Studies of Carbenium Ion on Unsaturated Carbon. II.[1] Exclusive Formation of Benzofurans *via* Vinyl Cations in the Solvolytic Reactions of 1-Aryl-2,2-bis(*o*-methoxyphenyl)vinyl Halides

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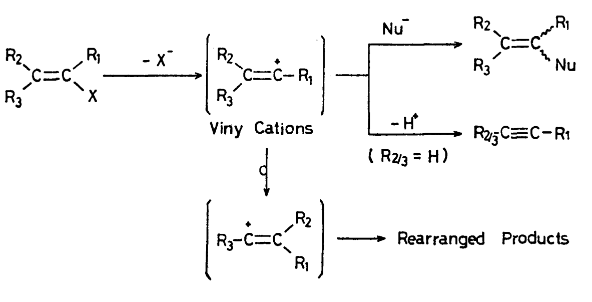
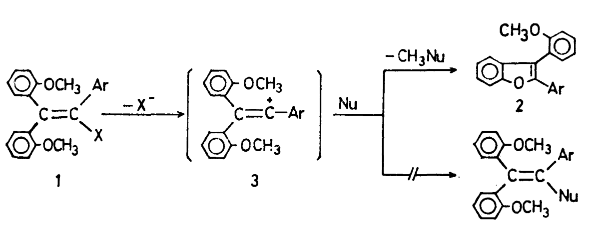
The reactions of 1-aryl-2,2-bis(*o*-methoxyphenyl)vinyl halides (**4**)—(**7**) in 80% aqueous ethanol (80% EtOH), acetic acid (AcOH), or 70% aqueous *N*,*N*-dimethylformamide gave benzofurans (**8**)—(**10**), respectively. The kinetic results *i.e.*, 1) first-order reaction rates, 2) large α-substituent effect ($\rho=-4.12$ against σ^+), 3) large leaving group effect ($k_{Br}/k_{Cl}=85$ in 80% EtOH and 28 in AcOH) and 4) the solvent effect ($m=0.53$), are consistent with the formation of the intermediate vinyl cations (**3**) which are captured exclusively by the *β*-*o*-methoxyl group. In the reaction of vinyl bromide (**7**), the formation of 7—9% of benzofuran (**11**) results from the *β*-*o*-methoxyphenyl migration in the vinyl cation (**17**) followed by cyclization. The exclusive intramolecular cyclization of the vinyl cations is discussed in terms of the proximity effect of the *β*-*o*-methoxyl group.

Extensive studies on solvolysis of vinyl derivatives in the last decade have definitely substantiated the vinyl cations as the reactive intermediates.[2] In these reactions, the products are generally those compounds derived from the nucleophilic attack of solvents or nucleophiles on the intermediate vinyl cations. Acetylenic compounds are obtained if *β*-hydrogens are present in the vinyl substrates. The same kinds of compounds are also formed by the rearrangement of vinyl cations.[3] Moreover, there are several examples of the participation of neighboring groups, such as *β*-sulfur atom,[4] *ω*-double bond,[5] or *ω*-triple bond,[6] which resulted in the formation of cyclized compounds. However, the selectivity of the cyclization is not high since the external nucleophilic attack to vinyl cations competes with the cyclization.



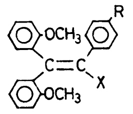
We found that in solvolytic conditions 1-aryl-2,2-bis(*o*-methoxyphenyl)vinyl halides (**1**) underwent a new type of internal cyclization to benzofurans (**2**) *via* vinyl cation intermediates (**3**). The most remarkable feature of these reactions is that the formation of benzofurans occurs exclusively and that no other product is obtained by an external nucleophilic attack to the vinyl cations even in the presence of strong nucleophiles.



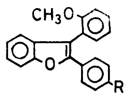
This paper describes the results of kinetics in relation to α-substituent group, solvent, and leaving group effects aimed at confirming the intermediacy of the vinyl cations (**3**) in the reaction of **1**.

Results

Products. Vinyl halides (**4**)—(**7**) were prepared by bromination or chlorination of the corresponding ethylenes, which is similar to the method used for the preparation of the 2-*p*-methoxyphenylvinyl derivatives.[7]



4 R=OCH$_3$, X=Br
5 R=OCH$_3$, X=Cl
6 R=CH$_3$, X=Br
7 R=H, X=Br



8 R=OCH$_3$
9 R=CH$_3$
10 R=H

The reaction of 2,2-bis(*o*-methoxyphenyl)-1-(*p*-methoxyphenyl)vinyl bromide (**4**) in 80% EtOH at 120 °C for 4 h in the presence of excess sodium hydroxide (NaOH) gave 2-(*p*-methoxyphenyl)-3-(*o*-methoxyphenyl)benzofuran (**8**); this was isolated and its structure was determined by microanalysis and by comparing its characteristic UV spectrum with other benzofuran derivatives. The NMR spectrum of the crude product was identical with that of the isolated **8**, which indicates the exclusive formation of **8**. The reactions of **4** in other solvent systems *i.e.*, AcOH and 70% aqueous *N*,*N*-dimethylformamide, always gave **8** in essentially quantitative yields. The selective formation of **8** was not affected by strong nucleophiles. In the presence of sodium azide, the reaction of **4** in 80% EtOH at 120 °C for 6 h also gave **8** as a sole product. The reaction of **4** in 80% EtOH at 120 °C for 4 h in the presence of 1.5 and 3 equivalents of sodium *p*-toluenethiolate afforded **8** exclusively, with 47 and 74% yields of methyl *p*-tolyl sulfide, respectively, which were derived from the capture of methyl moieties by the nucleophile *p*-toluenethiolate ions. A similar result, leading to a quantitative formation of **8**, was obtained in the reaction of the corresponding vinyl chloride (**5**) in basic 80% EtOH at 160 °C for 25 h.

