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Photochemistry of Vinyl Halides. Heterocycles from Reaction of Photogenerated Vinyl Cations with Azide Anion

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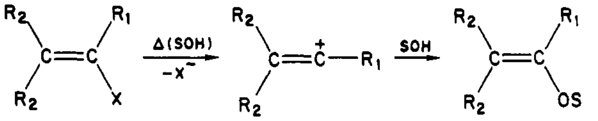
Irradiation of 1,2,2-tris(*p*-methoxyphenyl)vinyl bromide (**1a-Br**) and tetrabutylammonium azide in acetonitrile afforded 1,1,3,4,6,6-hexakis(*p*-methoxyphenyl)-2,5-diaza-1,3,5-hexatriene (**2a**). Formation of **2a** suggests the presence of azirine **3a** as a reactive intermediate and a route to synthesis of heterocycles in combination with azirine photochemistry. Irradiation of α-arylvinyl halides **1** and tetrabutylammonium azide in acetonitrile in the presence of dimethyl fumarate gave 1-pyrroline derivatives **5**. When the irradiation was performed in acetone, oxazoline derivatives **6** were obtained. The reaction of vinyl halides **1** with azide anion took place successfully even in a two-phase system, i.e., water–methylene chloride–tetrabutylammonium halide as a phase-transfer catalyst. In addition, photolysis of 2,2-bis(*p*-methoxyphenyl)-1-phenylvinyl bromide (**1f-Br**) in a two-phase system led to the formation of the β-aryl rearranged pyrrolines **5f**. This result indicates strong evidence for the intervention of vinyl cations in the photochemical reaction of the vinyl halide **1** and azide anion. The mechanistic points on the photochemical substitution and the scope and limitation of the reaction are discussed.

Introduction

Solvolysis of vinyl derivatives has been studied since 1964 and evidence for the generation of vinyl cations has been collected by kinetic and spectroscopic studies.[1] The generation of vinyl cations can be controlled by changing the substituents and the leaving groups. Although most vinyl cations can be generated by introducing good leaving groups on the α carbon and substituents which stabilize the vinyl cations or by using a solvent of high ionizing power, the products derived from vinyl cations are usually solvent-incorporated ones.



(1)

Rappoport and Kaspi carried out the reaction of tris(*p*-methoxyphenyl)vinyl *o*-nitrobenzenesulfonate in the presence of sodium azide in aqueous acetone at 35 °C and obtained an oily product which had a strong absorption band at 2110 cm^{-1} assignable to an N_3 stretching vibration.[2] Rappoport and Apeloig also reported that the reaction of 1,2-bis(*p*-methoxyphenyl)-2-phenylvinyl bromide in acetic acid in the presence of tetraethylammonium chloride gave the corresponding vinyl chloride.[3] These reactions have been performed in mechanistic studies on solvolysis of vinyl derivatives and not for the purpose of organic synthesis.

The conversion of vinyl derivatives by nucleophilic substitution is a useful synthetic method. However, the general method has not been known yet because vinyl derivatives do not undergo nucleophilic substitution unless an activating group is present at the β carbon of vinylic system.[4]

On the other hand, it has been reported recently that vinyl cations are formed by photolysis of vinyl halides.[5] The photolysis can be conducted even in a non-nucleophilic solvent. When the vinyl cations are trapped with azide anion, the corresponding azirines are formed in situ from the vinyl azides. Cycloaddition of the resulting nitrile ylides generated by the carbon–carbon bond cleavage of the azirines provides a one-pot synthesis of heterocycles from vinyl halides.

As discussed in a preliminary report,[5e] the photogenerated vinyl cation reacted with azide anion in the photolysis of vinyl bromides which had a *p*-methoxyphenyl group in the α position. This paper treats in detail the photolysis of α-aryl-substituted vinyl halides in the presence of azide anion and reveals the following points: (i) one-pot synthesis of heterocycles in combination with azirine photochemistry, (ii) extension to a two-phase photochemistry, and (iii) the scope and limitation of this reaction.

Results

Photolysis of Vinyl Halides 1 in the Presence of Azide Anion. Irradiation of 1,2,2-tris(*p*-methoxyphenyl)vinyl bromide (**1a-Br**) in the presence of tetrabutylammonium azide was carried out in acetonitrile through a Pyrex filter with a high-pressure mercury lamp (100 W) under a nitrogen atmosphere at 5 °C to give the 2,5-diaza-1,3,5-hexatriene **2a** (54%), *p*-methoxybenzaldehyde (23%), and *p*,*p*′-dimethoxybenzophenone (13%). The formation of the 2,5-diaza-1,3,5-hexatriene **2a** suggests the presence of 2,2,3-tris(*p*-methoxyphenyl)-2H-azirine (**4a**) derived from 1,2,2-tris(*p*-methoxyphenyl)vinyl azide (**3a**) (eq 2). It is well-known that diaza-1,3,5-hexatrienes **2** are formed by photolysis of the corresponding azirines **4**.[6]

To confirm the presence of azirines **4**, the method described in the photolysis of azirines was employed. Photolysis of the azirine gives the nitrile ylide, which undergoes 1,3-dipolar cycloaddition.[6]

