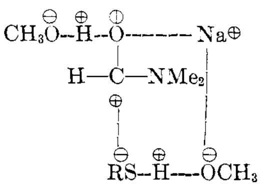

Figure 3

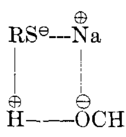

Figure 4

first reported case in which the fate of the reacting entity, $RS^{\ominus}Na^{\oplus}$, can be spectulated on with any reasonable certainty.

Experimental

Reagents.—The following materials were distilled under a nitrogen atmosphere through a 14-in. silvered column equipped with a tantalum-wire spiral: *n*-butyl mercaptan (Matheson Coleman, and Bell, b.p. 96–98°, $n^{20}{}_D$ 1.4411), cyclohexyl mercaptan [Columbia Organic Chemicals, b.p. 62–65° (12 mm.), $n^{20}{}_D$ 1.4925] benzyl mercaptan [Evans Chemetics Inc., b.p. 70° (3 mm.), $n^{20}{}_D$ 1.5776], and thiophenol [Matheson Coleman and Bell, b.p. 75° (5 mm.) $n^{20}{}_D$ 1.5805]. *p*-Aminothiophenol, *p*-nitrothiophenol and *p*-aminophenyl disulfide (Kek Labs) were used without further purification. All mercaptans were stored under a nitrogen atmosphere in a cold box.

Purification of Solvents.—Dimethylformamide, diglyme, *tert*-butyl alcohol, and methanol were dried over indicating Drierite and then distilled over 13X Linde Molecular Sieves to remove any water that was present. The sieves had previously been calcined under nitrogen at 750° for 4 hr. All solvents were stored in a nitrogen dry box.

Synthesis and Identification of Disulfides.—Each authentic disulfide was prepared according to the method described in Vogel.[11] One-tenth mole of each mercaptan was added to 50 ml. of a 15% sodium hydroxide solution in a flask equipped with a stirrer and nitrogen bubbler. Iodine (11.0 g.) was added over a 2-hr. period and each reaction mixture was then stirred overnight. *n*-Butyl and cyclohexyl disulfide were purified by distillation under reduced pressure through a 14-in. silvered column equipped with a tantalum wire spiral. Boiling points and indices of refraction agreed with those tabulated in Reid.[12] Phenyl and benzyl disulfides, when recrystallized from methanol, had respective melting points of 62 and 74° (reported[12] 62 and 74°, respectively). The yields of all disulfides varied between 65 and 80%.

In the isolation of disulfides from the oxidation reactions, the reaction mixture was neutralized with hydrochloric acid, diluted with an equal volume of water, and the disulfide removed by extraction with petroleum ether. The disulfides were purified as above and the physical properties agreed with the literature values. In addition, the infrared spectrum of each disulfide was identical to the synthesized materials. In the case of the phenyl, *p*-aminophenyl, and benzyl disulfides mixture melting points with the authentic disulfides showed no depression.

Preparation of Reaction Mixtures and Actual Oxidation Experiments.—All base-solvent systems were made up to the appropriate molarity in a specially adapted heavy-walled 500-ml. erlenmeyer flask in a nitrogen drybox. Each solvent contained 0.20 mole of the desired alkoxide base. One-tenth mole of each mercaptan was then added, the reaction flask sealed, and transferred to the oxidation apparatus which consisted of a polyethylene gas balloon, wet-test meter, drying tower, and a water-cooled condenser. Kinetic measurements were determined from the rate of oxygen consumption as a function of time using the previously derived first-order rate expression. This method of analysis as well as a detailed description of the apparatus employed have been discussed in detail previously.[1,13,14]

Acknowledgment.—The authors would like to acknowledge the experimental assistance of Mr. Joel Haberman. They would also like to thank the Esso Research and Engineering Co. for the privilege of publishing this research work and Dr. R. M. Skomoroski for helpful discussions.

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Telomerization by Free Radical Mercaptan Chain Transfer. I. Styrene and Ethanethiol[1]

George P. Scott and James C. Wang[2]

Department of Chemistry, State University of South Dakota, Vermillion, South Dakota

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One- and two-unit telomers (only) have been obtained from styrene using ethanethiol as a free radical chain transfer agent in the liquid phase. Reversibility of telomer formation under the conditions studied was found to be slight. Chain transfer constants for one- and two-unit telomers and also long chain polymers have been determined. The significance of the increase of transfer constant with chain length is discussed.