The reaction of 2,2-bis(*o*-methoxyphenyl)-1-*p*-tolylvinyl bromide (**6**) in basic 80% EtOH at 160 °C for 43 h gave 3-(*o*-methoxyphenyl)-2-*p*-tolylbenzofuran (**9**) as the sole product.

In contrast to 1-(*p*-methoxyphenyl)- and 1-*p*-tolylvinyl derivatives (**4**) and (**6**), the reaction of 1-phenylvinyl derivative (**7**) was much more sluggish; two different products were obtained. The NMR spectrum of the reaction of 2,2-bis(*o*-methoxyphenyl)-1-phenylvinyl bromide (**7**) in basic 80% EtOH at 160 °C for 204 h (95% reaction) showed two kinds of methoxyl singlets (at δ 3.45 and 3.34 in CCl_4) which were different from the methoxyl signals of the starting vinyl bromide (**7**). Integration of the two different methoxyl signals showed two products to be present in the ratio of 93: 7. The major one of these products was isolated as the picrate (mp 108—109 °C). Microanalysis of the picrate and the UV spectrum of the major product regenerated by alumina chromatography (see Table 1) showed the major one as a benzofuran derivative of $C_{21}H_{16}O_2$ (**10**). Attempts to isolate the minor product from the filtrate of the picrate (the major/minor ratio of 74/26) by formation of the picrate, by crystallization, and by thin-layer chromatography (silica gel) failed. However the high-pressure liquid chromatogram (alumina, hexane) of the filtrate showed two peaks and their UV spectra were measured by the stop-flow scanning method. As shown in Table 1, the UV spectrum of the major peak of the chromatogram showed λ_{max} at 306 nm, which was identical with that of the isolated major product (**10**). The minor peak, whose UV spectrum showed λ_{max} at 320 nm, was then assigned to the minor product (**11**). By consideration of the NMR and IR spectra of the reaction mixture and the UV spectrum of the minor product, the minor one has only one methoxyl group and can not be a product such as a ketone or ethyl vinyl ether which may be derived from external nucleophilic attack,[7] it was assigned as the isomeric benzofuran of the major one. The structures of isomeric **10** and **11** were determined as follows.

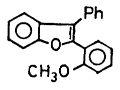
As shown in Table 1 benzofurans with 2-methoxyphenyl groups (**8**, **12**, and **13**) have higher λ_{max} than the benzofurans with 2-phenyl groups (**14** and **15**), or the benzofuran with 2-tolyl group (**9**). On the basis of this trend of chromophores, the major product (**10**) whose UV spectrum shows a lower λ_{max} (306 nm) than the minor one (320 nm) is assigned to a 2-phenyl-substituted benzofuran entity and then the minor one to a 2-methoxyphenyl-substituted benzofuran. Consequently, it is concluded that the major product (**10**) in the reaction of **7** is 3-(*o*-methoxyphenyl)-2-phenylbenzofuran and the minor one (**11**) is 2-(*o*-methoxyphenyl)-3-phenylbenzofuran.

The reactions of **7** in basic 50% EtOH at 160 °C for

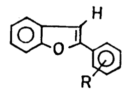
TABLE 1. ULTRAVIOLET SPECTRA OF 2-ARYL- AND 2,3-DIARYLBENZOFURANS IN CYCLOHEXANE

Compound	λ_{max} (nm)		
12[a]	325(20600),	310(33500),	303(30600)
	270(22000),	280(15900),	247(47000)
13[a]	327(33400),	312(33800),	298(19100)
	290(18200),	278(14600),	234(12100)
14[b]	316(24000),	304(32400),	296(25700)
	290(24000),	232(10700),	226(10700)
8	316(27500),	250(17400)	
9	307(24800),	238(17200)	
10	305(21400),	240(17700)	
	306(—)[c]	248(—)[c]	
11	320(—)[c]	263(—)[c]	
15[a]	305(22900),	237(22200)	

a) H. Taniguchi, unpublished results. b) Taken from Ref. 23. c) Measured by stop-flow scanning method of high-pressure liquid chromatography in hexane.



11



12 R=OCH_3-*p*
13 R=OCH_3-*o*
14 R=H

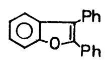


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TABLE 2. KINETICS OF SOLVOLYSIS OF TRIARYLVINYL HALIDES IN AQUEOUS ETHANOL

Compd	M×10^5	NaOH M×10^5	Solvent	Temp (°C)	$k\times10^4$ (s^{-1})	Method[a]
4	4700	10000	80% EtOH	120	2.52 ±0.04	t
	4700	40000	80% EtOH	120	2.22 ±0.03	t
	239	400	80% EtOH	120	2.44 ±0.03	u
	8.8	10.0	80% EtOH	120	2.46 ±0.03	u
	4700	10000	80% EtOH	130	5.47 ±0.07	t
	239	400	80% EtOH	130	5.71 ±0.13	u
	8.7	10.0	80% EtOH	130	5.11 ±0.03	u
	239	400	80% EtOH	140	13.92 ±0.23	u
	239	400	80% EtOH	150	24.12 ±0.44	u
				160	43.0[b]	
	148	300	70% EtOH	120	4.80 ±0.06[c]	u
	151	300	90% EtOH	120	0.98 ±0.04[c]	
5	3.52	16.0	80% EtOH	140	0.160±0.001	u
	3.64	80.0	80% EtOH	140	0.168±0.001	u
6	3.28	80.0	80% EtOH	160	0.617±0.006	u
7	635	1250	80% EtOH	160	0.026±0.001	n

a) t, titration method, u, UV method, n, NMR method. b) Extrapolated from data at lower temperature. c) Rates are averages of duplicate determinations.