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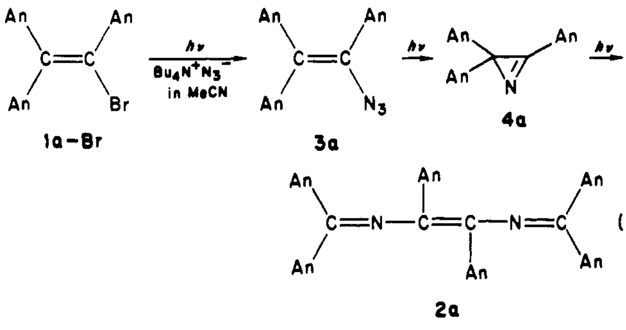
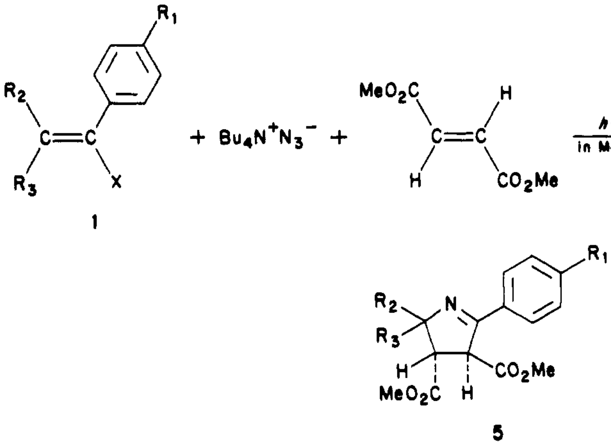


(2)

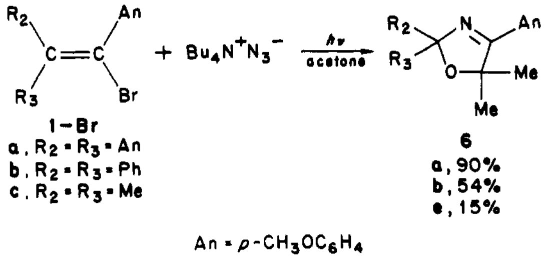
An = p-$CH_3OC_6H_4$

Irradiation of vinyl halides **1** was carried out in acetonitrile in the presence of tetrabutylammonium azide and dimethyl fumarate as a dipolarophile. As expected, *trans*-3,4-bis(methoxycarbonyl)-1-pyrroline derivatives **5** were formed. The trans stereochemistry of **5** was assigned on the basis of a 7-Hz coupling between two methine protons in the NMR spectrum, which was consistent with the result obtained by Padwa et al.[7] The results are given in Table I.



(3)

In order to obtain further evidence for the formation of the azirine **4** in situ, acetone was chosen as a dipolarophile. Irradiation of the vinyl bromides (**1a-Br** and **1b-Br**), respectively, was carried out in acetone in the presence of tetrabutylammonium azide with a Pyrex filter. After workup of the reaction mixture, 5,5-dimethyl-3-oxazoline derivatives **6a** and **6b** were isolated, respectively, by column chromatography on silica gel. When the vinyl bromide **1e-Br** was irradiated in a mixed solvent of acetone and acetonitrile in the presence of tetrabutylammonium azide without a Pyrex filter, oxazoline derivative **6e** was obtained in 15% yield similarly together with p-methoxybenzonitrile (18%) and 1-(p-methoxyphenyl)-2-methylpropene (7%). The formation of the oxazoline **6** provides further evidence that photolysis of the vinyl halide **1** in the presence of azide anion affords the azirine **4**.[8]



(4)

An = p-$CH_3OC_6H_4$

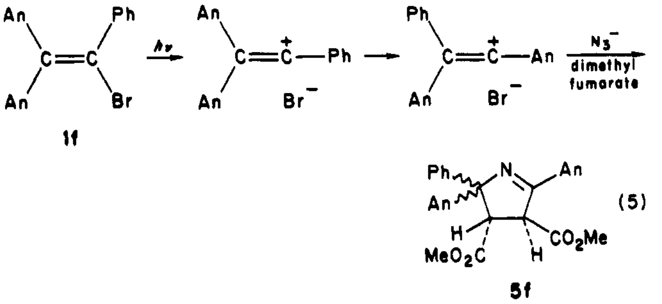
Table I. Photolysis of the Vinyl Halides 1 in the Presence of Azide Anion and Dimethyl Fumarate

	1				irradiatn		yield,^{c,d} %
	R_1	R_2	R_3	X	time,^{a} h	conditn^b	5
1a	MeO	An	An	Br	1	H	92
					1	T	88
1b	MeO	Ph	Ph	Br	3	H	86
					4	T	82
1c	Me	Ph	Ph	Br	6	H	75^e
1d	H	Ph	Ph	Br	12	H	45^e
1e	MeO	Me	Me	Br	2^f	H	14
					4^f	T	13^g

^{a} Irradiated through a Pyrex filter. ^{b} H: In a homogenous system (acetonitrile). T: In a two-phase system (CH_2Cl_2–H_2O). ^{c} Based on the vinyl halide 1. Conversion is nearly equal to 100%. ^{d} Isolated yield. ^{e} Determined by NMR with an internal standard, p-(*tert*-butyl)benzoic acid. ^{f} Irradiated through quartz. ^{g} p-Methoxybenzonitrile was also isolated in 21% yield.

In recent years many reactions have been conducted successfully under phase-transfer conditions.[9] A two-phase solution was prepared by mixing the vinyl bromide **1-Br**, dimethyl fumarate, sodium azide, methylene chloride, and water and irradiated after adding tetrabutylammonium bromide as a phase-transfer agent. After workup of the reaction mixture, the pyrroline **5** was isolated by column chromatography on silica gel and found to be identical with the product obtained by photolysis of the vinyl bromide **1-Br** with tetrabutylammonium azide in acetonitrile. The results are given in Table I.