The formation of short chain polymer fragments (telomers and cotelomers) by free radical chain transfer has been known for some time. However, its potential versatility as a synthetic tool has thus far received little application owing in part to separation problems and in part to lack of fundemental data on chain transfer in very short chains. A number of workers[3] have studied haloalkane agents and determined chain transfer constants for a few monomers measuring the relative rate of displacement (equation 1) to propagation (equation 2) for short chains containing n units. (Here M refers to monomer units and A and

$$B{-}M_n\cdot + A{-}B \xrightarrow{k_{dn}} B{-}M_n{-}A + B\cdot \qquad (1)$$

$$B{-}M_n\cdot + M \xrightarrow{k_{pn}} B{-}M_{n+1}\cdot \qquad (2)$$

B to fragments of the transfer agent, A–B. The sym-

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[2] Presented in part at the 141st National Meeting of the American Chemical Society, Division of Polymer Chemistry, Washington, D. C., March, 1962, and taken in part from the thesis of James C. Wang.

[3] (a) For a review and earlier references, see C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 243–259 and 313–326; (b) J. C. Robb and E. Senogles, *Trans. Faraday Soc.*, **58**, 708 (1962); (c) W. J. Kirkham and J. C. Robb, *ibid.*, **57**, 1757 (1961); (d) J. C. Robb and D. Vofsi, *ibid.*, **55**, 558 (1959); (e) W. I. Bengough and R. A. M. Thomson, *ibid.*, **57**, 1928 (1961); (f) **56**, 407 (1960).

bol B—$M_n\cdot$ represents the n-unit radical. The transfer constant $C_n = k_{dn}/k_{pn}$.)

Earlier work[3a] indicated that C_n was small when n = 1 but increased rapidly to a constant value for chains of four units or longer. Recent work[3b–f] using bromotrichloromethane as the transfer agent has included studies of individual rate constants and has shown a more complex variation of C_n with chain length. Kirkham and Robb[3c] ascribe this to a reactivity minimum of the growing radical chain at three or four monomer units length and suggest that the formation of a "semi bond" between the radical bearing carbon and the CCl_3 group may be involved.

Although telomer formation has been observed with mercaptan chain transfer agents[4], no corresponding studies of transfer constants or other kinetic data for short chains have been reported. This paper describes such a study involving telomer formation in the styrene–ethanethiol system.

The object of the study was to determine first whether telomers could be obtained from this system in appreciable quantities and whether their formation was significantly reversible in the liquid phase. It was then hoped to determine several telomerization chain transfer constants to be compared with the polymerization transfer constant, C_∞. Polymerization transfer constants for numerous primary alkanethiols with styrene have been reported[5]; however, the value for ethanethiol seems to have been omitted. It was, therefore, determined in this work.

Experimental[6]

Preparation and Characterization of the Telomers.—Ethanethiol (9.42 g.; 0.152 mole), redistilled styrene (22.73 g.; 0.218 mole) and azobisisobutyronitrile (AIBN; 2.0 mole % of the styrene) were sealed in a nitrogen filled pyrex reaction tube and heated for 6 hr. in a constant temperature bath at 50°. Excess mercaptan was removed by distillation at 0° using a water aspirator. The residue was distilled through a 7-in. Vigreux column under vacuum. After removal of the styrene, two fractions boiling over a narrow range were collected. Redistillation of these gave the two telomers. The one-unit telomer boiled at 68–69° (0.4 mm.), $n^{20}D$ 1.5395.

Anal. Calcd. for $C_{10}H_{14}S$: C, 72.34; H, 8.42; S, 19.25. Found: C, 72.47; H, 8.22; S, 19.13.

The two-unit telomer boiled at 145° (0.06 mm.), $n^{20}D$ 1.5685.

Anal. Calcd. for $C_{18}H_{22}S$: C, 80.00; H, 8.17; S, 11.81. Found: C, 79.73; H, 7.84; S, 11.88.

Sulfones of the telomers were prepared by adding an excess of a solution of equal volumes of 30% hydrogen peroxide and glacial acetic acid and allowing the mixture to stand in a water bath at 50° for 2 hr. The acetic acid and hydrogen peroxide were removed by evaporation on a steam bath. The products were recrystallized from an ethanol–water mixture.

The sulfone from the one-unit telomer melted at 78.5–79.5°. Fehnel and Resnick[7] report a melting point of 79–80° for this compound.