26 h (96% reaction), and in AcOH with excess silver acetate at 118 °C for 21 h (100% reaction) also gave these isomeric benzofurans in similar product ratios (the **10**/**11** ratios of 93/7 and 91/9, respectively).

Kinetics. Reaction rates of vinyl halides (**4**)—(**7**) in aqueous EtOH with NaOH and in AcOH with NaOAc were measured by titration of the formed bromide ions (titration method), and by measuring the UV spectra of the reaction mixtures (UV method). Since the results from the titration method were identical with those from the UV method within experimental errors, most of the measurements were made by the UV method. The reaction rates of **7** in 80% EtOH and of **5** in AcOH were followed by NMR spectroscopy (NMR method) as the reaction rates of these reactions were very sluggish.

The kinetic results in aqueous EtOH are summarized in Table 2. All the runs followed accurately the first-order kinetic law. The rate constants were not affected by the concentrations of the substrates and the added base(NaOH). Solvent polar effects were studied with **4** in 70, 80, and 90% EtOH. A plot of log *k* for **4** *vs.* Grunwald-Winstein's *Y* value8) is linear and the *m* value is 0.53 at 120 °C. The reactivity ratio of (**4**) 1650: (**6**) 24: (**7**) 1 suggests a large α-substituent effect. The Hammett plot of log *k* against σ^{+} 9) gave $\rho=-4.12$ (correlation coefficient r=0.999) in 80% EtOH at 160 °C. The bromide (**4**)/chloride (**5**) reactivity ratio in 80% EtOH at 140 °C is 85. Activation parameters for solvolysis of **4** in 80% EtOH are $\Delta H^{\ddagger}=26.8\pm0.4$ kcal/mol and $\Delta S^{\ddagger}=-7\pm1$ e.u. (120 °C).

Solvolysis rates of **4** and **5** in AcOH are shown in Table 3. The reactions obeyed good first-order kinetics up to 80% conversion. The bromide (**4**)/chloride (**5**) reactivity ratio in AcOH at 140 °C is 27.8.

Table 3. Kinetics of solvolysis of 2,2-bis-(*o*-methoxyphenyl)-1-(*p*-methoxyphenyl)vinyl bromide (**4**) and chloride (**5**) in acetic acid

Compd	$M\times10^{5}$	NaOAc $M\times10^{5}$	Temp. (°C)	$k\times10^{4}$ (s^{-1})	Method a)
4	988	1278	120	0.54 ± 0.01	u
	3.58	8.90	120	0.58 ± 0.01 b)	u
	3.30	7.76	140	3.33 ± 0.06	u
5	934	1864	140	0.12 ± 0.01	n

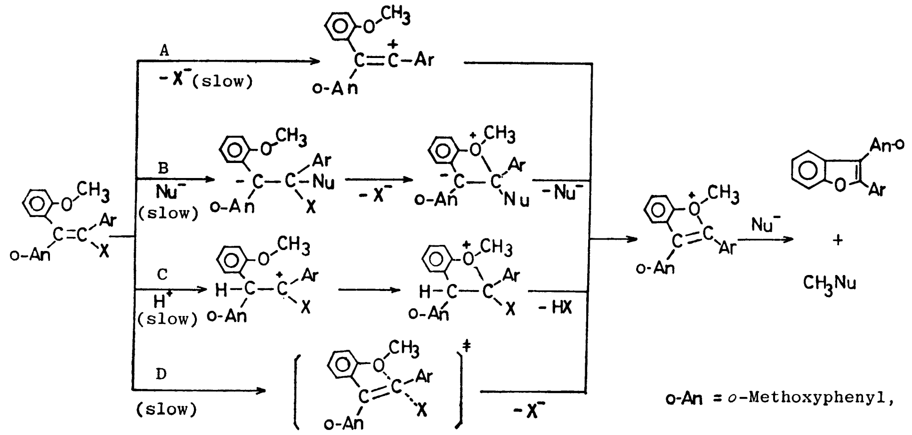
a) u, UV method; n, NMR method. b) Rate is an average of duplicate determinations.

Discussion

Evidence for the Vinyl Cation Intermediates. Several possible mechanisms for the exclusive intramolecular cyclization of 1-aryl-2,2-bis(*o*-methoxyphenyl)vinyl halides are shown in Scheme 1.

Path A *via* vinyl cation intermediates can be supported by the following criteria. The solvolysis rates fit first-order rate plots and do not depend on the base concentrations. The large α-substituent effect ($\rho=-4.12$ against σ^{+}) suggests the formation of a cation center on the α-carbon in the transition state. The solvent polar effect (m=0.53 at 120 °C) also indicates the cationic intermediate. Moreover, in addition to the electrophilic catalysis by the silver ions, the large leaving group effect ($k_{Br}/k_{Cl}=85$ in 80% EtOH and 27.8 in AcOH) suggests a heterolytic C–X bond fission in the rate-determining step. These reactivity ratios which depend on solvent,7,10) α-substituent,10,11) and leaving group7,12,13) effects are similar to those of the solvolysis of vinyl halides for which the intermediacy of vinyl cations has been established.