Photolysis of 2,2-Bis(p-methoxyphenyl)-1-phenylvinyl Bromide (1f-Br) in a Two-Phase System. To establish that a vinyl cation is generated even in a two-phase system, a mixture of the vinyl bromide **1f-Br**, tetrabutylammonium chloride, sodium azide, and dimethyl fumarate was irradiated in a two-phase solution of methylene chloride and water. Irradiation of this solution through a Pyrex filter for 4 h gave a stereoisomeric mixture of pyrroline derivatives **5f** in 84% yield. Both NMR spectra of these products showed typical AA′XX′ pattern of aromatic protons (p-$MeOC_6H_4C{=}N$): δ ($CDCl_3$) 6.78 (J = 8.5 Hz) and 7.80 (J = 8.5 Hz). Mass spectra indicated the presence of the fragments of $[An(Ph)CN{=}CAn]^+$ and $[AnCPh]^+$ in both cases, and the absence of those of $[An(An)CN{=}CPh]^+$ and/or $[AnCAn]^+$. These spectra suggest that formation of the pyrrolines **5f** involves a 1,2-anisyl shift across the double bond, which supports intervention of a vinyl cation[10] even in a two-phase system.



(5)

An = p-$CH_3OC_6H_4$

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Table II. Catalytic Reactions of the Vinyl Halides 1 with Azide Anion in a Two-Phase System

		1							
run		R_1	R_2	R_3	X	PTC	[PTC]/1[a]	irradiatn time, h	yield,[b] % 5
1	**1a**	OMe	An	An	Br	$Bu_4N^+Br^-$	0.56	2	79
2						$Bu_4N^+Br^-$	0.33	6	83
3						$Bu_4N^+Br^-$	0.11	2	25
4						$Bu_4N^+Br^-$	0.13	6	67
5						$Bu_4N^+Br^-$	0.11	12	77
6						$Bu_4N^+Cl^-$	0.36	6	92
7						$Bu_4N^+Cl^-$	0.10	12	74
8							0	12	0
9	**1b**	OMe	Ph	Ph	Br	$Bu_4N^+Br^-$	0.49	4	80
10						$Bu_4N^+Br^-$	0.19	12	64
11						$Bu_4N^+Br^-$	0.10	12	62
12					Cl	$Bu_4N^+Cl^-$	0.62	6	96
13						$Bu_4N^+Cl^-$	0.12	24	67
14						$Bu_4N^+Cl^-$	0.066	24	68
15	**1c**	Me	Ph	Ph	Br	$Bu_4N^+Br^-$	0.5	6	31
16					Cl	$Bu_4N^+Cl^-$	0.5	12	63
17	**1d**	H	Ph	Ph	Br	$Bu_4N^+Br^-$	0.5	12	22
18					Cl	$Bu_4N^+Cl^-$	0.5	12	40

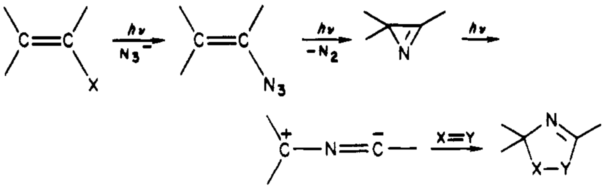
[a] Molar ratio of PTC (phase-transfer catalyst) to the vinyl halide 1. [b] Based on the vinyl halide 1.

Catalytic Reactions in the Photolysis of the Vinyl Halides 1 in a Two-Phase System. Irradiation of the vinyl halides 1 was carried out in a two-phase solution of methylene chloride and water similarly, with changing amounts of tetrabutylammonium halide. The results are given in Table II.

A decrease in the amount of tetrabutylammonium halide results in a decrease in the yield of the pyrroline **5**. When the vinyl bromide **1a-Br** was irradiated similarly in the absence of tetrabutylammonium halide for 12 h the pyrroline **5a** was not formed at all. Therefore, the reaction of the vinyl halide 1 with azide anion in a two-phase system requires a phase-transfer catalyst. From Table II, it is also found that the combination of the vinyl chloride **1-Cl** and tetrabutylammonium chloride is better than that of the vinyl bromide **1-Br** and tetrabutylammonium bromide.

Discussion

Formation of Heterocycles by Photolysis of Vinyl Halides in the Presence of Azide Anion and Dipolarophiles. The results obtained from the photolysis of vinyl halides in the presence of azide anion are consistent with those from the photolysis of azirines and support the presence of an azirine intermediate. The azirine should derive from the corresponding vinyl azide which is formed by substitution of the vinyl halide by azide anion.



(6)

The significance of this reaction is that heterocycles can be synthesized without the preparation of the vinyl azide or azirine. When a 1,3-dipolar cycloaddition is used, this method can be applied to the synthesis of various heterocycles.

The photochemical substitution reaction also was extended to a two-phase system. By use of the two-phase photochemistry, the following advantages are gained: (i) No expensive anhydrous or aprotic solvents are required. (ii) The experimental treatment becomes easier. (iii) Sodium azide is easily available and can be used directly, as tetrabutylammonium azide is not necessary. The successful two-phase photochemistry implies that the azide anion in the aqueous phase is transferred as tetrabutylammonium azide to the organic phase and behaves as it did in the case of photolysis in acetonitrile in the presence of tetrabutylammonium azide.

