Theoretical and Experimental Study on the Reaction Mechanism of Photolysis and Solvolysis of Arylvinyl Halides

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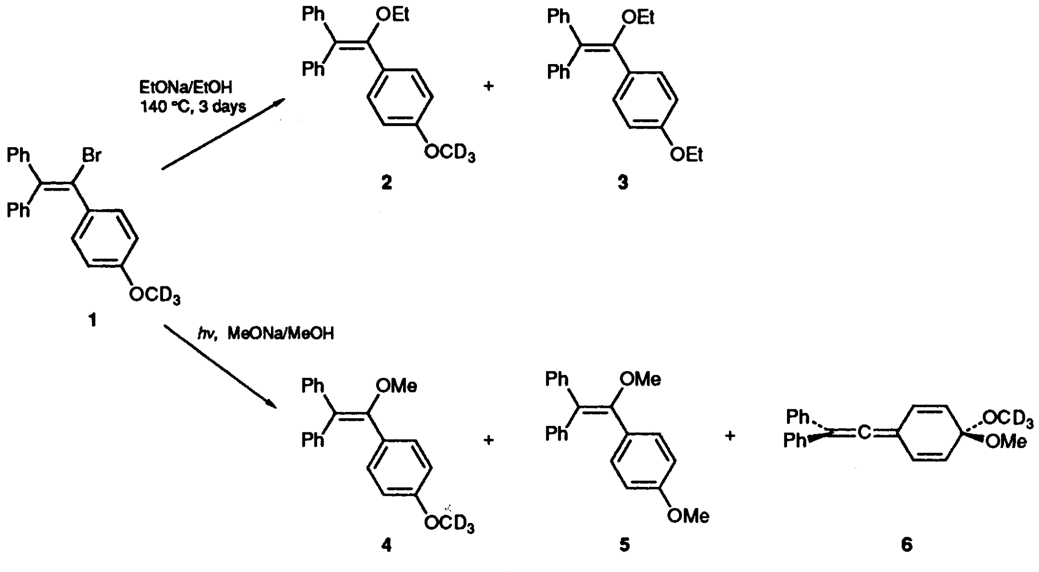
The reaction mechanisms of solvolysis and photolysis of arylvinyl halides have been studied in terms of *ab initio* molecular orbital calculations and experiments. The frontier orbital of the *p*-methoxyphenylvinyl cation requires that nucleophiles attack not only the vinylic carbon but also the *ipso* position of the *p*-methoxy group. The experimental results also show the possibility of a mechanism proceeding *via* the *ipso* intermediate. The solvolysis affords exclusively the vinyl type products because of the instability of the *ipso* intermediate. On the other hand, some of the *ipso* intermediate does not decompose to produce the vinyl cation under the mild conditions of photolysis. Substitution of the *p*-methoxy group in the anisyl fragment occurs in cases where the nucleophile has the ability to form a bond comparable with or stronger than the original C–O bond.

Since vinyl cations were confirmed in the solvolysis of halostyrenes,[1] much attention has been focused on these intermediates as active species in organic reactions. There are several methods of producing the intermediate.[1,2] Photolysis[3,4] has been a useful method to generate vinyl cations. Solvolysis of vinyl substrates is favoured by adding an α-aryl group to stabilize the cation or a good leaving group such as triflate.[1] Recently, we found that solvolysis of α-(*p*-methoxyphenyl)-β,β′-diphenylvinyl bromide **1** gave a different pattern of product distribution. Solvolysis at 140 °C in the presence of ethoxide anion resulted in conversion of the substrate into a mixture of vinyl ether derivatives, **2** and **3**, as shown in Scheme 1.[5] It is noteworthy that this reaction afforded **3** as a product in which both the Br and the CD_3O groups in **1** were substituted by ethoxy groups. Other nucleophiles, except for CN^-, did not replace the alkoxide group on the aromatic ring. Similar aromatic substitution reactions have been observed for benzylic cations.[6]