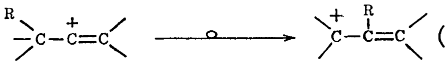
On the other hand, the possibilities of paths B–D, which may compete with the S_N1 mechanism in the solvolysis of vinyl derivatives,2) can be ruled out as follows. Path B involves an external nucleophilic attack on the double bond followed by displacement of the halogen by the *β*-*o*-methoxyl oxygen with elimination of the nucleophile. This pathway is unlikely in 80% EtOH or AcOH since the rate constants do not depend on the base concentrations. The nucleophilic addition-elimination mechanism was observed in the solvolysis of 9-(α-haloarylidene)fluorenes in 80% EtOH with strong nucleophiles,14) but the kinetic behavior of the fluorenyl systems are very different from those of our systems. Path C is a rate-determining electrophilic addition (protonation) followed by a methoxyl oxygen attack with elimination of the hydrogen halide.15,16) If path C could operate in our systems, the electrophilic addition should be faster in AcOH than in 80% EtOH. However, the solvolysis rates of **4** and **7** in 80% EtOH were faster than in AcOH ($k_{80\%\,EtOH}/k_{AcOH}$ of 4.4 for **4** at 120 °C and of 1.4 for **5** at 140 °C). Moreover, the



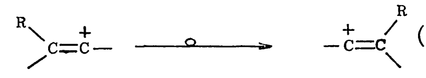
Scheme 1. Possible reaction paths for cyclization reaction.

effect of the leaving groups for the electrophilic addition-elimination route suggests the reactivity order: $k_{Cl} > k_{Br}$,[13] which is contrary to our systems. The exclusive cyclization to benzofurans and the lack of incorporation of the external nucleophiles suggest path D, which involves a one-step direct intramolecular S_N2-type attack of the β-*o*-methoxyl oxygen on the α-carbon with synchronous elimination of the halogen. However, such direct displacements at vinyl carbons are energetically unfavorable,[17] and have so far not been observed in vinyl systems. In path D, it could be expected that the solvolysis of 2-*o*-methoxyphenyl-substituted vinyl halides should be faster than that of the corresponding 2-*p*-methoxyphenyl-substituted vinyl derivatives in which the anchimeric acceleration by the β-methoxyl group is inherently impossible to operate. In practice, however, the solvolysis of 1,2,2-tris(*p*-methoxyphenyl)vinyl bromide (**16**)[7] is faster than that of **4** (k(**16**)/k(**4**) ratio of 1.7 in 80% EtOH at 120 °C and of 1.1 in AcOH at 120 °C). This result argues against the possibility of the anchimeric acceleration by the neighboring β-*o*-methoxyl group.

Cyclization vs. *2-*o*-Methoxyphenyl Migration.* As in the case of saturated carbenium ions, the rearrangement of the reactive vinyl cations to more stable cations is a characteristic feature of vinyl cation intermediates. In vinyl cations two types of rearrangements are known: to the double bond[18] (Eq. 1) and across the double bond[3,19] (Eq. 2).

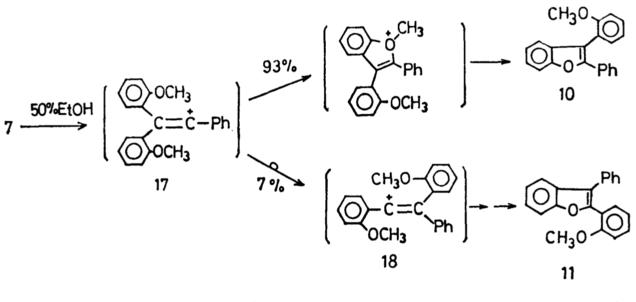


(Eq. 1)

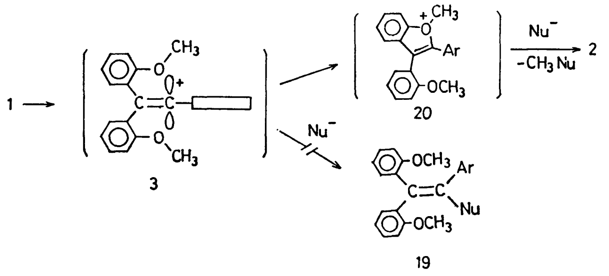


(Eq. 2)

Solvolysis of **7** gave small amounts of **11** (7, 7, and 9% in 50% EtOH, 80% EtOH, and AcOH with AgOAc, respectively) in addition to the normal cyclization product (**10**). Benzofuran (**11**) resulted from the 2-*o*-methoxyphenyl migration in the vinyl cation (**17**) to the more stable vinyl cation (**18**). The rearranged vinyl cation (**18**) is also exclusively attacked by the β-*o*-methoxyl oxygen. These results indicate that the nucleophilic attacks to the vinyl cation (**17**) are in the following ordering: internal nucleophilic attack (cyclization) > 2-*o*-methoxyphenyl group participation (migration) ≫ external nucleophilic attack.



In conclusion, it is a remarkable feature of the solvolytic reactions of 1-aryl-2,2-bis(*o*-methoxyphenyl)-vinyl halides (**1**) that exclusive cyclization to benzofurans (**2**) occurs in preference to the external nucleophilic attack to the vinyl cations (**3**) even in the presence of the strong nucleophiles. The origin of this exclusive cyclization can be discussed as follows. There exists a large steric hindrance between the aryl groups in **1**, because the substituents attached to the unsaturated carbons are held in the plane of the molecule. Vinyl cations (**3**) have the sp-hybridized structure and the α-aryl rings of the vinyl cations come to be perpendicular to the molecular plane in order to allow the π-orbital of the α-aryl groups to overlap well with the vacant *p*-orbital of the vinyl cations.[2] While some of the *cis* α-aryl and β-*o*-methoxyphenyl steric interaction is relieved in the sp-hybridized vinyl cations, the approach of the external nucleophiles to the cation center is still retarded because of the steric and electronic repulsions between the β-substituents and the approaching nucleophiles.[13,20] Moreover, even if such an external nucleophilic attack had occurred, the resulted vinyl derivatives (**19**) should be still sterically hindered. On the other hand, the intramolecular attack of the β-*o*-methoxy oxygen atoms upon the vinyl cations is entropically favorable since the β-*o*-methoxyl groups are located in suitable positions to attack the vacant *p*-orbital of the vinyl cations (**3**) and the resulted oxonium ions (**20**) are stabilized by the relief of the steric repulsion presented in the starting materials.[21] It seems likely that the proximity effect of the β-*o*-methoxyl group, in addition to the stability of the resulting product, is the driving force of the exclusive cyclization.