Photochemical Substitution via Vinyl Cations. In the homogeneous system as well as in the two-phase system, the formation of heterocycles by photolysis of vinyl halides proceeds via azirine intermediates, which should be derived from the corresponding vinyl azides. Therefore, the first step of the heterocycle formation is nucleophilic substitution of vinyl halides by azide anion.

Nucleophilic substitution reactions of vinyl halides are principally classified into (i) single step, so-called S_N2, (ii) multistep, (iii) S_N1, and (iv) $S_{RN}1$. Since the single step in a vinylic system cannot be accepted because of its high energy barrier,[4] the multistep, S_N1, and $S_{RN}1$ reactions are mainly responsible for the nucleophilic substitution of vinyl halides. The multistep,[4] i.e., addition–elimination process, is generally observed when the β substituent is electron withdrawing such as CN, NO_2, and CO_2R. The S_N1 process[1] occurs when the α substituent is electron donating and the leaving group is a good nucleofuge. This process involves a vinyl cation intermediate. The $S_{RN}1$ process[12] is a radical chain mechanism where a vinyl radical is concerned. Since the vinyl halides employed here are aryl-substituted ones and not activated at the β position, the multistep is excluded. By analogy with the photolysis of aryl-substituted vinyl halides,[5] it is reasonable to think that the photochemical substitution by azide anion proceeds via a vinyl cation. The $S_{RN}1$ process is also possible because photolysis of vinyl halides produces vinyl radicals.[11] However, the order (Cl > Br) for the yields of the products makes the $S_{RN}1$ mechanism an unlikely process.[12] In the photolysis of the vinyl bromide **1f-Br**, the pyrrolines **5f**, whose formation involves a 1,2-aryl migration across the double bond, are obtained in high yields. This 1,2-aryl migration strongly suggests the intervention of a vinyl cation in the photochemical substitution reaction. Consequently, the photochemical substitution reaction by azide anion may be depicted as in Scheme I.

The Scope and Limitation of Heterocycle Formation from Photochemical Substitution by Azide Anion. This method is very interesting as a one-pot synthesis

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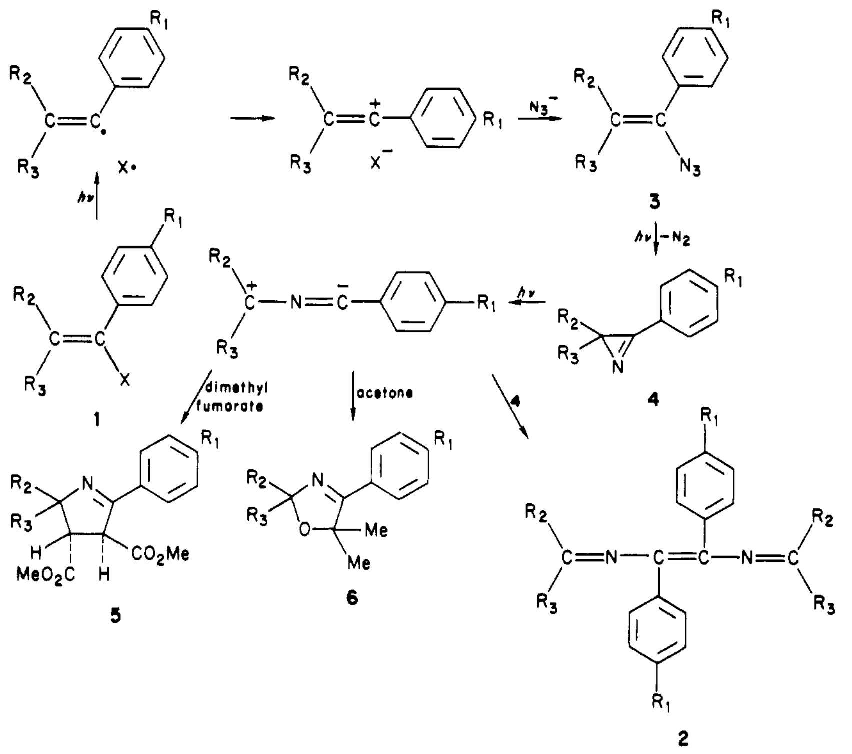
Scheme I



of heterocycles from vinyl halides. Some factors can be discussed concerning the formation of the pyrroline **5**, which can be applied to other substitution reactions of vinyl halides.

(a) Substitutent. As a factor affecting the yield of the pyrroline **5**, the effect of an α substituent on the vinyl halide **1** is most significant, as indicated by the order: $p\text{-}CH_3OC_6H_4 > p\text{-}CH_3C_6H_4 > C_6H_5$. This is consistent with the order of the stability of the resulting vinyl cation and implies that the stability of the vinyl cation generated by photolysis strongly influences the formation of the pyrroline **5**.

A β substituent also affects the formation of the pyrroline **5**. The difference in the effect between p-methoxyphenyl and phenyl groups is small but a methyl group leads to a large decrease in the yield of the pyrroline **5**. Consequently, the following order of the β substituent is obtained: $p\text{-}CH_3OC_6H_4 \geq C_6H_5 \gg CH_3$. This is due to the difference in light absorption between the vinyl halides **1**. The vinyl halides substituted by an aryl group at the β position absorb the light longer than 300 nm and can be photolyzed by a Pyrex filtered mercury lamp. On the other hand, the vinyl halides substituted by a methyl group at the β position do not absorb the light longer than 300 nm and must be irradiated without a Pyrex filter. Therefore, photolysis of the β-methyl-substituted vinyl halides causes the photodecomposition of the pyrroline or the intermediate to the benzonitrile derivative and leads to a low yield.