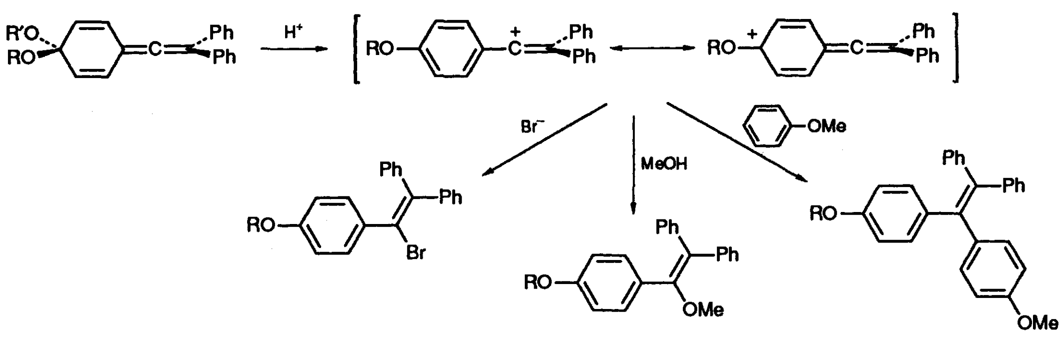
Photolysis of **1** also generates the vinyl cation to give vinyl ethers **4** and **5** under mild conditions.[7] This reaction also produces the product **6** which has a methoxy group added at the *ipso* position of the CD_3O group (hereafter, this type of molecule is called the *ipso* compound). The present experiments indicated that the vinyl/*ipso* ratio of the products depends on the temperature of the reaction. Other nucleophiles did not afford *ipso* products.[5] The *ipso* compounds decompose easily under acidic conditions to form arylvinyl cations. The cations react with several nucleophiles to afford the corresponding vinyl derivatives as shown in Scheme 2.[8]

The *p*-methoxy group in **1** is essential for its solvolysis and photolysis. This substituent has the ability to delocalize the positive charge not only on the vinyl but also on the aryl fragment in the cation. Therefore, it plays an important role in stabilizing the vinyl cation intermediate. In the case of the model cation **7**, we can consider two resonance structures **7v** and **7i**. According to these resonance forms, we can expect both the *ipso* and vinyl products to be formed. However, only the vinyl position seemed to be attacked by typical nucleophiles such as azide, cyanate, bromide and thiocyanate anions. Only the alkoxide anion leads to *ipso*-attack to form *ipso* adducts under photolysis conditions. Although the *ipso* position is open to all kinds of nucleophiles, the photolysis and solvolysis strongly depend on the nucleophile employed.[9] The resonance forms give no assistance with the interpretation of such experimental results.

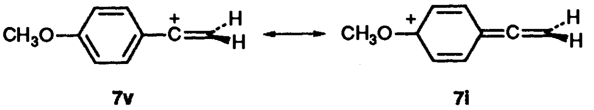
In order to understand the strange behaviour of the solvolysis



Scheme 1



Scheme 2



7v **7i**

and photolysis of α-arylvinyl halides, we have to know whether the reactions proceed under kinetic or thermodynamic control. The former effect is expected on consideration of the frontier orbitals of vinyl cations as the intermediates. The latter factor is estimated by the relative stability of the vinyl and *ipso* compounds as products. Molecular orbital (MO) calculations describe both properties well. Apeloig *et al.*[10] used this method (MINDO/3[11]) in order to investigate the intermediates by dissociative ionization of aryl-substituted vinyl bromides in the gas phase. The method was also useful for investigation of the reactivity of benzyl and related cations.[12] The substituent effect was also investigated for phenylmethyl cations with an electron-withdrawing group.[13]

In the present paper, our attention is focused on the reaction mechanism shown in Schemes 1 and 2. We have also studied the unique electronic and geometrical features of the reactants, intermediates and products. These properties are very much related to the mechanisms of solvolysis and photolysis.

Method of Calculations.—The *ab initio* MO calculations were performed using the GAUSSIAN86 program[14] at the Institute for Molecular Science. We also used the GAUSSIAN90 program for the Fujitsu S-4/1 Computer.[15] MINI1 basis sets[16] were used for geometry optimizations of ground state molecules by the energy gradient method.

We adopted model molecules such as vinyl cations **7** and **12**, α-anisylvinyl chloride **8**, vinyl ether **10** and their *ipso* isomers **9** and **11**. They have no substituents at the β-position for simplicity of calculations. While **8** is regarded as the reactant, **10** and **11** are the products of photolysis of solvolysis. **12** is a useful molecule to estimate the substituent effect in the benzene ring.

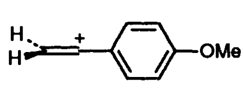
Results and Discussion

Experimental Results.—Solvolysis of α-arylvinyl bromides needed a high temperature of 140 °C for 3 days and produced only vinyl ethers **2** and **3**. The CD_3O group in **1** was displaced by the ethoxy group in **3**. The product ratio of **2**/**3** was 46/54.[7] The methoxy group in the anisyl fragment was not substituted with nucleophiles with the exception of cyanide and alkoxide anions. The vinyl/*ipso* ratio from the photolysis of **1** at 0 °C was 38/40.[7] We found no trace of *ipso* compounds in the products of the reaction at 45 °C. The photolysis using other nucleophiles gave only vinyl products.