Experimental

All melting points are uncorrected. NMR spectra were taken on a JEOL JNM-MH-60 spectrometer. All mass spectra were obtained with a JEOL JMS-07 spectrometer. UV spectra were recorded with HITACHI 124, Shimadzu UV-200S, and UV-202S spectrometers. All IR spectra were obtained with a Shimadzu IR-400 spectrometer. Aqueous ethanolic mixtures were prepared according to Grob.[10] Acetic acid was prepared by refluxing glacial acetic acid with 1% acetic anhydride and then fractionally distilling. Sodium acetate solutions were prepared by disolving analytical sodium carbonate in acetic acid. *N*,*N*-Dimethylformamide (DMF) was dried over phosphorus pentoxide overnight and the fraction boiling at 78—79.5 °C (28—30 mm) was collected and stored over molecular sieves. 70% aqueous DMF was obtained according to Kaufman.[11]

Preparation of Vinyl Halides. Vinyl halides were prepared by appropriate modifications of the methods used for the preparation of 2-*p*-methoxyphenyl-substituted vinyl halides.[7] Spectral data of the vinyl halides are given in Table 4.

*2,2-Bis(*o*-methoxyphenyl)-1-(*p*-methoxyphenyl)vinyl Bromide (4).* *1,1-Bis(*o*-methoxyphenyl)-2-(*p*-methoxyphenyl)ethanol:* A solution of *o*-methoxyphenylmagnesium bromide was prepared in the usual manner from magnesium (2.43 g, 0.1

mol), *o*-bromoanisole (18.71 g, 0.1 mol), and ether (80 ml). As soon as the metal reacted, ethyl *p*-methoxyphenylacetate (9.71 g, 0.05 mol) in ether (40 ml) was added and the reaction mixture was heated under reflux for 20 min and allowed to stand overnight. The aqueous solution was extracted twice with CH_2Cl_2 and the combined extracts and the ether layer were washed with water, dried over Na_2SO_4, and evaporated to dryness. The solid obtained (10.75 g, 59%) was recrystallized three times (CH_2Cl_2–EtOH) and gave white needles, mp 164—169 °C, of 1,1-bis(*o*-methoxyphenyl)-2-(*p*-methoxyphenyl)ethanol. IR(Nujol): 3500 cm^{-1} (OH). NMR ($CDCl_3$, δ): 3.44 (d-s, 6H, OCH_3), 3.66 (d-s, 5H, OCH_3 and CH_2), 4.83 (s, OH), 6.45—7.45 (m, 12H, arom.). Found: C, 75.54; H, 6.73%. Calcd for $C_{23}H_{24}O_4$: C, 75.80; H, 6.69%.

*2,2-Bis(*o*-methoxyphenyl)-1-(*p*-methoxyphenyl)ethylene*: Phosphoric acid (85%, 8 ml) was added to 1,1-bis(*o*-methoxyphenyl)-2-(*p*-methoxyphenyl)ethanol (7.3 g, 20.1 mmol) and the mixture was kept at 100 °C for 3 h with stirring. The cooled mixture was washed four times with water by decantation and the residual oil was dissolved in CH_2Cl_2 and dried over Na_2SO_4. After solvent removal, recrystallization from CH_2Cl_2–EtOH (1:4) gave 2,2-bis(*o*-methoxyphenyl)-1-(*p*-methoxyphenyl)ethylene, mp 99.5—100.5 °C (6.57 g, 95%). NMR ($CDCl_3$, δ): 3.50 (s, OCH_3), 3.61 (s, OCH_3), 3.70 (s, OCH_3), 6.52—7.25 (m, 13H, =CH– and arom.). UV: λ_{max} (cyclohexane); 285 nm (ε 19200) and 208 (37000).

*2,2-Bis(*o*-methoxyphenyl)-1-(*p*-methoxyphenyl)vinyl Bromide (4)*: 1. To 1,1-bis(*o*-methoxyphenyl)-2-(*p*-methoxyphenyl)ethanol (6.06 g, 0.017 mol) in AcOH (24 ml), bromine (2.75 g, 0.017 mol) was added and the mixture was kept for 30 min with stirring. The mixture was poured into water and extracted with ether. The ether extract was washed with saturated $NaHCO_3$ solution and water, and dried over Na_2SO_4. After solvent removal, the residual oil was chromatographed over neutral alumina. The solvent removal from the benzene fraction gave the solid (2.33 g, 33%). Recrystallization (benzene–EtOH 1:1) afforded white needles, mp 126.5—128 °C, of 2,2-bis(*o*-methoxyphenyl)-1-(*p*-methoxyphenyl)vinylbromide (**4**). Found: C, 65.20; H, 5.05%. Calcd for $C_{23}H_{21}O_3Br$: C, 64.95; H, 4.98%.

2. *N*-Bromosuccinimide (1.8 g, 10 mmol) and benzoyl peroxide (50 mg) were added to 2,2-bis(*o*-methoxyphenyl)-1-(*p*-methoxyphenyl)ethylene (3.5 g, 10 mmol) in CCl_4 (50 ml). The mixture was refluxed for 1 h with irradiation with a photographic reflector spot lamp. After cooling to 0 °C, the succinimide was filtered and the filtrate washed with water, dilute NaOH solution, and water again. After solvent removal, recrystallization (CH_2Cl_2–EtOH 1:1) gave **4** (4.52 g, 71%), mp 128—130 °C.

