# The Photochemistry of Unsaturated Nitrogen-Containing Compounds. III. The Mechanism of *cis*- and *trans*-Stilbene Formation from the Irradiation of Benzalazine

## ROGER W. BINKLEY

Department of Chemistry, Cleveland State University, Cleveland Ohio 44115

Received August 26, 1968

The direct irradiation of 4-methoxybenzalazine (9) in 2-propanol produces cis and trans isomers of stilbene, 4-methoxystilbene, and 4,4'-dimethoxystilbene; in addition, small quantities of benzalazine (1) and anisalazine (10) are also formed. cis- and trans-stilbene (2 and 3) and cis- and trans-4,4'-dimethoxystilbene (11 and 12) are shown not to arise from excitation of the small amounts of 1 and 10 produced photochemically. Irradiation of a mixture of 1 and 10 in 2-propanol also leads to cis and trans isomers of the unsubstituted, 4-methoxy-, and 4,4'-dimethoxystilbene systems; in this instance also the small amount of photochemically produced 4'-methoxybenzalazine (9) cannot account for cis- and trans-4-methoxystilbene (13 and 14) formed. Irradiation of trans-4-methoxystilbene system. Similarly, photolysis of a mixture of trans-stilbene (3) and trans-4,4'-dimethoxystilbene (12) gives none of the 4-methoxystilbene system. Irradiation of either benzalazine (1) with added trans-4,4'-dimethoxystilbene (13 or 14). These results along with previously reported observation on azine photochemistry are interpreted as requiring the azine to stilbene transformation to be an intermolecular process initiated by direct interaction between two azine systems. Possible mechanisms for this process are proposed and discussed.

In the initial publication in this series<sup>1</sup> it was reported that the irradiation of benzalazine (1) produced three photoproducts, benzaldimine, benzonitrile, and *trans*stilbene.<sup>2</sup> This original paper dealt primarily with the exploration of reaction conditions and determination of product identity, although some suggestions were made concerning possible reaction mechanisms. Since the completion of this initial study, the goal for further investigation of the photochemistry of **1** has been directed toward the determination of the mechanism for the reactions initiated by its excitation.

It is possible from an inspection of the results of benzalazine (1) photolyses to establish two classes of reaction products. The first category, which contains benzaldimine and benzonitrile, includes compounds derived from nitrogen-nitrogen bond cleavage. A study of the mode of formation of these two photoproducts is the subject of a previous paper.<sup>3</sup> The second classification, which includes  $cis^{-2}$  and transstilbene (2 and 3) consists of products resulting from a complete loss of nitrogen. The mechanism for formation of these latter two photoproducts is the subject of the work reported here.

$$C_{6}H_{5}CH = NN = CHC_{6}H_{5} \xrightarrow{1. h\nu \text{ in methanol}} 2. \text{ chromatographic separation} \\ C_{6}H_{5}C \equiv N + C_{6}H_{5}CHO + \\ C_{6}H_{5} = C_{6}H_{5} + C_{6}H_{5} + \\ H = H + C_{6}H_{5} + C_{6}H$$

In attempting to formulate a possible sequence of structural changes leading from an azine to a stilbene system, the mechanism shown in Scheme I represents one reasonable possibility. This process deserves special consideration due to the analogy between it and

SCHEME I

$$C_{6}H_{5}CH=NN=CHC_{6}H_{5} \xrightarrow{h\nu}$$

$$\begin{bmatrix} C_{6}H_{5} \\ N-CH \\ N-CH \\ N-CH \\ 0 \\ C_{6}H_{5} \end{bmatrix} \xrightarrow{h\nu (1)} C_{6}H_{5}CH=CHC_{6}H_{5} + N=N$$

the well-known photocyclization of dienes to cyclobutenes.<sup>4</sup> In focusing on a particular example it can be seen that the photochemical ring closure of the two conjugated carbon-nitrogen double bonds in 1 to form the cyclic azo compound 4 bears a strong resemblance to the known photochemical cyclization of 2,3-diphenylbutadiene (5) to give 1,2-diphenylcyclobutene<sup>5</sup> (6). A further parallel exists between the proposed decomposition of 4 as shown in Scheme I and the observed ring cleavage of 1,2-diphenylcyclobutene (6) to give ethylene and diphenylacetylene.<sup>5</sup>

$$CH_{2} = C(C_{6}H_{5})C(C_{6}H_{5}) = CH_{2} \xrightarrow{h\nu}$$

$$S \qquad isooctane$$

$$C_{6}H_{5} \qquad \downarrow \\ C - CH_{2} \xrightarrow{h\nu} C_{6}H_{5}C = CC_{6}H_{5} + CH_{2} = CH_{2}$$

$$C - CH_{2} \xrightarrow{h\nu} C_{6}H_{5}C = CC_{6}H_{5} + CH_{2} = CH_{2}$$

$$C_{6}H_{5} \qquad 6$$

A second mechanism for the photochemical formation of the stilbene system, one which is also based upon

<sup>(1)</sup> R. W. Binkley, J. Org. Chem., 33, 2311 (1968).

<sup>(2)</sup> Although not reported in ref 1, *cis*-stilbene has since been found to be a fourth product resulting from the irradiation of benzalazine (1). Its isolation and identification are described in the Experimental Section of this paper.

<sup>(3)</sup> R. W. Binkley, J. Org. Chem., in press.

<sup>(4)</sup> J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y. 1967, pp 502-515.

<sup>(5)</sup> E. H. White and J. P. Anholt, Tetrahedron Lett., 3937 (1965).

analogy to known photochemical processes, is shown in Scheme II. The beginning point in this second mechanism is the photochemical dimerization of two molecules of benzalazine (1) forming the substituted 1,2-diazetidine 7. Such a process is comparable to the reported photochemical dimerization of butadiene to cis- and trans-1,2-divinylcyclobutane.<sup>6</sup> The second step in the mechanistic sequence outlined in Scheme II

### SCHEME II



is the decomposition of 7 leading to cis- and transstilbene (2 and 3) and a conjugated azo compound.



This reaction is closely related to the proposed ring cleavage of substituted 1,2-diazetidine 8, a suggested intermediate in the photochemical conversion of N-pdimethylaminobenzylideneaniline to trans-azobenzene and cis-4,4'-bis(dimethylamino)stilbene<sup>7</sup> (Scheme III).



Since, based upon known photochemical processes, both of the two mechanisms just described can be classified as reasonable pathways leading to cis- and trans-stilbene (2 and 3) from benzalazine (1), an experimental test is needed to select between them. One basic difference between these two processes is that the first (Scheme I) is intramolecular while the second (Scheme II) is intermolecular; thus a suitable method of selection exists in the irradiation of a mixture of benzalazine (1) and a second, symmetrically substituted benzalazine to determine if any unsymmetrically substituted stilbene, the product of a crossover reaction,

(6) H. S. Hammond, N. J. Turro, and A. Fischer, J. Amer. Chem. Soc., 83, 4674 (1961).