Charge Distribution and Frontier Orbitals in Vinyl Cations.—It is interesting to see how the introduction of a methoxy group to **12** causes changes of charge distribution in the vinyl cation. Table 1 summarizes the geometrical parameters and the atomic charges optimized for vinyl cations, **7**, **12** and **12R**.* The positive charge on C(2) (0.200) of **12** is not so much different from that on C(8) (0.188). The total charge on the vinyl fragment (0.463) is smaller by 0.074 than that on the aryl fragment (0.537). The cation centre produced at C(2) is delocalized over the benzene ring as well. The charge distribution of **12R** is different from that of **12**—65.4% of the positive charge is localized in the vinyl fragment. The rotation of the terminal CH_2 plane prevents the cation centre from delocalizing over the benzene ring. Since the smaller interaction between the two fragments makes this geometry unstable, **12R** is less stable by 25.1 kcal mol^{-1} than **12**.†

The charge distribution in the vinyl cation is greatly influenced by the introduction of a *p*-methoxy group. The total charge on the vinyl fragment (0.378) of the substituted cation **7** is much smaller than that in the simple vinyl cation **12**. While the charge on C(4) (0.175) of the former is not so much different from that of the latter (0.171), the positive charge on C(8) (0.302) of **7** is much larger (by 0.114) than that of **12** (0.188). The introduction of the methoxy group makes the C(8) position to the more attractive site for nucleophiles. C(8) is more positive by 0.143 than C(2) in **7**. Therefore, the contribution of **7i** should be larger than that of **7v** in this molecule.

The change in the charge distribution leads to greater bond alternation in **7** than in **12**. This trend is clearly seen in the C(2)–C(3) and aromatic C–C bond lengths. While those of **7** are in the range 1.379–1.482 Å, those of **12** are between 1.404 and 1.444 Å. The optimized structures of **7** and **12R** are displayed in



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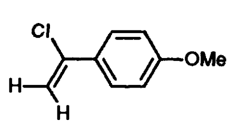

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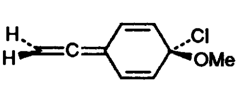

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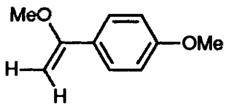

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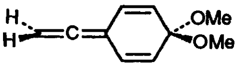

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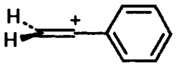

12

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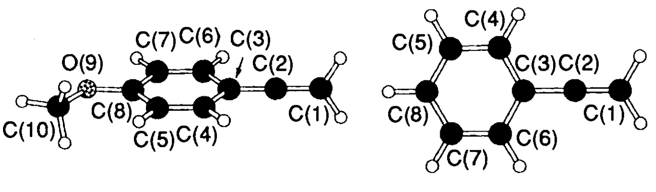
* **R** means that this molecule has the CH_2 plane parallel to the benzene ring as shown in Fig. 1.

† 1 cal = 4.184 J.

Table 1 Total energies, geometrical parameters and net atomic charges obtained for vinyl cations **7**, **12** and **12R**

	7	12	12R
Total energy[a]	−417.669 32	−304.543 65	−304.503 66
Lengths/Angles[b]			
C(1)–C(2)	1.325	1.324	1.327
C(2)–C(3)	3.379	1.404	1.496
C(3)–C(4), C(3)–C(6)	1.479, 1.482	1.466	1.434
C(4)–C(5), C(6)–C(7)	1.390, 1.384	1.406	1.418
C(5)–C(8), C(7)–C(8)	1.471, 1.476	1.444	1.427
C(8)–O(9)	1.368	—	—
O(9)–C(10)	1.492	—	—
H–C(1)–C(3)–C(4)	90.0	90.0	0.0
C(5)–C(8)–O(9)–C(10)	−179.8	—	—
Charge[c]			
C(1)	0.219	0.263	0.320
C(2)	0.159	0.200	0.334
(vinyl fragment)	0.378	0.463	0.654
C(3)	−0.100	−0.092	−0.066
C(4), C(6)	0.175, 0.161	0.171	0.082
C(5), C(7)	−0.001, 0.043	0.050	0.073
C(8)	0.302	0.188	0.102
O(9)	−0.312	—	—
C(10)	0.354	—	—
(Aryl fragment)	0.622	0.537	0.346

[a] Total energies in Hartree. [b] Bond lengths in Å and angles in degrees. [c] Atomic charges with hydrogens summed into heavy atoms.



7 **12R**

Fig. 1 Optimized structures of **7** and **12R**

Fig. 1. It is noteworthy that the terminal CH$_2$ plane is perpendicular to the benzene ring in **7**. O(9) and C(10) almost lie in the same plane as that of the benzene ring and they participate in the conjugation of the molecule.