The sulfone from the two-unit telomer melted at 67.5–68.5°.

Anal. Calcd. for $C_{18}H_{22}SO_2$: C, 71.48; H, 7.33; S, 10.59. Found: C, 71.33; H, 7.20; S, 10.32.

Reversibility of Telomer Formation.—A sample of one-unit telomer (2.30 g.) together with one mole % of AIBN was sealed in one leg of an evacuated H-shaped pyrex tube. The leg containing the telomer was placed in constant temperature bath at 50° for 24 hr. while the other leg was dipped in a Dry Ice–acetone bath. Only a small trace of material resulted in the cold leg of the tube. Gas chromatograms of material in both legs compared to gas chromatograms of prepared mixtures of one-unit telomer and ethanethiol indicated that not more than a few % of the telomer had decomposed.

A similar experiment with two-unit telomer likewise indicated very little decomposition at 50° for many hours. An additional experiment with one-unit telomer carried out in a similar manner but with excess mercaptan added, confirmed the stability of the telomer under these conditions (presumably in the presence of thiyl radicals).

Determination of the Polymerization Chain Transfer Constants.—Solutions containing freshly distilled styrene and small quantities of ethanethiol and AIBN were prepared in quantity. Several pyrex reaction tubes (30-ml. capacity) were filled nearly to the top with solution, sealed, and allowed to stand from 1–12 hr. in a constant temperature bath at 50°. Two aliquots (5.00 ml.) from each tube and from the original solutions were titrated amperometrically with 0.0050 *N* silver nitrate by the method of Kolthoff and Harris.[8] Titration was carried out in a closed flask, using a glycerine seal for the rotating electrode and a magnetic stirrer, to avoid loss of ethanethiol. The polymer was isolated from two aliquots (5.00 ml.) by precipitating in 50-ml. quantities of methanol. The supernatant methanol and styrene were decanted and evaporated rapidly at room temperature, and the small residue (about 0.1 to 0.2 part of the total) was added to the precipitated polymer. Solvent was removed by freeze drying and the precise weight of each yield determined.

Determination of Telomer Chain Transfer Constants.—Quantities of ethanethiol varying from 1–15 g. were placed in 30–60-ml. nitrogen filled Pyrex reaction flasks, the weight of the mercaptan being determined by the increase in weight of the flask. The flasks were cooled quickly in Dry Ice and acetone. After adding weighed quantities of styrene varying from 8–50 g, and (in most experiments) small weighed quantities of initiator. the flasks were quickly sealed and placed in a constant temperature bath set at 50 ± 0.1° with initial shaking to make the mixture homogeneous. After 0.5–3 hr., the tubes were cooled, unsealed, and connected directly to a water aspirator. Mercaptan was then removed by placing an ice bath around the tube and evaporating the mixture at 0°. In the majority of experiments, the weight of the residue was then determined, and the mixture was analyzed by gas chromatography on an ethylene glycol terephthalate column to determine the per cent of styrene approximately so that the degree of conversion could be estimated. The residue was then further distilled at a temperature of 50° under reduced pressure to remove most of the unchanged styrene. It should be pointed out that some polymerization may have occurred during this phase of the process; however, this should not affect the resulting quantities of telomers since the chromatogram showed that the mercaptan had been effectively removed at 0°.

The analysis of the final mixture was accomplished by running several gas chromatograms interspersed with chromatograms of mixtures of the pure telomers approximating the composition found. Ratios of the peak heights of each telomer to those of the corresponding standards were used to detemine quantities of telomers, and from these the ratio of one-unit telomer to two-unit telomer was calculated in each case.

Results

Observed Telomer Formation.—It was found to be relatively easy to isolate the one-unit telomer (the simple adduct) and the two-unit telomer from reaction mixtures obtained by reaction of ethanethiol with a moderate excess of styrene. These products and their sulfones gave analyses corresponding to the expected thioethers, $C_6H_5CH_2CH_2SCH_2CH_3$ and $C_6H_5CH_2CH_2CH(C_6H_5)CH_2SCH_2CH_3$. In spite of several attempts, however, no identifiable sample of any higher telomer was isolated either in pure from or as a mixture of diastereomers.

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(4) M. S. Kharasch and C. F. Fuchs, *J. Org. Chem.*, **13**, 97 (1948).