							Vie	1d of produce	to a much V 1.				
				Amt				mood to pr				4,4'-Dim	aethoxy-
			%	irradiated,		4-Methoxy-		Still	bene	4-Methos	xystilbene-	still.	bene
Run	Reactant	Time, hr	completion	lomn	Benzalazine	benzalazine	Anisalazine	cis	trans	cie	trans	cie	trans
T	4-Methoxybenzalazine	120	55	3.00	8.1		8.0	0.66	0.66	3.0	2.0	0.50	0.66
7	Benzalazine,	36	58	1.50		8.2		1.2	1.4	2.3	1.6	0.87	0.66
	anisalazine			1.50									
ŝ	Anisalazine	150	51	3.00	None	None		None	None	None	None	2.0	2.2
4	Benzalazine	63	63	3.00		None	None	5.3	3.3	None	None	None	None
5	4-Methoxybenzalazine,	120	57	3.00	12.4	135.0	15.5	0.60	09.0	3.0	2.1	0.50	0.70
	benzalazine,			0.08									
	anisalazine			0.08									
9	Benzalazine,	36	56	1.50	24.5	15.1	100	1.2	1.4	2.3	1.7	0.90	0.70
	anisalazine,			1.50									
	4-methoxy-benzalazine			0.08									
2	Benzalazine,	36	58	3.00		None	None	5.3	3.3	None	None	1.8	2.0
	trans-4,4'-dimethoxystilbene			0.04									
90	Anisalazine,	150	50	3.00	None	None		<b>2.1</b>	2.2	None	None	2.0	2.2
	trans-stilbene												
6	Benzalazine,	36	63	3.00		None	None	4.0	4.2	None	None	None	None
	cyclohexene			36.0									
a The	total stilbene yield varies from 3 t	to 5% depe	nding upon th	e azine syster	n being studied.	The exact per	centage yields	of each sti	ilbene in an	w given run	are shown i	in the Expe	erimental
Section.													

(readiations of Benzalazine (1), 4-Methoxybenzalazine (9), and Anisalazine (10)

<sup>(7)</sup> S. Searles, Jr., and R. A. Clasen, Tetrahedron Lett., 1627 (1965).

is formed. A second means of distinguishing between the two, is the irradiation of an unsymmetrically substituted benzalazine. The formation of any stilbene system other than an unsymmetrically substituted one would require an intermolecular process.

In order to investigate in depth the benzalazine (1) to *cis*- and *trans*-stilbene (2 and 3) conversion and, specifically, to determine if this process is inter- or intramolecular, the photochemistry of 4-methoxy-benzalazine (9), anisalazine (10), and mixtures of benzalazine (1) and anisalazine (10) was investigated.

### Results

The results of the irradiation of compounds 1, 9, and 10 are shown in Table I. Each entry describes a direct irradiation in 2-propanol<sup>8</sup> run under nitrogen atmosphere. The reaction mixtures in each case were separated into their individual components by column chromatography on silicic acid.

When benzalazine (1) is irradiated (run 4, Table I), the only azine or stillbene products formed are *cis*- and *trans*-stillbene (2 and 3); likewise, irradiation of anisalamethoxybenzalazine (9) are benzalazine (1) and anisalazine (10); in a similar manner, from the irradiation of mixtures of 1 and 10, 9 results. Since each of the azine systems studied was found to be stable under reaction conditions in absence of light and also stable during isolation, azines, other than starting material, obtained during irradiation must arise from photochemical reaction. In each case the azine photoproducts represent only a small portion of total azine concentration at the termination of reaction. In run 5 (Table I), where a small amount of benzalazine (1) and anisalazine (10)are added to the reaction mixture prior to the irradiation of 4-methoxybenzalazine (9), no noticeable change occurs in the relative amount of the stilbenes formed. Run 6 (Table I) describes a similar observation from the irradiation of 1 and 10 where a small amount of 9 had been added.

In Table II the results are presented of the irradiation of *trans*-stilbene (3), *trans*-4-methoxystilbene (14), and *trans*-4,4'-dimethoxystilbene (12) under the same conditions as the previously described azine irradiations. In each case the well-established *cis*-*trans* isomerization of stilbenes<sup>10</sup> occurred; however, transformation from one stilbene system to another did not take place.





#### Discussion

zine (10) (run 3, Table I) leads only to *cis*- and *trans*-4,4'-dimethoxystilbene (11 and 12). If, on the other hand, either 4-methoxybenzalazine (9) or a mixture of 1 and 10 is irradiated *cis*- and *trans*-stilbene (2 and 3), *cis*- and *trans*-4,4'-dimethoxystilbene (11 and 12), and *cis*- and *trans*-4-methoxystilbene (13 and 14) are isolated<sup>9</sup> (runs 1 and 2, Table I). (See eq 3 and 4.)

Also produced in low yield from the photolysis of 4-

The photochemical reactions of 4-methoxybenzalazine (9) (eq 3, run 1 in Table I) and the parallel reactions of an equimolar mixture of benzalazine (1)

(9) Since the yield reported for certain stilbene photoproducts is small (see Table I), sometimes representing only a few milligrams of material, it is important to establish the reliability of the measurement of these small quantities. The meas of each photoproduct isolated by chromatography was determined first by weighing and then by quantitative uv analysis. If these techniques indicated equivalent amounts of material present and if this same quantity was found by analysis of a different irradiation mixture, the value obtained was accented as being correct.

obtained was accepted as being correct. (10) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1967, pp 506-507 and 544-545.

<sup>(8)</sup> In addition to 2-propanol, the azine to stilbene transformation of benzalazine to cis- and trans-stilbene has also been studied in methanol, ethanol, 2-propanol containing benzhydrol, and cyclohexane. The stilbene yields in these four solvent systems showed no marked change from the corresponding yields in 2-propanol.

TABLE II IRRADIATION OF *trans*-Stilbene (3), *trans*-4-Methoxystilbene (14), and *trans*-4,4'-Dimethoxystilbene (12)

	Time,		Amt irradiated,	Stilbene		Yield of products, %- 			
Run	hr	Reactant	mmol	cis	trans	cis	trans	cis	trans
1	8	trans-Stilbene	1.00	48	34	0	0	0	0
<b>2</b>	16	trans-4-Methoxystilbene	1.00	0	0	44	38	0	0
3	16	trans-4,4'-Dimethoxy- stilbene	1.00	0	0	0	0	22	59
4	16	trans-Stilbene trans-4,4'-Dimethoxy- stilbene	$\begin{array}{c} 0.50\\ 0.50\end{array}$	27	14	0	0	10	31

and anisalazine (10) (eq 4, run 2 in Table I) leading in each case to *cis* and *trans* isomers of stilbene, 4-methoxystilbene, and 4,4'-dimethxoystilbene indicate that the azine to stilbene transformation is an intermolecular process. These two reactions, however, do not require an intermolecular reaction pathway since it is possible to explain in several other ways the formation of all three stilbene systems in both reactions. Before making a judgement concerning the indicated intermolecularity of these reactions, it is necessary to consider the various ways in which the three stilbene systems might arise during photolysis.