If the solvolysis is a kinetically controlled reaction, the frontier orbital of the vinyl cation intermediate governs the distribution of products. The lowest unoccupied MO (LUMO) is the frontier orbital of the ground state cation because a nucleophile is the other active species. The schematic representation of the LUMO of **7** is displayed in Fig. 2. The LUMO coefficients of C(2) (vinyl position) and C(8) (*ipso* position) in **7** are 0.619 and −0.511, respectively. On the other hand, those of C(2) and C(8) in **12** are 0.678 and −0.488. The difference in their absolute values for **7** (0.108) is almost half that (0.190) for **12**. The introduction of a *p*-methoxy group causes such a big change of the LUMO coefficients. We can expect that the major products of the solvolysis have vinyl geometry. However, according to the LUMO and the charge distribution, we cannot discard the possibility of the product and/or the intermediate having the *ipso* geometry.

Excited states of reactants and intermediates may be involved in the photolysis. To explore the excited states of the vinyl cation **7**, GVB[17] open shell singlet (OSS) calculations of **7-E*** were also performed with the same geometries obtained for the ground state molecules. It is well known that irradiation of ethylene causes rotation from two perpendicular CH$_2$ planes. We also expected this geometrical change for the photochemical reaction. Therefore, the GVB OSS energy of **7R-E** was calculated with the same geometry as the ground state except for the dihedral angle of the terminal CH$_2$ plane. The total energies of **7-E** and **7R-E** were calculated to be −417.579 01 and −417.596 48 Hartree, respectively. **7R-E** is more stable by 11.6 kcal mol^{-1} than **7-E**. Although both structures are not optimized in the OSS states, the excited cations probably have a rotated CH$_2$ plane. Therefore, the two singly occupied MOs (SOMO) of **7R-E**, displayed in Fig. 2, may relate to the photolysis. The p$_y$ atomic orbital of C(2) (1.001) occupies almost part of SOMO2. On the other hand, neither C(8) (0.212) nor C(2) (0.195) has the largest coefficient in SOMO1. Although almost half of the orbital is constructed with the p$_z$ orbital of C(1) (0.703), no reaction has been observed at the terminal carbon. Therefore, we cannot regard the excited cation as the active species of the photolysis.

Stability of Vinyl and ipso *Compounds*.—If the distribution of products is determined by thermodynamic stability of the products in photolysis and/or solvolysis, then the difference of free energies between the vinyl and *ipso* isomers is of importance. We can roughly estimate this from the total energies of the MO calculations. Table 2 summarizes the total energies of the reactants and products together with the optimized geometrical parameters. The optimized geometries of **8** and **11** are shown in Fig. 3. The total energies of the vinyl ether **10** and the *ipso* product **11** are calculated to be −531.648 74 and −531.570 01 Hartree, respectively. **10** is more stable by 49.4 kcal mol^{-1} than **11**. As their relative stability relates to the product distribution, the 6-31G//MINI1 [18,†] energies were calculated in order to obtain a better energy description. The total energies for **10** and **11** are −535.098 14 and −535.023 70 Hartree, respectively. The energy difference is 46.7 kcal mol^{-1} which is close to the MINI1 energy. Therefore, the vinyl ether should be the major product of solvolysis and photolysis, being consistent with our experimental results. The same trend is seen for **8** and **9**. It is possible to calculate the stabilization energy ΔE_{stab} ‡ for bond formation between **7** and nucleophiles. Those for the vinyl position are calculated to be −291.6 and −182.7 kcal mol^{-1} for CH$_3$O$^-$ and Cl$^-$, respectively. Those for the *ipso* position are −241.6 and −137.4 kcal mol^{-1}, respectively. The vinyl cation can bind CH$_3$O$^-$ more strongly than Cl$^-$ at both sites. Although the *ipso*-type molecule is unstable and its binding energy is small, this molecule should be an unstable intermediate of the reaction as discussed below.

The dihedral angle C(1)–C(2)–C(3)–C(4) between the vinyl and the anisyl fragments in **8** is calculated to be 30.4° as listed in Table 2. Therefore, the vinyl group does not lie in the same plane as the phenyl ring. This trend is similar to the result seen in styrene using very large basis sets.[19] This angle depends on the relative size of the substituent at the α-position. The C–C bond lengths in the benzene ring are in the range of 1.410 and 1.434 Å, slightly longer than those observed in benzene. On the other hand, the C(1)–C(2) and C(2)–C(3) bond lengths in the vinyl

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* E signifies that this molecule is in the excited state.

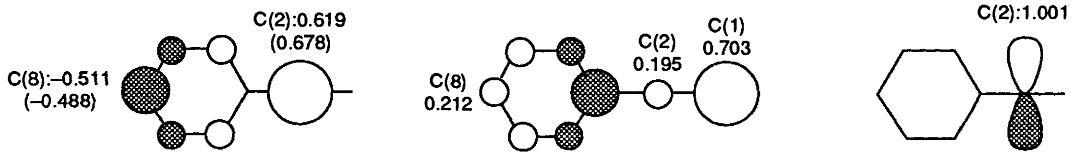
† 6-31G//MINI1 means the calculation which uses the 6-31G basis set and the optimized geometry by use of the MINI1 basis set.