(5) (a) R. A. Gregg, D. M. Alderman, and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 3740 (1948); (b) V. A. Dinaburg and A. A. Vanscheidt, *Zh. Obshch. Khim.*, **24**, 840 (1954); *Chem. Abstr.*, **49**, 8157d (1955).

(6) Boiling points and melting points are uncorrected. Microanalyses are by Galbraith Laboratories, Knoxville, Tenn.

(7) E. A. Fehnel and P. R. Resnick, *J. Org. Chem.*, **20**, 996 (1955).

(8) I. M. Kolthoff and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **18**, 161 (1946).

In most experiments small amounts of AIBN were used as the initiator; however, as the reaction of styrene with carbon tetrachloride,[3a] the process proceeded slowly in the absence of any initiator.

It has been suggested[3a] that both steps of mercaptan addition may be reversible. The experiments described above, appear to indicate a very slight tendency for the reaction to reverse. This was shown to be too small to complicate the determination of the chain transfer constants under the conditions used, although no quantitative estimate of the degree of reversibility can be made.

Determination of Chain Transfer Constants.—Fig. 1 shows the experimental linear variation of the logarithms of the per cents of styrene and ethanethiol remaining in five polymerizaition reactions. The slope of this line corresponds to the polymerization chain transfer constant.[5a] The value of the slope as determined by the method of least squares is 17.1 with a standard deviation of 0.51, the error at the 5% probability level being about ±1.4.

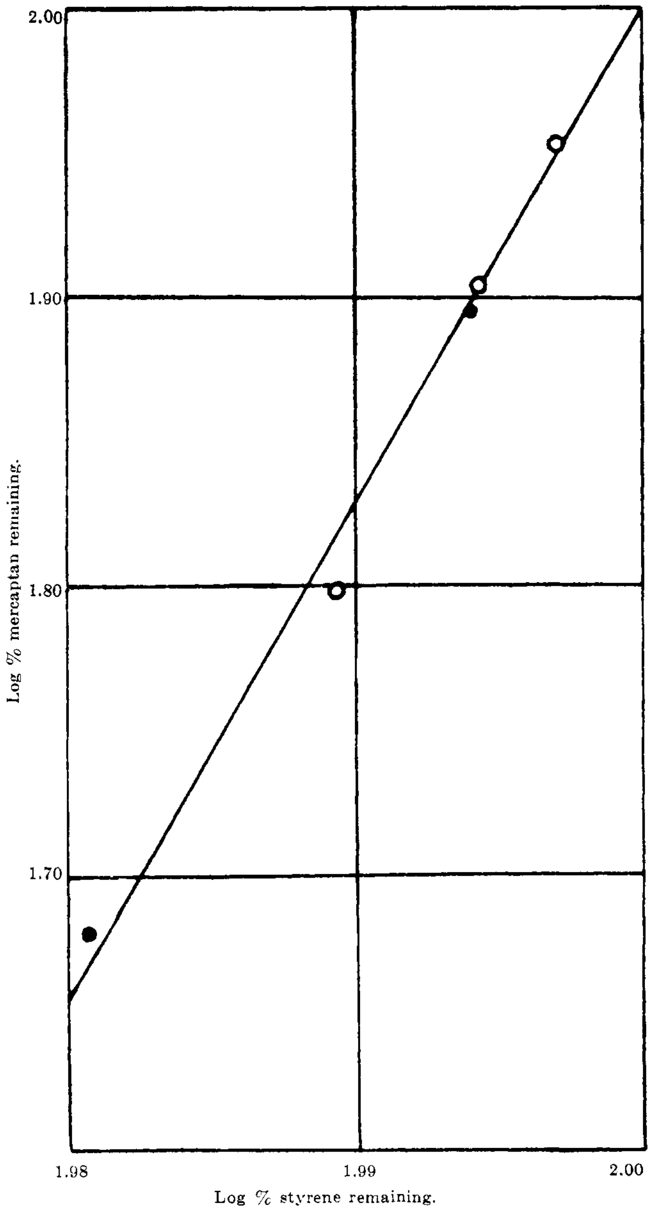

Fig. 1.—Determination of polymerization chain transfer constant: moles mercaptan per mole styrene; ○ = 9.4×10^{-4}; ● = 31.1×10^{-4}.