(b) Leaving Group. In general, in the photolysis of aryl-substituted vinyl halides the ease of formation of a vinyl cation follows the order: $X = Cl > Br > I$.[5] Since a vinyl cation is formed by an electron transfer in the radical pair generated by photolysis of the vinyl halide, a high electronegative halogen atom is favorable for the vinyl cation formation. In fact, even in a two-phase system vinyl chlorides gave higher yield than vinyl bromides.

(c) Tetrabutylammonium Halide. Tetrabutylammonium halide, which is a well-known phase-transfer catalyst, has been used extensively in two-phase reactions.[9] It is found that in this photochemical substitution of vinyl halides also tetrabutylammonium halide is useful and tetrabutylammonium chloride is better than tetrabutylammonium bromide.

Considering the hard and soft acids and bases principle is helpful to understanding the reaction. Ammonium ion is considered to be a soft acid because quaternary ammonium cation is large and polarizable.[13] The softness of the bases, Br^-, Cl^-, and N_3^-, is in the order: $Br^- > N_3^- \simeq Cl^-$.[14] Then, the ease of formation of the ammonium salt becomes the following order: $Bu_4N^+Br^- > Bu_4N^+N_3^- \simeq Bu_4N^+Cl^-$. Therefore, tetrabutylammonium chloride forms tetrabutylammonium azide in situ more easily than tetrabutylammonium bromide. This implies that tetrabutylammonium chloride forms a higher concentration of tetrabutylammonium azide in the organic phase than tetrabutylammonium bromide and the high concentration of tetrabutylammonium azide in the organic phase favors the reaction of a vinyl cation with azide anion.

Experimental Section

General Methods. All melting points are uncorrected. NMR spectra were taken on a HITACHI R-24B spectrometer. Mass spectra were obtained with a JEOL JMS-07 spectrometer. Ultraviolet spectra were recorded on a Shimadzu UV-200S spectrometer. IR spectra were obtained with a Shimadzu IR-400 spectrometer.

Preparation of Materials. Tetrabutylammonium azide was prepared by the method described in the literature.[15] The following vinyl halides were prepared by halogenation of the corresponding olefins described in the literature: **1a-Br**,[16] **1b-Br**,[17] **1b-Cl**,[18] **1c-Br**,[19] **1d-Br**,[20] **1d-Cl**,[21] **1e-Br**,[22] and **1f-Br**.[10b]

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Table III. Spectral Data for the Pyrroline 5

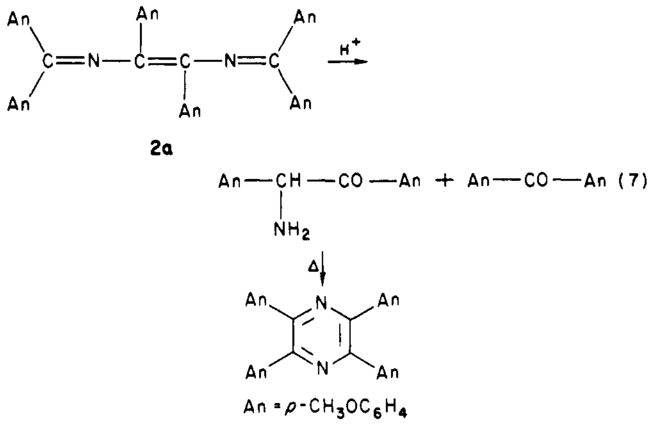
no.	NMR solvent: δ^a	IR ν(C=O), cm^{-1}	MS, m/e (M^+)
5a	$CDCl_3$: 3.26 (s, OCH_3), 3.49 (s, OCH_3), 3.63 (s, OCH_3), 3.75 (s, OCH_3), 4.71 (d, J = 7 Hz, CH), 4.90 (d, J = 7 Hz, CH), 6.49–6.90 (m, ArH), 7.64–7.90 (m, ArH)	1720	503
5b	$CDCl_3$: 3.20 (s, OCH_3), 3.46 (s, OCH_3), 3.75 (s, OCH_3), 4.40 (d, J = 7 Hz, CH), 4.93 (d, J = 7 Hz, CH), 6.77–7.96 (m, ArH)	1720	433
5c	CCl_4: 2.37 (s, CH_3), 3.15 (s, OCH_3), 3.43 (s, OCH_3), 4.23 (d, J = 7 Hz, CH), 4.75 (d, J = 7 Hz, CH), 6.65–7.80 (m, ArH)	1733	427
5d	CCl_4: 3.15 (s, OCH_3), 3.48 (s, OCH_3), 4.27 (d, J = 7 Hz, CH), 4.78 (d, J = 7 Hz, CH), 6.70–7.90 (m, ArH)	1733	389
5e	CCl_4: 1.10 (s, CH_3), 1.54 (s, CH_3), 3.16 (d, J = 7 Hz, CH), 3.57 (s, OCH_3), 3.65 (s, OCH_3), 3.74 (s, OCH_3), 4.50 (d, J = 7 Hz, CH), 6.58–7.60 (m, ArH)	1735	319

[a] The integration is consistent with the assignment.