One possible explanation for the formation of all three stilbene systems from the irradiation of 4-methoxybenzalazine (9) or a mixture of benzalazine (1) and anisalazine (10) is based upon the fact that, although in run 2 (Table I) the only azines in the reaction mixture at the outset were 1 and 10 and in run 1 (Table I) the only azine present at the start of reaction was 9, all three azines were isolated from both irradiation mixtures when the photolyses were terminated. The presence of 1, 9, and 10 in both reaction mixtures raises the possibility that each stilbene system is formed from direct excitation of the corresponding azine; however, if this proposal is correct, it requires that in run 2 (Table I), for example, the stilbene system formed in highest yield, cis- and trans-4-methoxystilbene (13 and 14), results from the irradiation of 4-methoxybenzalazine (9) which is not present in the original reaction mixture and represents only 6% of the total azine concentration when this irradiation is stopped (at 58% completion).

If 4-methoxybenzalazine (9) reacted to give *cis*- and trans-4-methoxystilbene (13 and 14) in much higher yield than the other azine to stilbene transformations [benzalazine (1) to cis- and trans-stilbene (2 and 3); anisalazine (10) to cis- and trans-4,4'-dimethoxystilbene (11 and 12) or if as the 4-methoxybenzalazine (9) was formed in run 2 (Table I) it reacted much more readily than either benzalazine (1) or anisalazine (10), it is conceivable that the sole source of cis- and trans-4methoxystilbene (13 and 14) in run 2 (Table I) could be 4-methoxybenzalazine (9); however, further consideration of Table I reveals that both of these possibilities are inconsistent with experimental result. First, in runs 1 and 4 of Table I it is evident that the 4methoxybenzalazine (9) to cis- and trans-4-methoxystilbene (13 and 14) reaction is not a much higher yield process than the other azine to stilbene transformations; in fact, benzalazine (1) reacts to give cisand trans-stilbene (2 and 3) in a somewhat higher yield (4.6%) than does 4-methoxybenzalazine (9) react to give cis- and trans-4-methoxystilbene (13 and 14) (2.4%). Second, a comparison of irradiation times and per cent conversions for 1, 9, and 10 should give a qualitative estimation of their relative reactivity since the uv spectra of all three azines are very similar and, thus, each of them absorbs approximately the same quantity of light during a given irradiation time. Such a comparison between runs 1 and 4 (Table I) show that benzalazine (1) actually reacts more rapidly than 4-methoxybenzalazine (9); therefore, the second of the possible explanations suggested above, that 9 reacts much more readily than the other azines, cannot be correct. On the basis of the above comparisons, the possibility that cis- and trans-4-methoxystilbene (13 and 14) arise as secondary products from the excitation of the small amount of photochemically produced 4-methoxybenzalazine (9) is not a workable explanation for 13 and 14 being the major stilbene systems formed in the irradiation of the benzalazine (1)-anisalazine (10) mixture; in addition, the further consideration of this possibility and the direct experimental test described below argue for the exclusion of this proposed explanation.

Considered from another point of view, the possibility that each stilbene system is formed from direct excitation of the corresponding azine again produces an unsatisfying explanation. If it is assumed that in run 2 of Table I the major stilbene photoproducts, cis- and trans-4-methoxystilbene (13 and 14), result solely from irradiation of 4-methoxybenazalazine (9), then it is also necessary to make the assumption that 9 is considerably more effective at the azine to stilbene transformation than are benzalazine (1) or anisalazine (10), since both 1 and 10 are present in the reaction mixture in much greater concentration than is 9. Making these two assumptions, however, requires an explanation for the fact that in run 1 (Table I) 4-methoxybenzalazine (9), the starting material, and hence, most abundant azine, loses its special effectiveness at the azine to stilbene transformation. In this case, any special reactivity would have to be ascribed to benzalazine (1) and anisalazine (10) since, even though 1 and 10 represent only a small portion of the azine concentration, cis- and trans-stilbene (2 and 3) and cis- and trans-4,4'-dimethoxystilbene (11 and 12) account for a substantial percentage of the stilbenes formed.

Although based upon the considerations discussed above it does not appear possible that in runs 1 and 2 (Table I) each stilbene system was formed from direct excitation of the corresponding azine, an experimental test was conducted to determine if deliberate addition of small quantities of benzalazine (1) and anisalazine (10) in run 1 and 4-methoxybenzalazine (9) in run 2 would affect the yield of the various stilbenes. The results of these experiments are described in runs 5 and 6

(Table I). In both cases the amount of each stilbene formed did not noticeably change as a result of these small azine additions (compare runs 1 and 5 and runs 2 and 6 of Table I). The conclusion derived both from these experiments and from consideration of the irradiations (runs 1-4, Table I) which have been discussed above is that, although the photochemical formation of benzalazine (1) and anisalazine (10) in run 1 (Table I) is an interesting photochemical process, the cis- and trans-stilbene (2 and 3) and cis- and trans-4,4'-dimethoxystilbene (11 and 12) produced in run 1 (Table I) do not arise in any significant quantity from the photolysis of 1 and 10; likewise, the cis- and trans-4methoxystilbene (13 and 14) formed in run 2 (Table I) do not arise from excitation of 4-methoxybenzalazine (9).

Even though a consideration of reactions 1-6 in Table I leads to the conclusion that the photochemical stilbene forming process is not, in general, one in which each azine molecule is transformed directly into the corresponding stilbene, several explanations still exist for rationalizing the presence of all three stilbene systems in irradiations where either 4-methoxybenzalazine (9) or a mixture of benzalazine (1) and anisalazine (10) are the starting materials. One such possibility is that in the irradiation of 9, for example, *cis*- and *trans*-4-methoxystilbene (13 and 14) may be the only stilbenes formed directly and that the *cis*- and *trans*-stilbene (2 and 3) and *cis*- and *trans*-4,4'-dimethoxystilbene (11 and 12) result from a photochemical reaction of 13 or 14, perhaps one such as that shown in Scheme IV.