‡ The stabilization energy for new bond formation is calculated as $\Delta E_{\text{stab}} = E_{\text{product}} - (E_{\text{cation}} + E_{\text{anion}})$, where E_{product}, E_{cation} and E_{anion} are the total energies of product, vinyl cation and nucleophile, respectively. We must take into account the basis set superposition error because we used the minimal basis set. However, the relative strength of C–O and C–Cl bonds will not change even if we used a larger basis set such as 6-31G**.

Table 2 Geometrical parameters and total energies optimized for the products vinyl chloride **8**, vinyl ether **10** and their *ipso* isomers, **9** and **11**

	ipso			Vinyl	
	9	**11**		**8**	**10**
Total energy	−0.163 34[a]	−0.570 01[b]		−0.235 16[a]	−0.648 74[b]
Lengths/angles[c]					
C(1)–C(2)	1.326	1.326	C(1)–C(2)	1.353	1.357
C(2)–C(3)	1.340	1.339	C(2)–C(3)	1.524	1.531
C(3)–C(4)	1.515	1.516	C(2)–Cl–(O)	1.863	1.444
C(4)–C(5)	1.352	1.351	C(3)–C(4)	1.420	1.427
C(5)–C(8)	1.550	1.566	C(4)–C(5)	1.420	1.411
C(3)–C(6)	1.514	1.516	C(5)–C(8)	1.427	1.435
C(6)–C(7)	1.353	1.351	C(3)–C(6)	1.427	1.417
C(7)–C(8)	1.554	1.571	C(6)–C(7)	1.410	1.421
C(8)–O(9)	1.453	1.474	C(7)–C(8)	1.434	1.426
C(8)–Cl–O(11)	1.972	1.482	C(8)–O(9)	1.423	1.425
C(1)–C(2)–C(3)	179.9	180.0	C(1)–C(2)–C(3)	126.5	124.2
H–C(1)–C(3)–C(4)	90.0	89.7	C(1)–C(2)–C(3)–C(4)	30.4	23.4
C(4)–C(5)–C(8)–O(9)	131.5	119.6	H–C(1)–C(2)–Cl–(O)	182.7	173.9
C(4)–C(5)–C(8)–Cl–O(11)	−113.3	−127.0	C(4)–C(5)–C(8)–O(9)	177.4	−179.9
			C(7)–C(8)–C(9)–O(10)	−179.8	0.7

[a] Total energies +875.0 in Hartree. [b] Total energies +531.0 in Hartree. [c] Bond lengths in Å and angles in degrees.



7 (LUMO) 7R-E(SOMO1) 7R-E(SOMO2)

Fig. 2 Schematic representation of the LUMO of **7** and two SOMOs of **7R-E**. Values are the MO coefficients of these frontier orbitals. Those in parentheses are LUMO coefficients of **12**. The contribution from the methoxy group is omitted.

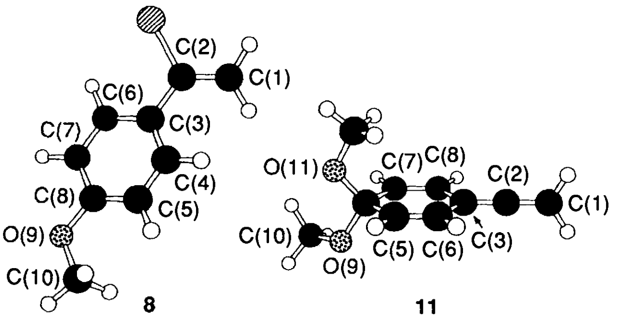
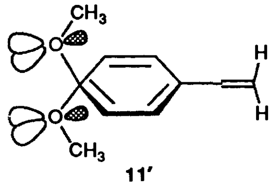


Fig. 3 Optimized structures of **8** and **11**



11′

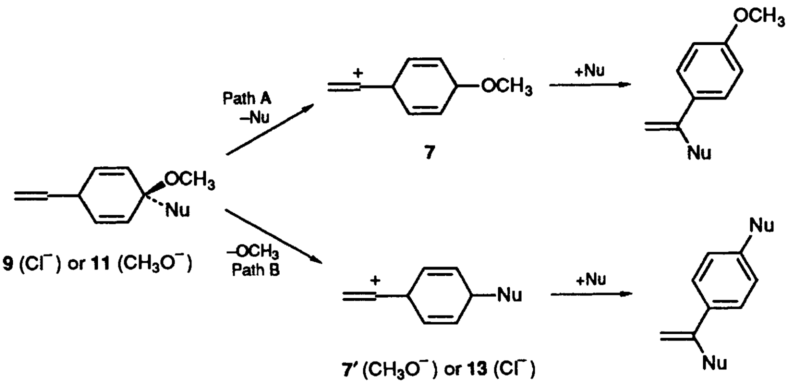
fragment are 1.353 and 1.524 Å, respectively. The former is close to a C–C double bond length and the latter to a single bond length. The methoxy group participates in conjugation with the benzene ring since the dihedral angle C(7)–C(8)–O(9)–C(10) is −179.8°. The geometrical features of **10** are similar to **8**.