1-Chloro-1-(*p*-methylphenyl)-2,2-diphenylethylene (1c-Cl). Chlorination of 1-(*p*-methylphenyl)-2,2-diphenylethylene[23] (13.52 g) was conducted in acetic acid (300 mL). After chlorination the reaction mixture was poured into water (500 mL) and extracted with ether. The ethereal soltuion was washed with water and saturated sodium hydrogen carbonate solution and dried over anhydrous sodium sulfate. After evaporation of the solvent, benzene (100 mL) and DBU (9 mL) were added and the solution was refluxed for 4 h. Then, the reaction mixture was poured into water, extracted with ether, washed with water and saturated sodium chloride solution, and dried over anhydrous sodium sulfate. After evaporation of the solvent the residue was cooled to solidify the product. Recrystallization from ethanol–benzene gave crystals of the vinyl chloride **1c-Cl**: 3.61 g; mp 131–136 °C; NMR (CCl_4) δ 2.24 (s, 3 H, CH_3) and 6.68–7.15 (m, 14 H, ArH). Anal. Calcd for $C_{21}H_{17}Cl$: C, 82.75; H, 5.62. Found: C, 82.32; H, 5.56.

Photolysis of 1,2,2-Tris(*p*-methoxyphenyl)vinyl Bromide (1a-Br) in the Presence of Tetrabutylammonium Azide. The vinyl bromide **1a-Br** (429 mg, 1 mmol) was irradiated in acetonitrile (100 mL) in the presence of tetrabutylammonium azide (2 mmol) through a Pyrex filter with a high-pressure mercury lamp (100 W) under nitrogen atmosphere at 5 °C for 1 h. After evaporation of the acetonitrile the products were extracted with ether. The ethereal solution was washed with water and saturated sodium chloride solution and dried over anhydrous sodium sulfate. Evaporation of the ether gave orange crystals. The orange crystals were filtered off and recrystallized from ethanol–benzene: 150 mg, mp 219–221 °C; NMR ($CDCl_3$) δ 3.73 (s, 6 H, OCH_3), 3.82 (s, 12 H, OCH_3), and 6.50–7.62 (m, 24 H, ArH); UV (ethanol) λ_{max} (log ϵ) 278 nm (4.55) and 413 (3.68); MS, *m/e* (relative intensity) 718 (M^+, 100), 359 ($M^+/2$, 45), 344 (11), 226 (89), and 211 (85). Anal. Calcd for $C_{46}H_{42}N_2O_4$: C, 76.86; H, 5.89; N, 3.90. Found: C, 76.50; H, 5.95; N, 3.63.

The acid-catalyzed hydrolysis of the orange crystals was carried out in order to determine the structure. The orange crystals (100 mg) were dissolved in 2 N hydrochloric acid (10 mL)–ethanol (50 mL) to give a red-brown solution, which was refluxed for 20 min. The pale yellow reaction mixture was separated into an organic layer and an aqueous layer. The organic layer was obtained by extraction with ether–benzene, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent gave crystals, 70 mg (mp 143–144 °C), which were identified as 4,4′-dimethoxybenzophenone by comparison with an authentic sample (lit.[24] mp 144–145 °C). The aqueous layer was basified by adding 1 N sodium hydroxide solution to pH 9–10, extracted with ether, washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent gave an oily material, 30 mg, which showed the NMR spectrum in $CDCl_3$: δ 2.78 (s, NH_2), 3.70 (s, OCH_3), 3.77 (s, OCH_3), 5.38 (s, CH), and 6.65–7.95 (m, ArH). From the NMR spectrum, the oily material was assigned to 1-amino-1-(*p*-methoxyphenyl)-4′-methoxyacetophenone, which was further confirmed by condensation to the pyrazine derivative. The amino ketone was refluxed in ethanol for 2 h. After checking the disappearance of the amino group in the NMR spectrum the crude product was purified by column chromatography on alumina with ether eluent, giving white crystals: mp 273–274 °C; NMR ($CDCl_3$) δ 3.31 (s, OCH_3) and 6.67–7.91 (m, ArH); MS, *m/e* 504 (M^+). From the spectral data described above the white crystals were assigned to 2,3,5,6-tetrakis(*p*-methoxyphenyl)pyrazine.[25] Consequently, the orange crystals were assigned to 1,1,3,4,6,6-hexakis(*p*-methoxyphenyl)-2,5-diaza-1,3,5-hexatriene (**2a**) on the basis of the spectral data, elemental analysis, and chemical behavior.



(7)

On the other hand, the mother liquor which was obtained by filtration of the diazahexatriene **2a** was submitted to column chromatography on silica gel with hexane–ether eluents. The isolated products were the vinyl bromide **1a-Br** (96 mg), *p*-methoxybenzaldehyde[26] (24 mg), and 4,4′-dimethoxybenzophenone[24] (25 mg).

Photolysis of Vinyl Halides 1 in the Presence of Tetrabutylammonium Azide and Dimethyl Fumarate. Irradiation of 1,2,2-tris(*p*-methoxyphenyl)vinyl bromide (**1a-Br**) (1 mmol) with tetrabutylammonium azide (2 mmol) was carried out in acetonitrile (100 mL) in the presence of dimethyl fumarate (4 mmol) through a Pyrex filter by use of a high-pressure mercury lamp (100 W) for 1 h. After evaporation of the solvent the products were extracted with ether, washed with water and saturated sodium chloride solution, and dried over anhydrous sodium sulfate. After removal of the solvent the crude mixture was separated by column chromatography on silica gel with hexane–ether eluents. *trans*-3,4-Bis(methoxycarbonyl)-2,5,5-tris(*p*-methoxyphenyl)-1-pyrroline (**5a**) was obtained in 92% yield. The spectral data are given in Table III.