*2,2-Bis(*o*-methoxyphenyl)-1-(*p*-methoxyphenyl)vinyl Chloride (5).* To 2,2-bis(*o*-methoxyphenyl)-1-(*p*-methoxyphenyl)ethylene (2.79 g, 8.05 mmol) in CCl_4 (20 ml), chlorine (0.6 g, 8.475 mmol) was added over the period of 120 min. After the solution was stirred for an additional 90 min, the solvent was evaporated and a white solid (2.68 g, 87%) precipitated. Recrystallization (CH_2Cl_2–EtOH) gave 2,2-bis(*o*-methoxyphenyl)-1-(*p*-methoxyphenyl)vinyl chloride (**5**), mp 112—113 °C. Found: C, 72.38; H, 5.63%. Calcd for $C_{23}H_{21}O_3Cl$: C, 72.53; H, 5.56%.

*2,2-Bis(*o*-methoxyphenyl)-1-*p*-tolylvinyl Bromide (6).* *1,1-Bis(*o*-methoxyphenyl)-2-*p*-tolylethanol*: To *o*-methoxyphenylmagnesium bromide (23.8 g, 0.112 mol) in ether (100 ml), dry benzene (40 ml) and then ethyl *p*-tolylacetate (10.0 g, 0.056 mol) in dry benzene (44 ml) were added, and the solution was allowed to stand overnight. After the solution was refluxed for 20 min, 2M-HCl (90 ml) was added and the reaction mixture was extracted with CH_2Cl_2. Work-up of the reaction mixture gave the solid. Recrystallization (CH_2Cl_2–EtOH 1:2) gave 1,1-bis(*o*-methoxyphenyl)-2-*p*-tolylethanol (15.11 g, 77.5%), mp 168—169 °C. NMR($CDCl_3$, δ): 2.20 (s, CH_3), 3.42 (d-s, 6H, OCH_3), 3.68 (s, CH_2), 4.84 (s, OH), 6.65—7.50 (m, 12H, arom.). IR(Nujol): 3570 cm^{-1} (OH). Found: C, 79.03; H, 6.98%. Calcd for $C_{23}H_{24}O_3$: C, 79.28; H, 6.94%.

*2,2-Bis(*o*-methoxyphenyl)-1-*p*-tolylethylene*: 1,1-bis(*o*-methoxyphenyl)-2-*p*-tolylethanol (10.0 g, 0.028 mol) was treated with phosphoric acid (85%, 15 ml) at 100 °C for 3 h. Work-up of the reaction mixture gave 2,2-bis(*o*-methoxyphenyl)-1-*p*-tolylethylene (8.69 g, 92%), mp 87.2—88.8 °C (EtOH). NMR (CCl_4, δ): 2.20 (s, CH_3), 3.43 (s, OCH_3), 3.56 (s, OCH_3), 6.55—7.20 (m, 13H, =CH– and arom.). UV: λ_{max} (cyclohexane); 283 nm (ε 17800), 220 (26900). Found: C, 83.58; H, 6.82%. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71%.

*2,2-Bis(*o*-methoxyphenyl-1-*p*-tolylvinyl Bromide (6)*: Bromine (0.97 g, 6.05 mmol) in CCl_4 (10 ml) was added slowly to 2,2-bis(*o*-methoxyphenyl)-1-*p*-tolylethylene (2.0 g, 6.09 mmol) in CCl_4 (15 ml) while cooling, with stirring which continued for an additional 30 min. Solvent removal gave the solid and recrystallization (CH_2Cl_2–EtOH 1:5) gave white needles, mp 123—124 °C, of 2,2-bis(*o*-methoxyphenyl)-1-*p*-tolylvinyl bromide (**6**) (3.25 g, 87.5%). Found: C, 67.17; H, 5.33%. Calcd for $C_{23}H_{21}O_2Br$: C, 67.49; H, 5.17%.

*2,2-Bis(*p*-methoxyphenyl)-1-phenylvinyl Bromide (7).* *1,1-Bis(*o*-methoxyphenyl)-2-phenylethanol*: To *o*-methoxyphenylmagnesium bromide(*o*-bromoanisole, 22.47 g, 0.12 mol, magnesium, 2.67 g, 0.11 mol) in ether (100 ml), ethyl phenylacetate (8.2 g, 0.05 mol) in dry benzene (70 ml) was added slowly and heated under reflux for 4 h. On cooling, 2M-HCl (70 ml) was added and a work-up of the reaction mixture similar to that of 1,1-bis(*o*-methoxyphenyl)-2-(*p*-methoxyphenyl)ethanol gave the precipitate (10.23 g, 61%). Recrystallization (CH_2Cl_2–EtOH) gave 1,1-bis(*o*-methoxyphenyl)-2-phenylethanol, mp 154 °C. NMR ($CDCl_3$, δ): 3.43 (d-s, 6H, OCH_3), 3.72 (s, CH_2), 4.83 (broad s, OH), 6.64—7.46 (m, 13H, arom.). IR (Nujol): 3560 cm^{-1} (OH). Found: C, 78.92; H, 6.63%. Calcd for $C_{22}H_{22}O_3$: C, 79.01; H, 6.63%.

*2,2-Bis(*o*-methoxyphenyl)-1-phenylethylene*: 1,1-Bis(*o*-methoxyphenyl)-2-phenylethanol (5.0 g, 0.015 mol) was treated with phosphoric acid (11 ml) at 100 °C for 3 h. Work-up of the reaction mixture gave 2,2-bis(*o*-methoxyphenyl)-1-phenylethylene (4.59 g, 97%), mp 91—92 °C. NMR (CCl_4, δ): 3.41 (s, OCH_3), 3.57 (s, OCH_3), 6.55—7.15 (m, 14H, =CH– and arom.). UV: λ_{max} (cyclohexane) 284 nm (ε 16000), 250 (12500). Found: C, 83.24; H, 6.40%. Calcd for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37%.

