J. Am. Chem. Soc. 1991, 113, 7255–7261

2000 of formaldehyde is present in the reactive form, most being present as the unreactive hydrate, while half the acetaldehyde is in the free form. If, from the data in Table III, we calculate the rate constant for enolate reacting with the total aldehyde, the values of log k are 3.02 for formaldehyde and 3.10 for acetaldehyde. For comparison, the rate constant for reprotonation of acetaldehyde enolate is given as log $k = 2.80$ (Table I). Thus, we expect formaldehyde to show simple behavior up to slightly higher concentrations than acetaldehyde, even though it is inherently more reactive!

Other condensations with formaldehyde will be expected to be similarly prone to changes in the rate-determining step. Most other carbonyl compounds will be less acidic than acetaldehyde and so will have faster reprotonation rates, but they will also be more powerful nucleophiles and so have faster rates of attack on formaldehyde. For acetophenone the reprotonation is governed by log $k = 3.60$, while our predicted rate of addition is governed by log $k_{\text{micro}} = 7.42$ (expressed in terms of free formaldehyde) or log $k = 4.10$ expressed in terms of total formaldehyde. The situation is clearly similar to that for reaction of acetaldehyde with formaldehyde, and the rate-determining step should change at high concentrations. Similar conclusions result for acetone.

Our predictions for aldol additions to trifluoroacetophenone indicate that the expected rate constants are larger than the corresponding rate constants for acetophenone; for the reaction of acetone with trifluoroacetophenone the observable rate constant is predicted to be 4.5 $M^{-1}\,s^{-1}$, and the microscopic rate constant for reaction of acetone enolate with trifluoroacetophenone is predicted to be 6.5×10^5 $M^{-1}\,s^{-1}$. By contrast, for the reaction of acetone with acetophenone[71] we find that the observed rate constant is 3.2×10^{-4} $M^{-1}\,s^{-1}$ and the calculated microscopic rate constant is 47 $M^{-1}\,s^{-1}$. Thus, the polar substituent has led to a large increase in the rate as well as a large increase in the equilibrium constant. Recently, Thornton et al. have reported studies of the effect of polar substituents on the relative rates of aldol condensations.[72] For the condensation in diethyl ether as the solvent of the enolate of pinacolone with 1,3-dimethoxyacetone or acetone, they report a relative rate of 3.0×10^4, favoring the ketone with the electron-withdrawing groups. The closest comparison is with our k_{micro} values, where we found a rate ratio of 1.4×10^4. Since the σ^* value for CF_3 is 2.61, which is significantly greater than twice the σ^* value for CH_3OCH_2, i.e. $2 \times 0.66 = 1.32$, this appears anomalous. There is likely to be a solvent effect favoring reaction in ether because the transition state will have less concentrated charge than the initial or final states and so will be selectively favored in the less polar solvent. Both our predictions and Thornton's experimental results agree that there are large rate effects to be obtained from substitution by polar groups near the reaction centers for the aldol condensation.

Acknowledgment. I thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

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Ipso Substitution of Triarylvinyl Cations by Alkoxide Anions

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Abstract: Photolysis and solvolysis of triarylbromoethanes **1** in the presence of alkoxide anions in alcohols resulted in significant formation of products derived from ipso substitution by alkoxide anions. Photolysis of 1-aryl-1-bromo-2,2-diphenylethenes **1Aa** and **1Ab** with 10 mol equiv of alkoxide anions gave 1-alkoxy-1-aryl-2,2-diphenylethenes **2A** and 3,3-dialkoxy-6-(2,2-diphenylvinylidene)-1,4-cyclohexadienes **3A** (ipso adducts). However, the photolysis with weak bases such as TEA, pyridine, $NaHCO_3$, and K_2CO_3 did not give ipso adducts **3A** but only enol ethers **2A**. Interestingly, photolysis of 2,2-bis(p-alkoxyphenyl)-1-bromo-1-phenylethenes **4a** and **4b** with NaOEt in ethanol afforded ipso adducts **6a** and **6b**, respectively, which had a 1,2-aryl-rearranged structure. Furthermore, solvolysis of 1-bromo-1-(p-methoxyphenyl)ethenes **1Aa**, **1Ba**, and **1Ca** in ethanol containing 10 mol equiv of NaOEt at 120–130 °C for 1–3 days provided p-ethoxyphenyl-substituted enol ethers **2bb**, p-ethoxyphenyl-substituted bromoethenes **1b**, and p-methoxyphenyl-substituted enol ethers **2ab**, respectively. The major formation of p-ethoxyphenyl-substituted compounds (ipso-substituted products) suggests that there is no large difference in ipso substitution between vinyl cations generated by photolysis and solvolysis. On the basis of the results obtained above the factors affecting ipso attack on arylvinyl cations are discussed.

Ipso substitution at an aromatic ring has been focused on destabilized benzylic cations which bear electron-withdrawing groups on the α carbon.[1] The electron-withdrawing groups increase the electron demand of the cationic center toward the aromatic ring and cause the charge delocalization of the aromatic ring. Such delocalization is favorable for ipso substitution.