Irradiation of the vinyl halides **1b–e** with tetrabutylammonium azide was carried out in the presence of dimethyl fumarate under the conditions similar to the photolysis of **1a-Br**, except for the vinyl bromide **1e-Br** which was irradiated without a Pyrex filter. After workup of the reaction mixture and separation by column chromatography on silica gel with hexane–ether eluents, the pyrroline **5** was obtained as an amorphous solid. The spectral data are given in Table III. Satisfactory analytical values (±0.3% for C,H,N) were reported for **5a–d**. The pyrroline **5e** did not give

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[26] *p*-Methoxybenzaldehyde was identical with a commercial sample.

a correct analysis but the spectral data were consistent with those of *trans*-3,4-bis(methoxycarbonyl)-5,5-dimethyl-2-phenyl-1-pyrroline except for the *p*-methoxy substituent.[7]

Photolysis of Vinyl Halides 1 in the Presence of Tetrabutylammonium Azide and Acetone. Irradiation of the vinyl bromide **1a-Br** (1 mmol) with tetrabutylammonium azide (2 mmol) was carried out for 1 h in acetone (100 mL) through a Pyrex filter by use of a high-pressure mercury lamp (100 W) under nitrogen atmosphere at 5 °C. After evaporation of the solvent the crude products were extracted with ether, washed with water, and dried over anhydrous sodium sulfate. After evaporation of the ether the products were separated by column chromatography on silica gel with hexane–ether eluents. The products obtained were 1,1,2-tris(*p*-methoxyphenyl)ethylene, 16 mg (5%), and 5,5-dimethyl-2,2,4-tris(*p*-methoxyphenyl)-3-oxazoline (**6a**), 373 mg (90%). The ethylene was identified by comparison with an authentic sample.[27] The oxazoline **6a** was assigned by the spectral data and elemental analysis: NMR (CCl_4) δ 1.50 (s, 6 H, CH_3), 3.61 (s, 6 H, OCH_3), 3.67 (s, 3 H, OCH_3), and 6.52–7.84 (m, 12 H, ArH); UV (ethanol) λ_{max} (log ϵ) 275 nm (4.32); MS, *m/e* 401 (M^+). Anal. Calcd for $C_{27}H_{27}NO_4$: C, 74.80; H, 6.52; N, 3.36. Found: C, 74.57; H, 6.54; N, 3.17.

Similar irradiation of **1b-Br** for 3 h gave 5,5-dimethyl-2,2-diphenyl-4-(*p*-methoxyphenyl)-3-oxazoline (**6b**) in 58% yield: NMR (CCl_4) δ 1.51 (s, 6 H, CH_3), 3.66 (s, 3 H, OCH_3), and 6.60–7.82 (m, 14 H, ArH); MS, *m/e* 357 (M^+). Anal. Calcd for $C_{24}H_{23}O_2N$: C, 80.64; H, 6.49; N, 3.92. Found: C, 80.52; H, 6.63; N, 3.94.

Irradiation of the vinyl bromide **1e-Br** (2 mmol) with tetrabutylammonium azide (4 mmol) was carried out in acetone (20 mL)–acetonitrile (90 mL) for 8 h without a Pyrex filter by use of a high-pressure mercury lamp (100 W). After workup of the reaction mixture, the following products were obtained. 1-(*p*-Methoxyphenyl)-2-methylpropene[28] and *p*-methoxybenzonitrile[29] were identified by comparison with authentic samples. 2,2,5,5-Tetramethyl-4-(*p*-methoxyphenyl)-3-oxazoline (**6e**) was identified on the basis of spectral data: NMR (CCl_4) δ 1.40 (s, 6 H, CH_3), 1.50 (s, 6 H, CH_3), 3.77 (s, 3 H, OCH_3), and 6.58–7.80 (m, 4 H, ArH). MS, *m/e* (relative intensity %) 233 (M^+, 5), 218 (100), 177 (66), 175 (49), 149 (18), 134 (34), and 100 (21). The fragmentation pattern is similar to that of 2,2,5,5,-tetramethyl-4-phenyl-3-oxazoline.[8]

Photolysis of Vinyl Halides 1 in the Presence of Dimethyl Fumarate in a Two-Phase System. A two-phase solution was prepared by mixing the vinyl bromide **1-Br** (1 mmol), dimethyl fumarate (4 mmol), sodium azide (10 mmol), methylene chloride (90 mL), and water (10 mL) in an immersion-type photoreactor. Irradiation of this solution was carried out with a high-pressure mercury lamp (100 W) under nitrogen atmosphere at 10 °C after adding 1.5 mmol of tetrabutylammonium bromide as a phase-transfer agent. After irradiation the methylene chloride was evaporated, and the products were extracted with ether, washed with water and saturated sodium chloride solution, and dried over anhydrous sodium sulfate. After evaporation of the ether, the products were isolated by column chromatography on silica gel with ether–hexane eluate. The products were the same as those obtained in the homogeous photolysis. The results and conditions are given in Table I. In the case of the vinyl bromide **1e-Br**, *p*-methoxybenzonitrile[29] was obtained along with the pyrroline **2e**.