*2,2-Bis(*o*-methoxyphenyl)-1-phenylvinyl Bromide (7)*: 2,2-bis(*o*-methoxyphenyl)-1-phenylethylene (3.50 g, 0.01 mol) was treated with *N*-bromosuccinimide (2.00 g, 0.012 mol) and benzoyl peroxide (50 mg) in CCl_4 (70 ml) in a manner similar to that used preparation of **4**. The solid obtained (3.87 g, 89%) was recrystallized (CH_2Cl_2–EtOH 2:5) to give white needles, mp 142—143 °C, of 2,2-bis(*o*-methoxyphenyl)-1-phenylvinyl bromide (**7**). Found: C, 66.85; H, 4.85%. Calcd for $C_{22}H_{19}O_2Br$: C, 66.84; H, 4.84%.

*Reaction of 2,2-Bis(*o*-methoxyphenyl)-1-(*p*-methoxyphenyl)vinyl Bromide (4).* *Reaction in 80% EtOH*: Vinyl bromide (**4**) (70 mg, 0.164 mmol) in 80% EtOH (20 ml) containing NaOH (0.5 mmol) was kept in a sealed ampoule at 120 °C for 8 h. The solvent was removed and ether was added, then the inorganic salt was removed, dried over Na_2SO_4, and the ether was evaporated to give 3-(*o*-methoxyphenyl)-2-(*p*-methoxyphenyl)benzofuran (**8**) exclusively. The NMR spectrum and the thin-layer chromatogram of the crude product showed no

TABLE 4. SPECTRAL DATA OF VINYL HALIDES (**4**)—(**7**)

Compd	NMR (CCl_4, δ)	λ_{max} (cyclohexane) nm (ε)	MASS (m/e)
4	3.46 (s, 3H, OCH_3)	285 (13400)	426, 424 (M^+)
	3.65 (s, 3H, OCH_3)	240 (17000)	345 (M^+–Br)
	3.70 (s, 3H, OCH_3)		330 (M^+–CH_3Br)
	6.34—7.25 (m, 12H, arom.)		
5	3.43 (s, 3H, OCH_3)	284 (15500)	382, 380 (M^+)
	3.58 (s, 3H, OCH_3)	240 (16400)	330 (M^+–CH_3Cl)
	6.42—7.23 (m, 12H, arom.)		
6	2.21 (s, 3H, OCH_3)	283 (11500)	410, 408 (M^+)
	3.47 (s, 3H, OCH_3)	235 (sh, 20000)	329 (M^+–Br)
	3.73 (s, 3H, OCH_3)		314 (M^+–CH_3 Br)
	6.40—7.30 (m, 12H, arom.)		
7	3.43 (s, 3H, OCH_3)	284 (10500)	396, 394 (M^+)
	3.73 (s, 3H, OCH_3)		315 (M^+–Br)
	6.40—7.25 (m, 13H, arom.)		300 (M^+–CH_3Br)

product other than **8**. Recrystallization (EtOH) gave white plates, mp 125—126 °C. NMR (CCl_4, δ): 3.58 (s, OCH_3), 3.68 (s, OCH_3), 6.58—7.62 (m, 12H, arom.). MS (m/e): 330 (M^+). Found: C, 80.13; H, 5.26%. Calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49%.

Reaction in AcOH: Vinyl bromide (**4**) (70 mg, 0.164 mmol) in AcOH (7 ml) with Na_2CO_3 (85 mg, 0.8 mmol) was refluxed for 27 h. The cooled solution was poured into water, extracted with ether, washed with saturated $NaHCO_3$ solution and water, dried over Na_2SO_4, and then the solvent was evaporated to give the precipitate. Recrystallization (EtOH) gave white needles, mp 124.5—125.5 °C, of **8**. The NMR spectrum of the crude product showed that **8** was probably the only product.

Reaction in 70% Aqueous DMF: Vinyl bromide (**4**) (120 mg, 0.283 mmol) in 70% aqueous DMF (20 ml) was kept in a sealed ampoule at 140 °C for 16 h. The NMR spectrum of the crude product showed the presence of **8** as the sole product.

Reaction in the Presence of Sodium Azide: Vinyl bromide (**4**) (70 mg, 0.165 mmol) in basic (NaOH, 0.4 mmol) 80% EtOH (20 ml) in the presence of sodium azide (650 mg, 10.0 mmol) was kept in a sealed ampould at 120 °C for 6 h. The NMR spectrum of the crude product showed the quantitative formation of **8**.

Reaction in the Presence of Sodium p-*Toluenethiolate*: Vinyl bromide (**4**) (210 mg, 0.49 mmol) and *p*-toluenethiol (87.1 mg, 0.7 mmol) in basic (NaOH, 0.7 mmol) 80% EtOH (7 ml) was sealed in an ampoule and kept at 120 °C for 4 h. After work-up of the solution, the NMR spectrum of the reaction mixture (in CCl_4) showed the presence of **8** (100%) and methyl *p*-tolyl sulfide (47%) (CH_3 at δ 2.02 and SCH_3 at 2.33) which was assigned by comparison with an authentic sample.[22] Since it was hoped that more of the methyl moiety would be trapped by the nucleophile *p*-toluenethiolate ions, the reaction of **4** (200 mg, 0.47 mmol) in basic (NaOH, 1.4 mmol) 80% EtOH (7 ml) in the presence of *p*-toluenthiol (1.4 mmol) was conducted under the same conditions. The NMR spectrum of the reaction mixture this time showed **8** (100%) and methyl *p*-tolyl sulfide (74%).