In order to test experimentally the possibility that two molecules of 4-methoxystilbene might interact photochemically in an exchange reaction to produce a molecule of stilbene and one of 4,4'-dimethoxystilbene, trans-4-methoxystilbene (14) was irradiated. The irradiation of 14 is described in run 2 of Table II. Although cis-trans isomerization occurred during this reaction, neither the stilbene nor the 4,4'-dimethoxystilbene system was formed. In a similar experiment where a mixture of trans-stilbene (3) and trans-4,4'dimethoxystilbene (12) was irradiated (run 4, Table II), none of the 4-methoxystilbene system was formed. The results from these experiments exclude the possibility that the formation of all six stilbenes during the irradiation of either 4-methoxybenzalazine (9) or a mixture of benzalazine (1) and anisalazine (10) arises from a secondary photochemical reaction between two stilbene systems.

Although the potentiality of two stilbene molecules reacting with each other in a crossover process as an explanation for the formation of all three stilbene systems in reactions 1 and 2 (runs 1 and 2 of Table I) has been excluded, a direct intermolecular reaction between two azine molecules leading to a molecule of a stilbene is not the only remaining possibility. A plausible explanation for the product distribution in runs 1 and 2 (Table I) is that in the irradiation of 4-methoxybenzalazine (9), for example, the only stilbenes formed directly are *cis*- and *trans*-4-methoxystilbene (13 and 14); however, once these compounds are produced, they undergo a reaction such as that shown in Scheme V. In this example a molecule of 13





combines photochemically with one of 9 leading ultimately to the stilbene and the 4,4'dimethoxystilbene systems. The first step of this proposed process is, in effect, a photochemical Diels-Alder reaction; similar processes are known in the photochemistry of conjugated dienes<sup>6</sup> (eq 2). The second step, the one producing the two stilbenes, is initiated by the wellestablished photolytic loss of nitrogen from an azo compound.<sup>11</sup>

The possibility that azine and stilbene molecules interact photochemically and, thereby, effect the identity of the stilbene systems isolated was tested directly first by addition of trans-4,4' dimethoxystilbene (12) to a benzalazine (1) irradiation (run 7, Table I) and second by the addition of trans-stilbene (3) to an anisalazine (10) irradiation (run 8, Table I). If an interaction between azine and stilbene molecules was occurring, it would have been reflected in both of these

(11) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., pp 230-232. In examining possible reaction mechanisms which are consistent with the experimental results from the various azine and stilbene irradiations, it is important to consider related work which has been reported on the mechanism of thermal decomposition of azines. In studying the thermal reaction of benzalazine (1) to give *trans*-stilbene (3), Zimmerman and Somasekhara found an intermolecular process to be operative.<sup>12</sup> They explained this reaction on the basis of a chain mechanism in which phenyldiazomethane was shown to be the chain carrying species. These authors also

$$\begin{array}{l} \operatorname{Ar\bar{C}H} \overset{\sim}{N} = N + \operatorname{ArCH} = NN = \operatorname{CHAr} \xrightarrow{\Delta}_{C_{6}H_{6}} \\ \left[ \begin{array}{c} \operatorname{ArCHN} = N\bar{C}HAr \\ \operatorname{ArCHN} = N \\ \operatorname{ArCHN} = N \\ \end{array} \right] \longrightarrow \operatorname{ArCH} = \operatorname{CHAr} + \operatorname{Ar\bar{C}H} \overset{+}{N} = N + N_{2} \end{array}$$

irradiated a mixture of phenyldiazomethane and benzalazine (1) and observed that no apparent reaction occurred; in particular, no *cis* or *trans* stilbene (2 and 3)was formed. This experiment shows that the mechanism for the photochemical azine to stilbene reaction cannot be the same as that for the corresponding thermal reaction; in other words, the photochemical reaction does not involve phenyldiazomethane as a chain carrying species.

A second intermolecular mechanism which was considered as a candidate for explaining the formation of *trans*-stilbene (3) from pyrolysis of benzalazine  $(1)^{12}$ suggests another chain mechanism, one in which phenylcarbene is the chain carrying species. The *trans*-stilbene (3) forming step in this process is the attack of phenylcarbene on a second molecule of benzalazine (1). Evidence from three sources argues against such a process being operative in the photochemical reaction. First, the previously described

$$C_6H_5CH: + C_6H_5CH=NN=CHC_6H_5\xrightarrow{no}$$
  
reaction

 $C_6H_5CH = CHC_6H_5 + C_6H_5CHN = \dot{N}$ 

irradiation of a mixture of benzalazine (1) and phenyldiazomethane by Zimmerman and Somasekhara<sup>12</sup> is reported by these authors to have produced phenyl carbene in the presence of 1 but resulted in no stilbene formation. Second, the ether produced from the known insertion of an aryl carbene into an oxygenhydrogen bond of an alcohol<sup>13</sup> was not observed in the reactions described in the present study even though these irradiations were conducted in 2-propanol; in addition, the ether-forming reaction with solvent should have disrupted any intermolecular reaction between phenyl carbene and benzalazine (1). Finally, the addition to the irradiation mixture of cyclohexene (run 9, Table I), a compound known to produce cyclopropane adducts with phenyl carbene,<sup>14</sup> gave no indication of such adducts; also there was no decrease in the amount of *cis*- and *trans*-stilbene formed when cyclohexene was added to the reaction mixture. The results from these experiments exclude the possibility that phenyl carbene is an intermediate in the azine to stilbene conversion.

Based upon considerations made thus far the following facts are clear: (a) stilbene photoproducts undergo *cis-trans* isomerism but do not interact with each other to produce new stilbenes; (b) stilbenes formed photochemically do not react with unconsumed azine to give new stilbenes; (c) the azine to stilbene reaction must be, at least in part, intermolecular (a small amount of intramolecular azine to stilbene reaction is not inconsistent with the observations made here; however, the fact that such a process must be a minor one is evident from a consideration of run 2 in Table I where the major stilbene products must arise *via* intermolecular reaction); (d) the azine to stilbene reaction does not involve phenyldiazomethane or phenylcarbene.

There are two related mechanisms for the azine to stilbene conversion, both of which possess reasonable analogy to known reactions and are consistent with the facts listed above. Each involves the photochemically initiated direct interaction between two azine systems. The first of these, one which is pictured in Scheme II, has already been considered in the introductory portion of this paper. At the time of this earlier consideration analogy between this mechanism and the known photochemical transformations of butadiene<sup>6</sup> and of N-p-dimethylaminobenzylideneaniline<sup>7</sup> was described. This reaction sequence is given again, in greater detail, in Scheme VI in order to show the manner in which a symmetrically substituted stilbene could arise from the irradiation of 4-methoxybenzalazine (9). The process by which an unsubstituted or unsymmetrically substituted stilbene would result from irradiation of 9 is completely analogous.