Bond lengths for C(2)–C(3), C(3)–C(4), C(4)–C(5) and C(5)–C(8) in the *ipso* product **11** are calculated to be 1.339, 1.516, 1.351 and 1.566 Å, respectively. There is bond alternation in the molecule. It is important to point out that **11** has the terminal CH_2 plane perpendicular to the benzene ring like an allene molecule shown in Fig. 3. Because of the repulsion between lone pair orbitals of O(9) and O(11), the two methoxy groups cannot take up a conformation like **11′**.

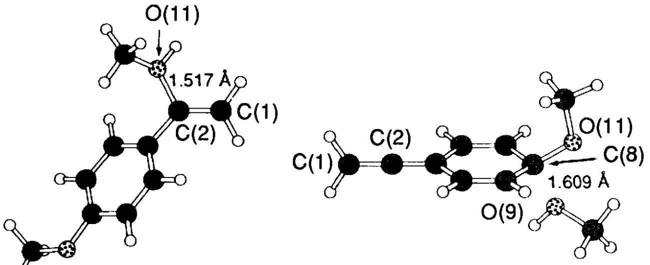
Substituent in Aryl Fragment of Final Product.—The resonance structures of **7v** and **7i** explain neither why the CD_3O group is displaced only by the alkoxide or cyanide ion in the solvolysis nor why the products of the reactions are dependent on the nucleophiles used. The present MO calculations suggest the solution for the two problems. Although the LUMO coefficients indicate the major product to have the vinyl geometry, they also suggest the possibility of the *ipso* intermediate. We have to consider the reaction *via* the *ipso* intermediate, as in Scheme 3.

While vinyl ethers as the products are too stable to decompose to vinyl cations again, the *ipso* intermediates are unstable and we can expect their decomposition of vinyl cations under solvolytic conditions. We examined two nucleophiles, Cl^- as a soft base and CH_3O^- as a hard base. As **9** has two different substituents at the *ipso* position, we can consider two paths which reproduce two kinds of vinyl cation from the intermediate. One is path A which liberates the introduced nucleophile and affords **7** again. The other is path B which loses the original methoxy group and produces the substituted vinyl cation **13**. The relative strength of the C–O and the C–Nu bond determines the substituent in the aryl group of the final product.

In order to ascertain which cation, **7** or **13**, is easily regenerated from **9**, we optimized cation **13**. The sum of the total energies of **7** and Cl^- is −874.944 34 Hartree and that of **13** and



Scheme 3



14 **15**

Fig. 4 Optimized structures of **14** and **15**. Values in the figure are the bond length between the protonated oxygen and C(2) or C(8).

CH_3O^- is $-874.741\ 35$ Hartree. The energy difference is very large, being as much as 127.3 kcal mol^{-1}. The breaking of the C–O bond from **9** leads to a much less stable vinyl cation than the cleavage of the C–Cl bond. Although we must consider the solvent effect, the MO calculations indicate that the Cl^- should be the leaving group from **9**. This means that the methoxy group cannot be replaced by the Cl^-. In fact, we have not obtained vinyl products where the methoxy group in the aryl fragment is substituted with nucleophiles except for cyanide and alkoxide anions.[7] On the other hand, methoxide anion as the nucleophile forms a new C–O bond as strong as the old C–O bond. We can expect, in part, the displacement of the old group by the new one *via* the formation of the *ipso* intermediate. Therefore, the *ipso* intermediate was required for the displacement of the *p*-methoxy group to occur in both the solvolysis and the photolysis.

Protonation of the ipso *Intermediate.*—It is important to know what change occurs when a proton attacks the oxygen atom of the methoxy group of the vinyl position of **10** and that of the *ipso* position of **11** for the reaction of Scheme 2. Fig. 4 displays the optimized structures of **14** and **15** which are considered to be the intermediates of Scheme 2 because both have a proton at O(11) or O(9). Total energies were calculated to be $-531.982\ 29$ and $-531.927\ 03$ Hartree, respectively. **14** is more stable than **15** by 34.7 kcal mol^{-1}. Both molecules retain the geometrical features of the parent molecules. The C(2)–O(11) length of **14** and C(8)–O(9) length in **15** were calculated to be 1.517 and 1.609 Å. They are longer by 0.073 and 0.130 Å than the corresponding lengths in **10** and **11**, respectively. Protonation makes the C–O bond longer and weaker in **15** than in **14**. This result shows that protonation at O(9) of **15** causes the change whereby it easily releases one of the methoxy groups to form the vinyl cation. On the other hand, it is difficult to remove the methoxy group at the α-position of **14** by protonation at O(11).