*Reaction of 2,2-Bis(*o*-methoxyphenyl)-1-(*p*-methoxyphenyl)-vinyl Chloride (5)*. Vinyl chloride (**5**) (60 mg, 0.16 mmol) in basic (NaOH, 0.5 mmol) 80% EtOH (20 ml) was sealed in an ampoule and kept at 160 °C for 25 h. After work-up of the reaction mixture, the NMR spectrum of the crude product showed the dominant formation of **8**.

*Reaction of 2,2-Bis(*o*-methoxyphenyl)-1-*p*-tolylvinyl Bromide (6)*. Vinyl bromide (**6**) (60 mg, 0.15 mmol) in 80% EtOH containing NaOH (0.5 mmol) was kept in a sealed ampoule at 160 °C for 43 h. Work-up of the reaction mixture gave the precipitate of 3-(*o*-methoxyphenyl)-2-*p*-tolylbenzofuran (**9**). The NMR spectrum (in CCl_4) of the crystallized product, mp 89—90 °C, which was identical with that of the crude product, had peaks at δ 2.29 (s, CH_3), 3.56 (s, OCH_3), 6.75—7.44 (m, 12H, arom.). UV: λ_{max} (80% EtOH); 306 nm (ε 26800), 240 (sh, 17200). MS (m/e): 314 (M^+). Found: C, 83.82; H, 5.85%. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77%.

*Reaction of 2,2-Bis(*o*-methoxyphenyl)-1-phenylvinyl Bromide (7)*. With protection from light, vinyl bromide (**7**) (0.31 g, 0.78 mmol) in AcOH (20 ml) containing silver acetate (0.84 g, 5 mmol) was refluxed for 21 h (100% reaction), followed by filtration, and the solvent was evaporated. Work-up of the reaction mixture gave an oil (0.23 g) which could not be induced to crystallize. An NMR spectrum (in CCl_4) of the crude product showed two different methoxyl proton peaks (singlet at δ 3.58 and 3.31) in addition to aromatic proton peaks (multiplet at δ 6.8—7.7) indicating the possibility of two different products, each one of which would have one methoxyl group. Integration of these methoxyl proton peaks showed two products to be present in the ratio of 91 : 9, respectively. Similarly, the reaction of **7** (63 mg, 0.16 mmol) in basic (NaOH, 0.5 mmol) 80% EtOH (20 ml) in a sealed ampoule at 160 °C for 204 h (95% reaction) and the reaction of **7** (55 mg, 0.136 mmol) in basic (NaOH, 7.0 mmol) 50% EtOH (14 ml) at 160 °C for 26 h (96% reaction) gave the two products in similar product ratios (93 : 7 for both). Twice attempted separation of the two products by thin-layer chromatography (TLC) on silica gel (benzene–hexane 1 : 2 or 1 : 3) gave only poor separations, as judged by the small changes in the relative NMR intensities of the two different methoxyl proton peaks. By treating the reaction mixture (0.103 g) with a hot saturated solution of picric acid in EtOH (3 ml) and allowing the solution to cool, a picrate was separated in orange-red needles (0.122 g), which were then recrystallized (EtOH), mp 108—109 °C. Found: C, 61.02; H, 3.62; N, 7.86%. Calcd for $C_{27}H_{19}O_9N_3$ (1 : 1 π-complex of picric acid and $C_{21}H_{16}O_2$): C, 61.25; H, 3.62; N, 7.94%. The picrate was split by chromatography on alumina and eluted with benzene to give a pale yellow oil. All attempted crystallizations failed. The NMR spectrum of this oil (in CCl_4) showed only one methoxyl singlet at δ 3.45 and an aromatic 13H multiplet at δ 6.9—7.7, indicating the isolated major product. MS (m/e): 330 (M^+). The UV spectrum in cyclohexane showed a characteristic absorption at 305 nm of 2-phenylbenzofuran chromophor; its structure was assigned to 3-(*o*-methoxyphenyl)-2-phenylbenzofuran (**10**), as discussed in Table 1. Attempts to isolate the minor product from the filtrate of the picrate by TLC or by formation of the picrate failed. The high-pressure liquid chromatogram of the filtrate (by Shimadzu 840 instrument; column, Varian-Aerograph Micro Pack AL-10 $2.2\phi \times 0.25$ m; eluent, hexane; flow rate, 0.4 ml/min) showed two separated peaks and their UV spectra were recorded by the stop-flow method, as shown in Table 1. The assignment of these peaks was previously discussed.

Kinetics. *Titration Method*: Kinetic runs were achieved according to a method similar to Rappoport's.7) Titration of the bromide ions against standard silver nitrate using Eosin or Uranin indicators (Fajans method) showed ambiguous end-points of titration, so this method was abandoned. Titrimetrirate constants were determined by the Volhald method as follows. The reaction mixtures in ten to fifteen sealed ampoules, each of which was quenched at appropriate times, were diluted with water ten times. A weighted quantity of the standard silver nitrate was added to each solution. After addition of concd nitric acid (2 ml), nitrobenzene (3—5 ml), and iron alum solution (2 ml), back-titration by the standard 0.01 M potassium thiocyanate gave a sharp end-point.

UV Method: The reaction mixtures of UV concentration in ten to fifteen ampoules were quenched at appropriate intervals and the change in the absorbance (at 300—310 nm) of the reaction mixture was followed by an UV spectrometer. In some runs, concd reaction mixtures were diluted to UV concentration and their UV spectra were measured.

NMR Method: Five to six sealed ampoules, each of which contained vinyl halides (50 mg) in 80% EtOH or AcOH with buffers, were quenched at appropriate times. After work-up of the reaction mixtures, rate constants were obtained by following the relative NMR intensities of the different methoxyl peaks of vinyl halides and benzofurans.

All rate constants are calculated by the least-squares method.

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