It is of interest to note that the mechanism described in Scheme VI also provides a possible pathway for the photochemical syntheses of azines not present in the reaction mixture at the initiation of irradiation; thus, one mode for decomposition of the substituted 1,2diazetidine 15, produced by irradiation of 4-methoxybenzalazine (9), leads to the formation of the conjugated azo system 16 (path A). The further loss of nitrogen from 16 logically yields benazalazine (1). The actual existence of 16 is not required for benazlazine (1) formation since the intermediate 15 could decompose directly to give the 4,4-dimethoxystilbene system, molecular nitrogen, and two C6H5CH-N radicals The dimerization of these radicals produces (path B). benzalazine (1). This phenomenon of photochemical azine formation already has been presented and discussed<sup>15</sup> and will be the subject of a forthcoming paper.

The second of these two related mechanisms also begins with the photochemical dimerization of two azine systems. This process is shown in Scheme VII, using, in this instance, 4-methoxybenazlazine (9) as the starting material. This mechanism differs from that just discussed only by the manner in which the two

<sup>(12)</sup> H. E. Zimmerman and S. Somasekhara, J. Amer. Chem. Soc., 82, 5865, (1960).

<sup>(13)</sup> W. Kirmse, L. Horner, and H. Hoffmann, Ann., 614, 19 (1958).

<sup>(14)</sup> G. L. Closs and L. E. Closs, Tetrahedron Lett., 26 (1960).

<sup>(15)</sup> R. W. Binkley, Abstracts, First Central Regional Meeting American Chemical Society, Akron, Ohio, May 1968, No. 116.





17



CH <sub>3</sub> O-CH=CH-OCH <sub>3</sub>
11 and 12

azines dimerize. In the reaction sequence now under consideration (Scheme VII) the dimerization of two molecules of 9 produces a six-membered heterocyclic ring in a photochemical Diels-Alder reaction. As was mentioned above, photochemically initiated Diels-Alder reactions are well known in other diene-type systems<sup>6,16-18</sup> (see eq 2). The second step of the proposed process is the photochemical loss of nitrogen from the cyclic azo system 17 to yield 4,4-dimethoxystilbene and benzalazine (1).

The two mechanisms which have just been discussed

(Schemes VI and VII) actually represent variations of the same basic process, namely, the photochemical dimerization of two azine molecules as the critical step in stilbene formation. A choice between the two based upon the existing experimental data is not possible; in fact, it cannot be stated with certainty that either of these two processes represents the correct mechanism. What is certain is that both of them are consistent with the four experimentally derived requirements previously mentioned; in addition, a systematic consideration of the accumulated evidence has excluded other simple reaction pathways which provided reasonable potential mechanisms.

In conclusion, it is certain that the azine to stilbene transformation is to a large extent an intermolecular reaction. This reaction, unlike the corresponding thermal one, does not involve phenyldiazomethane. Phenylcarbene is also not important in this photochemical process. The mechanisms shown in Schemes VI and VII represent reasonable ways in which two azine molecules could interact to produce a molecule of stilbene. Both of these are consistent with the available experimental data but neither of them is required by these data. They represent at this point the most likely explanations for the azine to stilbene transformation.

#### Experimental Section<sup>19</sup>

Since the weights of the various stilbene photoproducts obtained from chromatography of the irradiation mixtures were generally small, each weight was checked by quantitative uv analysis. In all experiments reported the direct weight and the amount of material present determined by uv analysis were always in agreement. The per cent yields given are based upon reacted starting material. Each irradiation described was run with constant stirring using a 100-W Hanovia high pressure quartz mercury-vapor lamp which had been lowered into a

<sup>(16)</sup> J. P. Simons, Trans. Faraday Soc., 56, 391 (1960).

<sup>(17)</sup> G. O. Schenck, J. Kuhls, and C. H. Krauch, Ann., 693, 20 (1966).

<sup>(18)</sup> J. A. Barltrop and B. Hesp, J. Chem. Soc., 5182 (1965).

<sup>(19)</sup> All melting points were taken on a Fisher-Johns block and are corrected.

water-cooled quartz immersion well. Prepurified nitrogen was passed through the solutions for 1.0 hr prior to irradiation and a slow stream of nitrogen was continued during photolysis. No filter was used. Although benzonitrile and benzaldehyde were detected in most reaction mixtures, no attempt was made to analyze for these or other aldehydes and nitriles.

Irradiation of 4-Methoxybenzalazine<sup>12</sup> (9) in 2-Propanol.—In a typical run 714 mg (3.00 mmol) of 4-methoxybenzalazine in 900 ml of anhydrous 2-propanol was irradiated for 120 hr at 25°. After termination of irradiation, the solvent was removed by distillation *in vacuo* below 35°, leaving a deep yellow solid which was chromatographed on an  $80 \times 2.5$  cm silicic acid column slurry packed in 1:9 ether-hexane; 20-ml fractions were collected. The column was eluted as follows: 0.5 l. of hexane, 0.5 l. of 1:99 ether-hexane, 0.5 l. of 1:49 ether-hexane, 0.5 l. of 1:24 ether-hexane, 0.5 l. of 1:12 ether-hexane, 0.5 l. of 1:6 ether-hexane, 0.5 l. of 1:3 ether-hexane, and 0.5 l. of 1:1 etherhexane.

Fractions 20-23 yielded 1.2 mg (0.0067 mmol, 0.4%) of a clear oil, identified as cis-stilbene by comparison of the ir and uv spectra with an authentic sample.<sup>20</sup> Fractions 23-33 gave 1.2 mg (0.0066 mmol, 0.4%) of crystalline *trans*-stilbene, mp 123–124° (lit.<sup>21</sup> mp 124°). It was identical in ir spectrum with and a mixture melting point showed no depression with an authentic sample.<sup>20</sup> Fractions 68-75 yielded 6.3 mg (0.030 mmol, 1.8%) of a clear oil shown to be cis-4-methoxystilbene by ir and uv spectral comparison with an independently synthesized sample.22 Fractions 76-91 afforded 4.9 mg of white solid, mp 129-135°, recrystallized for hexane to leave 4.2 mg (0.020 mmol, 1.2%) of white needles, mp 134-135°, identical in ir spectrum and showing no mixture melting point depression with a sample of trans-4-methoxystilbene (lit.<sup>12</sup> mp 132-134°) synthesized according to the procedure of Adkins and Zartman.<sup>23</sup> Fractions 105-111 yielded 1.2 mg (0.0050 mmol, 0.3%) of cis-4,4'-dimethoxystilbene, identical in ir and uv spectra with a sample synthesized according to the procedure of Schlenk.<sup>24</sup> Fractions 112-118 gave 1.6 mg (0.0066 mmol, 0.4%) of a white crystalline solid, mp 209-212°, identical in ir spectrum and showing no mixture melting point depression with an authentic sample<sup>25</sup> of trans-4,4'-dimethoxystilbene (lit.<sup>26</sup> mp 212°). Fractions 129-138 afforded 18.1 mg of yellow solid, mp 88-93°, recrystallized from hexane to give 16.8 mg (0.081 mmol, 4.9%) of yellow needles, mp 93-94°, shown by ir and uv spectroscopy to be benzalazine (lit.<sup>27</sup> mp 93°). Fractions 148-170 produced 322 mg of unreacted 4-methoxybenzalazine, mp 84-86° (lit.<sup>12</sup> mp 83-84°). Fractions 180-201 gave 216 mg (0.080 mmol, 4.9%) of yellow crystals, mp 164–165°, shown by ir spectroscopy and mixture melting point comparison to be anisalazine (lit.<sup>27</sup> mp 168°).