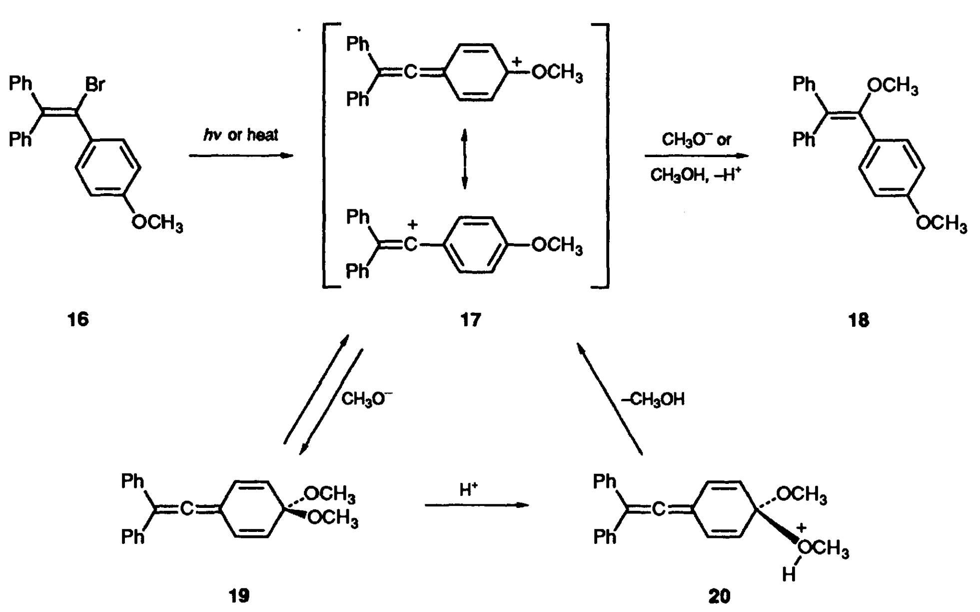
Reaction Mechanism.—According to both the MO calculations and the experimental results, Scheme 4 is considered to be the mechanism for photolysis and solvolysis. The photolysis or solvolysis of α-arylvinyl bromide **16** initially produces the vinyl cation **17**. Nucleophiles attack both C(2) and C(8) and form the vinyl ether **18** and the *ipso* intermediate **19**. As the *ipso* intermediate is unstable and the solvolysis requires the severe conditions of 120 °C for 3 days, the *ipso* intermediate decomposes to form the vinyl cation again. The methoxy group is exchanged in part with a nucleophile if the inserted group in the *ipso* intermediate forms a bond comparable with or stronger than the original C–O bond. **18** is too stable to lose its alkoxy group replaced at the α-position. This is the case where the solvolysis of **1** forms **2** and **3**. As observed in the previous experiments,[7] weaker nucleophiles such as Br^-, SCN^- or alcohol do not produce the substituted products in the aryl fragment because they can form only a very weak C–Nu bond at the *ipso* position. The solvolysis is well-explained by the decomposition following the formation of the *ipso* intermediate.

A mechanism similar to the solvolysis was considered for the photochemical reaction. Both **18** and **19** are formed by the reaction between **17** and methoxide anion. As the photolysis does not require severe conditions like solvolysis, a portion of the *ipso* adduct does not decompose to reproduce vinyl cation and, therefore, we could isolate the *ipso* compound as the product. Another portion of the *ipso* intermediate releases one of the methoxy groups and regenerates the vinyl cation. If we use a higher temperature, such as 45 °C, in photolysis, all *ipso* intermediates decompose as observed. The reaction *via* the *ipso* intermediate explains the three kinds of product of photolysis *i.e.* **4**, **5** and **6**.

The reactant in Scheme 2 has the *ipso* geometry. The protonation of one of the methoxy groups in **19** produces the cation **20**. Now that the C–O bond at the *ipso* position is very weak, **20** releases methanol to form **17**. When we add nucleophiles such as Br^-, SCN^- or MeOH, vinyl products are obtained. Even if these nucleophiles attack at the *ipso* position to form the intermediate (like **9**), it easily decomposes to form vinyl cation again. Vinyl products are very stable and, consequently, were the sole products obtained.