It has been pointed out[3a] that the following simple expression involving telomerization transfer constants can be obtained directly from the rate expressions for the addition and displacement reactions (1 and 2),

$$d[B\text{—}M_n\text{—}A] / \sum_{n+1}^{\infty} d[B\text{—}M_i\text{—}A] = C_n[AB]/[M] \qquad (3)$$

where [AB], [M], and $[B\text{—}M_n\text{—}A]$ = concentrations of transfer agent, monomer, and n-unit telomer, respectively. If the extent of reaction is kept low (10% or less), the left-hand side can be approximated by measured ratios of product concentrations, and values for C_n can be determined.

The denominator of the left-hand side of equation 3 refers to the total concentrations of all telomers having more than n monomer units. However, in the course of this work, it was soon found that the quantity of telomers having more than two units formed at low conversions was too small to obtain even a rough approximation of the denominator in the expression for the second chain transfer constant; in fact at a one to one mole ratio of transfer agent to monomer, almost no mixture of high telomers was obtained. It was therefore concluded that the chain transfer constant C_2 was relatively large.

This situation is better adapted to the use of equation 4, which is readily derived from 3, for determination of the chain transfer constants,

$$\frac{d[B\text{—}M_n\text{—}A]}{d[B\text{—}M_{n+1}\text{—}A]} = C_n[AB]/[M] + C_n/C_{n+1} \qquad (4)$$

(where the left side is the ratio of n-unit telomer to n + 1-unit telomer). Thus the ratio of concentrations of one-unit to two-unit telomer at low conversion should show a simple linear relationship to the ratio of reactants. The first chain transfer constant should correspond to the slope and the second chain transfer constant should equal this slope divided by the intercept. Sets of these ratios determined in ten experiments are listed in Table I and the plot (Fig. 2) shows a good approximation of the linear relationship.

TABLE I

DATA FOR CALCULATION OF TELOMER CHAIN TRANSFER CONSTANTS

Run no.	Mole ratio EtSH/styrene	Mole % AIBN (compared to EtSH)	Time, hr.	% Styrene consumed	Mole ratio, one-unit/ two-unit
1	1.00	0.20	1.0	6.6	7.53
2	1.01	.20	2.5	11.0	7.38
3[a]	1.00	.20	6.0	25.0	7.28
4	0.753	.27	0.5		5.48
5	.502	.40	.5		3.76
6	.501	.39	1.0		3.77
7	.310	.00	1.0	3.0	2.48
8	.200	.98	1.5	2.6	1.75
9	.196	1.11	3.0	5.4	1.58
10	.068	0.00	1.0		0.88

[a] Not plotted in Fig. 2 or used in direct calculation of the slope.

The slope, as determined by the least squares method, is 7.15 and the intercept 0.24, corresponding to values of 7.15 for C_1 and 30 for C_2. The standard deviations are 0.12 for slope and 0.074 for the intercept, corresponding to limits of error of about ±0.3 for C_1 and ±10 for C_2 at the 5% probability level. However, examination of the results for runs number 1–3, 8, and 9 in Table I shows that a small but significant constant error is introduced by the change in mercaptan to monomer ratio as the reaction proceeds. Correction for this would raise the line slightly especially at the lower end. The resulting change in slope is small, but the relative change in intercept is substantial.[9]

Discussion

It is of interest to note that Sivertz[10] in reporting a study of the kinetics of addition of butanethiol to styrene estimated a value for the average k_p of 230 at thiol concentrations at which the propagation was assumed to be chiefly due to the one-unit radical. Combination of this with his value of 1.24×10^3 for K_d indicates a value of about 5.4 for C_1, which is comparable to the value reported above for the styrene–ethanethiol system.

The increase by a factor of 2.4 in the styrene ethanethiol transfer constant going from C_1 to C_∞ is substantially less than has been reported for the haloalkanes.[3] Since the electronegativity of sulfur on the Pauling scale is essentially the same as carbon, it seems unlikely that any polar effect would account for even this difference. Models indicate, however, that there should be appreciably less interference with the formation of the transition state for addition of monomer units to the one-unit radical as compared to radicals possessing two or more styrene units. Results indicate that the value for C_2 is certainly substantially higher than C_1 and may possibly be even higher than C_∞.