Irradiation of a Mixture of Benzalazine (1) and Anisalazine (8) in 2-Propanol.—Benzalazine (312 mg, 1.50 mmol) and anisalazine (402 mg, 1.50 mm) in 900 ml of anhydrous 2-propanol were irradiated at 25°. After 36 hr, the solvent was removed by distillation *in vacuo* below 30°, leaving an oily yellow solid which was chromatographed on an  $81 \times 2.5$  cm silicic acid column slurry packed in 1:10 ether-hexane; 20-ml fractions were collected. The column was eluted as follows: 0.5 l. of hexane, 0.5 l. of 1:99 ether-hexane, 0.5 l. of 1:12 ether-hexane, 0.5 l. of 1:2 ether-hexane.

Fractions 21-24 yielded 2.2 mg (0.012 mmol, 0.7%) of cisstilbene, identified by ir and uv spectroscopy. Fractions 25-36 gave 2.9 mg of white crystals, mp 118-122°, yielding after one recrystallization from hexane 2.5 mg (0.014 mmol, 0.8%) of trans-stilbene, mp 122-124°. Fractions 74-82 afforded 4.8 mg (0.023 mmol, 1.3%) of cis-4-methoxystilbene, also identified by ir and uv spectroscopy. Fractions 83-90 gave 3.3 mg (0.016 mmol, 0.9%) of trans-4-methoxystilbene, mp 133-135°. Fractions 95-101 yielded 2.1 mg (0.0087 mm, 0.5%) of cis-4,4'dimethoxystilbene, identified by ir and uv spectroscopy. Fractions 109-114 produced 1.6 mg (0.0066 mmol, 0.4%) of trans4,4'-dimethoxystilbene, mp 209-210°. Fractions 118-139 yielded 51 mg of benzalazine, mp 91-93°. Fractions 150-163 afforded 26.7 mg of yellow solid, mp 75-80°, recrystallized from ether-hexane to give 19.5 mg (0.082, 4.7%) of 4-methoxybenzalazine, mp 84-85°. Fractions 166-186 gave 288 mg of yellow solid, mp 150-160°, recrystallized from methanol to give 267 mg of anisalazine, mp 164-165°.

Test of the Stability of 4-Methoxybenzalazine (9) under Reaction and Isolation Conditions.—4-Methoxybenzalazine (238 mg, 1.00 mmol) was dissolved in 300 ml of anhydrous 2-propanol, stirred for 120 hr at 25° under nitrogen and the solvent removed by distillation *in vacuo* below 35°. The residual solid was chromatographed on an 80  $\times$  2.5 cm silicic acid column slurry packed in 1:9 ether-hexane; 20-ml fractions were collected. The column was eluted as follows: 0.5 l. of hexane, 0.5 l. of 1:49 ether-hexane, 0.5 l. of 1:24 ether-hexane, 1.0 l. of 1:12 ether-hexane, and 0.5 l. of 1:6 ether-hexane. Fractions 145-165 afforded 236 mg of 4-methoxybenzalazine, mp 86-86°. No stilbenes or other azines were present.

Test of the Stability of Benzalazine (1) and Anisalazine (8) under Reaction and Isolation Conditions.—Benzalazine has previously been shown to be stable under reaction and isolation conditions.<sup>1</sup> Anisalazine was subjected to procedure identical with that described above for 4-methoxybenzalazine and found to be stable.

Irradiation of Benzalazine (1) in 2-Propanol.—Benzalazine (624 mg, 3.00 mmol) in 900 ml of anhydrous 2-propanol was irradiated at 25°. After 36 hr, the solvent was removed by distillation *in vacuo* below 30°, leaving a yellow oil which was chromatographed on a  $78 \times 2.5$  cm column of silicic acid slurry packed in 1:10 ether-hexane; 20-ml fractions were collected. The column was eluted as follows: 1.0 l. of hexane, 0.5 l. of 1:24 ether-hexane, and 0.5 l. of 1:12 ether-hexane.

Fractions 22-26 yielded 9.6 mg (0.053 mmol, 2.8%) of *cis*stilbene, identified by ir spectroscopy. Fractions 27-38 afforded 6.0 mg (0.033 mmol, 1.8%) of *trans*-stilbene, mp 120-123°. Fractions 135-149 gave 237 mg of unreacted benzalazine, mp 90-93°.

Irradiation of Anisalazine (10) in 2-Propanol.—Anisalazine (805 mg, 3.00 mm) in 900 ml of 2-propanol was irradiated at  $25^{\circ}$ . After 150 hr, the solvent was removed by distillation *in vacuo* below 30°, leaving a yellow solid which was chromatographed on an 80  $\times$  2.5 cm silicic acid column slurry packed in 1:10 ether-hexane; 20-ml fractions were collected. The column was eluted as follows: 0.5 l. of 1:49 ether-hexane, 0.5 l. of 1:24 ether-hexane; 0.5 l. of 1:12 ether-hexane, 0.5 l. of 1:6 ether-hexane, 0.5 l. of 1:3 ether-hexane, and 0.5 l. of 1:1 ether-hexane.

Fractions 51-59 gave 4.8 mg (0.020 mmol, 1.3%) of cis-4,4'-dimethoxystilbene, identified by ir and uv spectroscopy. Fractions 60-72 yielded 5.2 mg (0.022 mmol, 1.4%) of trans-4,4'-dimethoxystilbene, mp 207-208°. Fractions 98-127 produced 385 mg of unreacted anisalazine, mp 159-164°.

Irradiation of 4-Methoxybenzalazine (9) with Small Amounts of Benzalazine (1) and Anisalazine (10) Added.—4-Methoxybenzalazine (714 mg, 3.00 mmol), benzalazine (17 mg, 0.08 mmol), and anisalazine (21 mg, 0.08 mmol) dissolved in 2propanol were irradiated for 120 hr at  $25^{\circ}$ . After completion of irradiation, the solvent was removed by distillation *in vacuo* below 30°, leaving a yellow solid which was chromatographed on an  $85 \times 2.5$  cm silicic acid column slurry packed in 1:9 ether-hexane; 20-ml fractions were collected. The column was eluted as follows: 0.5 l. of hexane, 0.5 l. of 1:99 ether-hexane, 0.5 l. of 1:49 ether-hexane, 0.5 l. of 1:24 ether-hexane, 0.5 l. of 1:12 ether-hexane, 0.5 l. of 1:6 ether-hexane, 0.5 l. of 1:3 ether-hexane, and 0.5 l. of 1:1 ether-hexane.