Photolysis of 2,2-Bis(*p*-methoxyphenyl)-1-phenylvinyl Bromide (1f-Br) in a Two-Phase System. A mixture of the vinyl bromide **1f-Br** (1 mmol), tetrabutylammonium chloride (1.5 mmol), sodium azide (10 mmol), dimethyl fumarate (4 mmol), methylene chloride (90 mL), and water (10 mL) was irradiated through a Pyrex filter in a similar manner for 4 h. After workup of the reaction mixture the crude materials were submitted to column chromatography on silica gel and a mixture of two isomers of the pyrrolines **5f** was isolated with ether–hexane eluate. One isomer solidified on standing and was isolated by filtration. **5f-A**: NMR ($CDCl_3$) δ 3.20 (s, 3 H, OCH_3), 3.49 (s, 3 H, OCH_3), 3.77 (s, 6 H, OCH_3), 4.32 (d, *J* = 7 Hz, 1 H, CH), 4.87 (d, *J* = 7 Hz, 1 H, CH), 6.74–7.80 (m, 13 H, ArH); IR 1726 cm^{-1} (C=O); MS, *m/e* (relative intensity %) 473 (M^+, 23), 414 (13), 329 (61), 314 (16), 196 (100), and 181 (61). Anal. Calcd for $C_{28}H_{27}O_6N$: C, 71.02; H, 5.75; N, 2.96. Found: C, 70.84; H, 5.75; N, 2.85. **5f-B**: NMR ($CDCl_3$) δ 3.24 (s, 3 H, OCH_3), 3.45 (s, 3 H, OCH_3), 3.61 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 4.31 (d, *J* = 7 Hz, 1 H, CH), 4.86 (d, *J* = 7 Hz, 1 H, CH), and 6.44–7.85 (m, 13 H, ArH); IR 1726 cm^{-1} (C=O); MS, *m/e* (relative intensity %) 473 (M^+, 46), 414 (19), 329 (100), 314 (35), 196 (71), and 181 (27). Anal. Calcd for $C_{28}H_{27}O_6N$: C, 71.02; H, 5.75; N, 2.96. Found: C, 70.99; H, 5.73; N, 2.81. The stereochemistry of the two isomers **5f-A** and **5f-B** was not determined.

Catalytic Reactions in the Photolysis of Vinyl Halides 1 in a Two-Phase System. A mixture of the vinyl bromide **1a-Br** (100 mg, 0.235 mmol), sodium azide (2.35 mmol), dimethyl fumarate (0.940 mmol), methylene chloride (13 mL), water (2 mL), and the described amounts of tetrabutylammonium halide in Table II was placed in a quartz tube and irradiated through a Pyrex filter with a high-pressure mercury lamp (100 W) under nitrogen atmosphere at 10 °C. After evaporation of the methylene chloride the products were extracted with ether, washed with water and saturated sodium chloride solution, and dried over anhydrous sodium sulfate. After evaporation of the ether the NMR spectra of the products were taken in $CDCl_3$ by using *p*-(*tert*-butyl)benzoic acid as an internal standard, and the yield of the pyrroline **5** was determined. The results are given in Table II.

Similar irradiations in two-phase solutions were conducted with vinyl halides **1b-Br** and **Cl**. The vinyl halide **1b-Br** or **Cl** (100 mg), sodium azide, and dimethyl fumarate in the molar ratio 1:10:4 were dissolved in methylene chloride (13 mL)–water (2 mL) solution together with the corresponding tetrabutylammonium halide. Irradiation of this solution was carried out in the same manner as the photolysis of **1a-Br**. After workup of the reaction mixture the yield of the pyrroline **5b** was determined in the same manner.

A mixture of the vinyl halide **1c** or **1d** (0.274 mmol), sodium azide (2.74 mmol), dimethyl fumarate (1.10 mmol), tetrabutylammonium halide (0.137 mmol), methylene chloride (13 mL), and water (2 mL) was placed in a quartz tube and irradiated in the same manner as the photolysis of **1a-Br**. The results are given in Table II.

Registry No. **1a-Br**, 25354-46-5; **1b-Br**, 25354-48-7; **1b-Cl**, 33686-66-7; **1c-Br**, 83248-27-5; **1c-Cl**, 92937-58-1; **1d-Br**, 1607-57-4; **1d**-Cl, 18084-97-4; **1e-Br**, 40811-05-0; **1f-Br**, 41038-34-0; **2a**, 72031-50-6; **5a**, 72031-51-7; **5b**, 73514-71-3; **5c**, 92901-76-3; **5d**, 92901-77-4; **5e**, 73514-72-4; ($2\alpha,3\alpha,4\beta$)-**5f**, 92901-80-9; ($2\alpha,3\beta,4\alpha$)-**5f**, 92901-81-0; **6a**, 72031-53-9; **6b**, 92901-79-6; **6c**, 72031-54-0; $Ph_2C{=}CHC_6H_4$-*p*-CH_3, 56982-84-4; An_2CO, 90-96-0; AnCOCH(NH_2)An, 92901-78-5; AnCHO, 123-11-5; $Bu_4N^+N_3^-$, 993-22-6; $(CH_3)_2CO$, 67-64-1; $AnCH{=}C(CH_3)_2$, 877-99-6; AnCN, 874-90-8; NaN_3, 26628-22-8; $Bu_4N^+Br^-$, 1643-19-2; $Bu_4N^+Cl^-$, 1112-67-0; 2,3,5,6-tetrakis(*p*-methoxyphenyl)pyrazine, 21885-49-4; dimethyl fumarate, 624-49-7.

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(29) *p*-Methoxybenzonitrile was identical with a commercial sample.