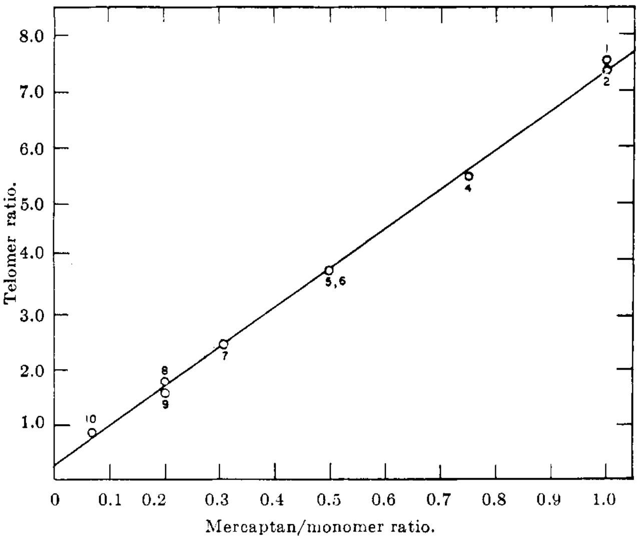

Fig. 2.—Relationship between one-unit to two-unit telomer mole ratio and ethanethiol to styrene mole ratio.

Information about the chain transfer constants C_3 to C_5 would be especially interesting for comparison with the bromotrichloromethane–styrene system[3c]; however, a different approach will probably be required because of the difficulty in isolating higher telomers.

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[9] Extrapolation of results from runs 1–3, 8 and 9 to zero per cent styrene consumed and substitution of the resulting ratios in equation 4 would lead to values of 7.03 for C_1 and 14 for C_2.

[10] C. Sivertz, *J. Phys. Chem.*, **63**, 34 (1959).

Photodimers of 4'-Substituted 2-Styrylpyridines[1]

J. L. R. Williams, J. M. Carlson, G. A. Reynolds, and R. E. Adel

Research Laboratories, Eastman Kodak Company, Rochester, New York

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Photodimers of 2-styrylpyridine and 5-ethyl-2-styrylpyridine substituted with CH_3O, CH_3, NO_2, and $(CH_3)_2N$ in the 4'-positions have been prepared. Irradiation of the free bases or the methiodide salts in solution gave difficultly separable mixtures of dimers, *cis* isomers, and *trans* isomers. Irradiation of the methiodide salts in the solid state yielded the dimeric salts in the cases of 2-styrylpyridine, 5-ethyl-2-styrylpyridine, and to a lesser degree with 4'-methyl-2-styrylpyridine. All other methiodide salts failed to dimerize when irradiated as solids. Solid-state dimerization of the methosulfate derivatives except the two 4'-dimethylamino-substituted derivatives was achieved. The dimeric methosulfates were then converted by anion exchange to the corresponding methiodide salts. Photodimerizations of the substituted styrylpyridine hydrochlorides in aqueous solution were successful in all cases except those of the 4'-nitro-substituted derivatives. Irradiation of suspensions of the hydrochloride salts in heptane gave similar results.

In preceding papers[2,3] the preparation of two photodimers of *trans*-2-styrylpyridine (Ia) was described and their relationship to the *trans–cis* photoisomerization of *trans*-2-styrylpyridine (Ia) was demonstrated. Solid-state irradiation of the methiodide (Ic) and the hydrochloride (Ie) salts to *trans*-2-styrylpyridine (Ia) produced dimers with the same configurations, as indicated by physical data. Solution irradiation of Ia produced only a mixture of *cis* and *trans* isomers. On the other hand, solution irradiation of the methiodide (Ic) or the hydrochloride (Ie) gave mixtures of *cis* and *trans* isomers as well as dimers. Dimer Id, obtained by irradiation of 2-styrylpyridine hydrochloride (Ie), in solution or in the solid state, followed by isolation and quaternization of the dimeric free base (Ib), was identical with dimer Id, obtained by solid-state irradiation of *trans*-2-styrylpyridine methiodide (Ic). In order to extend the dimerization study to substituted derivatives of *trans*-2-styrylpyridine and *trans*-5-ethyl-2-styrylpyridine, a group of derivatives with CH_3O, CH_3, NO_2, and $(CH_3)_2N$ in the 4'-positions were prepared.[4]

In the present work, it was found that 5-ethyl-2-styrylpyridine methiodide (VIc) photodimerized quan-

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[1] Contribution no. 2331 from the Kodak Research Laboratories.

[2] J. L. R. Williams, *J. Org. Chem.*, **25**, 1839 (1960).

[3] J. L. R. Williams, S. K. Webster, and J. A. VanAllan, *ibid.*, **26**, 4893 (1961).

[4] J L. R. Williams, *et al.*, *J. Org. Chem.*, in press.