Experimental

Solvolysis of Vinyl Bromide.—In this study deuteriated vinyl bromide **1** was used in order to classify the types of the products, *i.e.*, vinyl and *ipso* products. A solution of vinyl bromide **1** (170 mg, 0.46 mmol) in absolute ethanol (14 cm^3) containing NaOEt (4.6 mmol) was placed in a Pyrex ampoule, degassed, and sealed. The mixture was heated in an oil bath at 140 °C for 3 days. After evaporation of the solvent, the product mixture was extracted with diethyl ether several times, and the combined layers were washed and dried. The products were analysed by ^1H NMR spectroscopy (400 MHz) in $CDCl_3$ and compared with authentic samples. The product ratio (46:54) of the major



Scheme 4

Table 3

Temp./ °C	Irr. time/ h	Products (% yield) 4	5	6
0	3	26	12	40
45	3	79	21	0

ethyl enol ethers **2** and **3** was calculated by the integration of ethoxy and methoxy groups. Authentic samples of **2** and **3** were prepared according to the procedure outlined by Rappoport and Gal.[20]

Photolysis of Vinyl Bromide.—A solution of vinyl bromide **1** (736 mg, 2 mmol) in CH_2Cl_2 (20 cm^3) and MeOH (100 cm^3) containing NaOMe (20 mmol) was irradiated with a Pyrex-filtered high-pressure Hg lamp (100 W) under an N_2 atmosphere. After evaporation of the solvent at 5–10 °C, the products were extracted with diethyl ether, and the organic layer was washed and dried. The products were analysed by ^1H NMR spectroscopy and compared with authentic samples and the characteristic olefinic and methoxy protons of the *ipso* adduct **6**. The characteristic signals [3.19 (s, OMe), 5.85 (d, *J* 10*, =CH), 6.47 (d, *J* 10, =CH_2)] of the *ipso* adduct **6** were confirmed by comparison with ^1H NMR spectra of other isolated *ipso* adducts. The results of photolyses at 0 and 45 °C are summarized in Table 3. Yields were determined by ^1H NMR spectroscopy using hexamethylbenzene as an internal reference.

Materials.—Preparation of 1-Bromo-1-(*p*-$[^2H_3]$methoxyphenyl)-2,2-diphenylethene **1** was carried out using the procedure described by Carter and Hey,[21] m.p. 127–130 °C (EtOH) (lit.,[21] 130 °C); $\delta_H(CDCl_3)$ 6.50–7.30 (m, ArH); *m/z* 369 (24, $M^+ + 2$), 367 (24, M^+), 288 (100, $M^+ - Br$).

1-*Ethoxy*-1-(p-$[^2H_3]$*methoxyphenyl*)-2,2-*diphenylethene* **2**. M.p. 102–103 °C (lit., 101–102 °C); $\delta_H(CDCl_3)$ 1.19 (t, *J* 7, Me), 3.67 (q, *J* 7, CH_2), 6.62–7.32 (m, ArH); *m/z* 333 (83, M^+), 304 (22, $M^+ - Et$), 276 (100, $M^+ - Et - CO$).

1-*Ethoxy*-1-(p-*ethoxyphenyl*)-2,2-*diphenylethene* **3**. M.p. 90–92 °C (hexane); $\delta_H(CDCl_3)$ 1.19 (t, *J* 7, Me), 1.36 (t, *J* 7, Me), 3.67 (q, *J* 7, CH_2), 3.97 (q, *J* 7, CH_2), 6.60–7.31 (m, ArH); *m/z* 344 (99, M^+), 315 (23, $M^+ - Et$), 287 (100, $M^+ - Et - CO$) (Found: C, 83.4; H, 7.0. Calc. for $C_{24}H_{24}O_2$: C, 83.69; H, 7.02%).

Authentic samples of **4** and **5** were prepared by photolysis of the corresponding vinyl bromides in MeOH containing triethylamine.[6]

1-*Methoxy*-1-(p-$[^2H_3]$*methoxyphenyl*)-2,2-*diphenylethene* **4**. M.p. 143–144 °C (EtOH); $\delta_H(CDCl_3)$ 3.46 (s, Me), 6.64–7.30 (m, ArH); *m/z* 319 (100, M^+), 276 (100, $M^+ - Me - CO$).

1-*Methoxy*-1-(p-*methoxyphenyl*)-2,2-*diphenylethene* **5**. M.p. 145–147 °C (EtOH); $\delta_H(CDCl_3)$ 3.45 (s, Me), 3.75 (s, Me), 6.63–7.30 (m, ArH); *m/z* 316 (100, M^+), 301 (10, $M^+ - Me$), 273 (78, $M^+ - Me - CO$) (Found: C, 83.4; H, 6.35. Calc. for $C_{22}H_{20}O_2$: C, 83.52; H, 6.37%).

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* Coupling constants are in Hz.

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