Fractions 22-26 yielded 1.2 mg (0.0060 mmol, 0.5%) of cis-stilbene, identified by ir and uv spectroscopy. Fractions 27-37 gave 1.2 mg (0.006 mmol, 0.4%) of trans-stilbene, mp 120-124°. Fractions 79-88 afforded 6.3 mg (0.030 mmol, 1.8%) of cis-4-methoxystilbene, identified by ir and uv spectroscopy. Fractions 89-96 gave 4.4 mg (0.021 mmol, 1.2%) of trans-4-methoxystilbene, mp 133-134°. Fractions 109-115 yielded 1.2 mg (0.0050 mmol, 0.3%) of cis-4,4'-dimethoxystilbene, identified by ir and uv spectroscopy. Fractions 116-121 gave 1.9 mg (0.0070 mmol, 0.5%) of trans-4,4'-dimethoxystilbene, mp 206-210°. Fractions 131-145 afforded 31 mg of yellow crystals, mp 88-90°, recrystallized form hexane to give 26 mg (0.124 mmol) of benzalazine, mp 93-94°. Fractions 155-173 produced

<sup>(20)</sup> Matheson Coleman and Bell, Norwood, Ohio 45212.

<sup>(21)</sup> A. Michaelis and H. Lange, Ber., 8, 1314 (1875).

<sup>(22)</sup> L. Zechmeister and W. H. McNeeley, J. Amer. Chem. Soc., 64, 1919 (1942).

<sup>(23)</sup> H. Adkins and W. Zartmen, Org. Syn., 17, 89 (1943).

<sup>(24)</sup> W. Schlenk and E. Bergmann, Ann., 463, 123 (1928).

<sup>(25)</sup> Aldrich Chemical Co., Inc., Milwaukee, Wisc.

<sup>(26)</sup> H. Wiechell, Ann., 279, 341 (1894).

<sup>(27)</sup> T. Curtius and R. Jay, J. Prakt. Chem., [2] 39, 45 (1889).

320 mg of 4-methoxybenzalazine, mp 82-85°. Fractions 180-200 gave 52 mg of yellow crystals, mp 155-164°, recrystallized from ethanol to give 42 mg (0.155 mmol) of anisalazine, mp 163-164°.

Irradiation of a Mixture of Benzalazine (1) and Anisalazine (10) with a Small Amount of 4-Methoxybenzalazine (9) Added.— Benzalazine (312 mg, 1.50 mmol), anisalazine (402 mg, 1.50 mmol), and 4-methoxybenzalazine (19 mg, 0.080 mmol) in 900 ml of 2-propanol were irradiated at 25°. After 36 hr, the solvent was removed by distillation *in vacuo* below 30°, leaving a yellow oil which was chromatographed on a 79  $\times$  2.5 cm silicic acid column slurry packed in 1:10 ether-hexane; 20-ml fractions were collected. The column was eluted as follows: 0.5 l. of hexane, 0.5 l. of 1:99 ether-hexane, 0.5 l. of 1:49 ether-hexane, 0.5 l. of 1:24 ether-hexane, 0.5 l. of 1:12 ether-hexane, 0.5 l. of 1:6 ether-hexane, 0.5 l. of 1:3 ether-hexane, and 0.5 l. of 1:2 ether-hexane.

Fractions 19–23 yielded 2.2 mg (0.012 mmol, 0.7%) of cisstilbene, identified by ir and uv spectroscopy. Fractions 24-33 gave 2.5 mg (0.014 mmol, 0.8%) of trans-stilbene, mp 121-124°. Fractions 74-82 afforded 4.8 mg (0.023 mmol, 1.3%) of cis-4methoxystilbene, identified by ir and uv spectroscopy. Fractions 83-93 gave 3.6 mg (0.017 mmol, 0.9%) of trans-4-methoxystilbene, mp 131-135°. Fractions 100-104 yielded 2.2 mg (0.0087 mmol, 0.5%) of cis-4,4'-dimethoxystilbene, identified by ir and uv spectroscopy. Fractions 105-113 produced 2.2 mg of white solid, mp 200-210°, recrystallized from ethanol to give 1.7 mg (0.0070 mmol, 0.4%) of trans-4,4'-dimethoxystilbene, mp 207-210°. Fractions 118-138 yielded 69 mg of yellow solid, mp 81-87°, recrystallized from hexane to give 53 mg of benzalazine, mp 90-92°. Fractions 145-163 afforded 42 mg of yellow solid, mp 79-86°, recrystallized from ether-hexane to give 36 mg (0.151 mmol) of 4-methoxybenzalazine, mp 84-86°. Fractions 170-187 gave 279 mg of yellow solid, mp 155-160°, recrystallized from ethanol to give 260 mg of anisalazine, mp 163°.

Irradiation of Benzalazine (1) with Added trans-4,4'-Dimethoxystilbene (12).—Benzalazine (624 mg, 3.00 mmol) and trans-4,4'-dimethoxystilbene (10 mg, 0.04 mmol) in 900 ml of anhydrous 2-propanol were irradiated at 25°. After 36 hr, the solvent was removed by distillation *in vacuo* below 30°, leaving a yellow oil which was chromatographed on an  $80 \times 2.5$  cm silicic acid column slurry packed in 1:10 ether-hexane; 20-ml fractions were collected. The column was eluted as follows: 1.0 l. of hexane, 0.5 l. of 1:49 ether-hexane, 0.5 l. of 1:24 etherhexane, 0.5 l. of 1:12 ether-hexane, and 0.5 l. of 1:6 etherhexane.

Fractions 23–27 yielded 9.6 mg (0.053 mmol, 2.8%) of *cis*stilbene, identified by ir and uv spectroscopy. Fractions 28–40 afforded 6.0 mg (0.033 mmol, 1.8%) of *trans*-stilbene, mp 120–124°. Fractions 99–107 gave 4.3 mg (1.8 mmol) of *cis*-4,4'-dimethoxystilbene, identified by ir and uv spectroscopy. Fractions 108–120 produced 4.8 mg of *trans*-4,4'-dimethoxystilbene, mp 205–209°. Fractions 135–150 gave 240 mg of benzalazine, mp 90–92°.

Irradiation of Anisalazine (10) with Added trans-Stilbene (3).—Anisalazine (805 mg, 3.00 mmol) and trans-stilbene (10 mg, 0.05 mmol) in 900 ml of 2-propanol were irradiated at 25°. After 150 hr of irradiation, the solvent was removed by distillation *in vacuo* below 30°, leaving a yellow solid which was chromatographed on a  $75 \times 2.5$  cm column of silicic acid slurry packed in 1:10 ether-hexane; 20-ml fractions were collected. The column was eluted as follows: 1.0 l. of hexane, 0.5 l. of 1:24 ether-hexane, 0.5 l. of 1:12 ether-hexane, 0.5 l. of 1:16 ether-hexane, 0.5 l. of 1:3 ether-hexane, and 0.5 l. of 1:1 ether-hexane.

Fractions 20-24 afforded 3.8 mg (0.021 mmol) of *cis*stilbene, identified by ir and uv spectroscopy. Fractions 25-40 gave 4.0 mg (0.022 mmol) of *trans*-stilbene, mp 123-124°. Fractions 50-59 gave 4.8 mg (0.020 mmol) of *cis*-4,4'-dimethoxystilbene, identified by ir and uv spectroscopy. Fractions 60-72 yielded 5.2 mg (0.022 mmol) of *trans*-4,4'-dimethoxystilbene, mp 207-208°. Fractions 100-135 produced 375 mg of unreacted anisalazine, mp 157-164°.

Irradiation of Benzalazine (1) in 2-Propanol with Added Cyclohexene.—Benzalazine (624 mg, 3.00 mmol) and cyclohexene (2.46 g, 30.0 mmol) in 900 ml of 2-propanol were irradiated at 25°. After 36 hr, the solvent was removed by distillation *in vacuo* below 30°, leaving a yellow oil which was chromatographed on a  $79 \times 2.5$  cm column of silicic acid slurry packed in 1:10 ether-hexane; 20-ml fractions were collected.

The column was eluted as follows: 1.0 l. of hexane, 0.5 l. of 1:49 ether-hexane, 0.5 l. of 1:24 ether-hexane, and 0.5 l. of 1:12 ether-hexane.

Fractions 21-26 yielded 7.2 mg (0.040 mmol, 2.1%) of *cis*stilbene, identified by ir and uv spectroscopy. Fractions 27-40 gave 7.6 mg (0.042 mmol, 2.2%) of *trans*-stilbene, mp 122-124. Fractions 131-150 afforded 241 mg of unreacted benzalazine, mp 91-93°.

Irradiation of trans-4-Methoxystilbene (14) in 2-Propanol. trans-4-Methoxystilbene (210 mg, 1.00 mmol) in 300 ml of anhydrous 2-propanol was irradiated for 16 hr at 25°. After irradiation, the solvent was removed by distillation *in vacuo* below 35°, leaving a clear oil which was chromatographed on an  $80 \times 2.5$  cm column of silicic acid slurry packed in 1:9 ether-hexane; 20-ml fractions were collected. The column was eluted as follows: 0.5 l. of hexane, 0.5 l. of 1:99 ether-hexane, and 0.5 l. of 1:49 ether-hexane.

Fractions 65-72 gave 93 mg of *cis*-4-methoxystilbene, identified by ir and uv spectroscopy. Fractions 73-85 afforded 80 mg of *trans*-4-methoxystilbene, mp 132-134°. Neither the stilbene or the 4,4'-dimethoxystilbene system was present in the reaction mixture.

Irradiation of trans-Stilbene (3) in 2-Propanol.—trans-Stilbene (180 mg, 1.00 mmol) in 300 ml of 2-propanol was irradiated for 8 hr at 25°. After irradiation, the solvent was removed by distillation *in vacuo* below 35°, producing a clear oil which was chromatographed on a  $80 \times 2.5$  cm column of silicic acid slurry packed in 1:9 ether-hexane; 20-ml fractions were collected. The column was eluted as follows: 0.5 l. of hexane, 0.5 l. of 1:99 ether-hexane, 0.5 l. of 1:49 ether-hexane.

Fractions 19–23 produced 88 mg of *cis*-stilbene, identified by ir and uv spectroscopy. Fractions 24-38 gave 61 mg of *trans*stilbene, mp 120–124°. Neither the 4-methoxy- or the 4,4'dimethoxystilbene system was present in the irradiation mixture.

Irradiation of trans-4,4'-Dimethoxystilbene (12) in 2-Propanol.—trans-4,4'-Dimethoxystilbene (240 mg, 1.00 mmol) in 300 ml of 2-propanol was irradiated for 16 hr at 25°. After irradiation, the solvent was removed by distillation *in vacuo* below 30°, leaving a white solid which was chromatographed on an 85 × 2.5 cm silicic acid column slurry packed in 1:9 etherhexane; 20-ml fractions were collected. The column was eluted as follows: 0.5 l. of hexane, 0.5 l. of 1:99 ether-hexane, 0.5 l. of 1:49 ether-hexane, 0.5 l. of 1:24 ether-hexane, and 0.5 l. of 1:12 ether-hexane.

Fractions 89–97 gave 53 mg of cis-4,4'-dimethoxystilbene, identified by ir and uv spectroscopy. Fractions 100–113 produced 142 mg of *trans*-4,4'-dimethoxystilbene, mp 205–207°. Neither the stilbene nor the 4-methoxystilbene systems were produced.

Irradiation of a Mixture of trans-Stilbene (3) and trans-4,4'-Dimethoxystilbene (12) in 2-Propanol.—trans-Stilbene (90 mg, 0.50 mmol) and trans-4,4'-dimethoxystilbene (120 mg, 0.50 mmol) in 300 ml of anhydrous 2-propanol was irradiated for 16 hr at 25°. After irradiation, the solvent was removed by distillation in vacuo below 30°, leaving an oily solid which was chromatographed on an  $80 \times 2.5$  cm column of silicic acid slurry packed in 1:9 ether-hexane; 20-ml fractions were collected. The column was eluted as follows: 0.5 l. of hexane, 0.5 l. of 1:49 ether-hexane, 0.5 l. of 1:24 ether-hexane, and 0.5 l. of 1:12 ether-hexane.

Fractions 19–23 produced 49 mg of *cis*-stilbene, identified by ir and uv spectroscopy. Fractions 24–35 gave 25 mg of *trans*stilbene, mp 122–125°. Fractions 91–97 produced 21 mg of *cis*-4,4'-dimethoxystilbene, identified by ir and uv spectroscopy. Fractions 99–108 gave 74 mg of *trans*-4,4'-dimethoxystilbene, mp 207–209°. None of the 4-methoxystilbene system was formed.

**Registry No.**—1, 588-68-1; 3, 103-30-0; 8, 2009-41-8; 9, 19019-27-3; 10, 2299-73-2; 12, 15638-14-9; 14, 1694-19-5; 2-propanol, 67-63-0.

Acknowledgment.—Appreciation is gratefully expressed to the Research Corporation for support of this work. The author also wishes to thank Mr. Timothy L. Hottel for the construction of equipment used in this study.