On the other hand, it is impossible, in α-arylvinyl cations, to introduce the electron-withdrawing group onto the α carbon because there are no bonds displaced at the α carbon. Also introduction of electron-withdrawing groups onto the β position does not accelerate the formation of arylvinyl cations[2] but causes vinylic substitution via addition–elimination mechanism.[2,3] A strong

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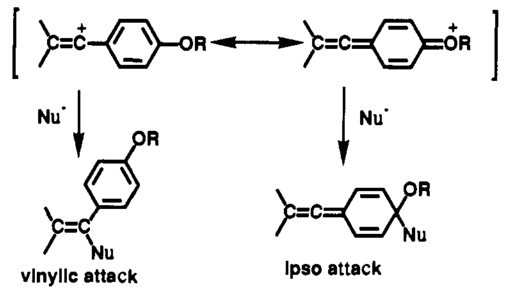
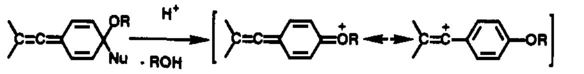
Scheme I



electron-releasing group such as an alkoxy group at the para position delocalizes the charge and stabilizes α-arylvinyl cations. As a result, there is a possibility that substitution by nucleophiles at the ipso position takes place even in the α-arylvinyl cations.

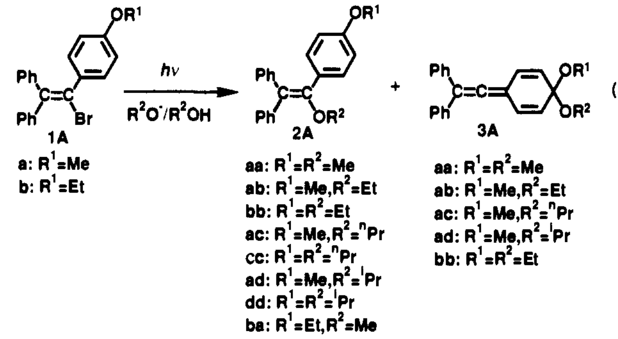
Recently we have reported the ipso substitution of triarylbromoethenes by cyanide or alkoxide anions under photochemical conditions.[4] It has been found that the ipso substitution strongly depends on the α substituent and nucleophiles. This paper describes comprehensively the novel ipso substitution of arylvinyl cations, its scope, and the factors affecting it.

Although the ipso substitution on arylvinyl cations is restricted with respect to the substituent, nucleophiles, and others, it provides unique ipso adducts in the case of alkoxide ions such as nucleophiles and is developed for regeneration of arylvinyl cations.[4]



(1)

Ipso Substitution of Triarylbromoethenes 1 by Photolysis. Photolysis of 1-aryl-1-bromo-2,2-diphenylethene (**1A**) was carried out in an alcohol in the presence of the corresponding alkoxide anion (10 equiv). The products identified were 1-alkoxy-1-aryl-2,2-diphenylethenes (**2A**) and 3,3-dialkoxy-6-(2,2-diphenylvinylidene)-1,4-cyclohexadienes (**3A**). The enol ether-type of product **2A** has been observed previously in photolysis of triarylbromoethenes in methanol.[5]



(2)

Enol ethers **2Aab**, **2Aac**, **2Aad**, and **2Aba** may be contaminated with minor enol ethers **2Abb**, **2Acc**, **2Add**, and **2Aaa**, respectively.

Alcoholysis of the photoproducts obtained just after photolysis with ethanol or methanol at room temperature leads to almost quantitative yields of enol ethers whose ether group is derived from the solvent. For unequivocal structure assignment these enol ethers were further hydrolyzed with acidic aqueous ethanol to the corresponding ketones for verification, which were isolated and identified. Table I indicates that ipso adducts **3A** were found as a major product in either case except for the photolysis with ^{t}*BuOK*. Ethoxide and 1-propoxide ions are preferable to methoxide and 2-propoxide ions for the formation of ipso adducts **3A**. The combination of 1-bromo-1-(p-ethoxyphenyl)ethene **1Ab** and ethoxide anion gave the best yield of ipso adduct **3Ab**, which was isolated as crystals.

Scheme II

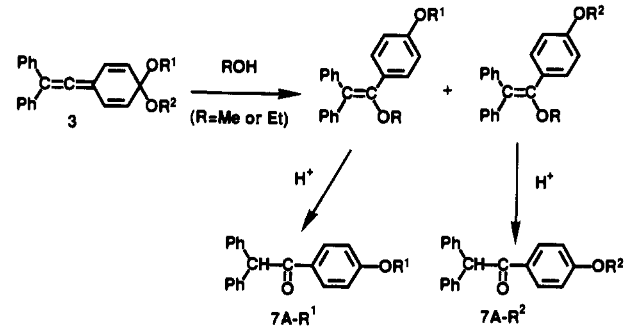
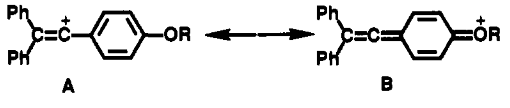


Table I. Photolysis of Arylvinyl Bromides **1A** in the Presence of Alkoxide Ions

bromide **1A**	alkoxide ion	solvent	products (%) **2A**	products (%) **3A**
1Aa	NaOMe	MeOH	38 (**2Aaa**)	47 (**3Aaa**)
	NaOEt	EtOH	14 (**2Aab** + **2Abb**)	73 (**3Aab**)
	NaO^{n}Pr	^{n}PrOH	18 (**2Aac** + **2Acc**)	74 (**3Aac**)
	NaO^{i}Pr	^{i}PrOH	57 (**2Aad** + **2Add**)	38 (**3Aad**)
	KO^{t}Bu	^{t}BuOH	0	0
1Ab	NaOMe	MeOH	31 (**2Aba** + **2Aaa**)	67 (**3Aab**)
	NaOEt	EtOH	0	88 (**3Abb**)
1Aa	TEA	MeOH	79 (**2Aaa**)	0
	TEA	EtOH	70 (**2Aab**)	0
	TEA	^{n}PrOH	80 (**2Aac**)	0
	TEA	^{i}PrOH	86 (**2Aad**)	0
	pyridine	MeOH	80 (**2Aaa**)	0
	K_2CO_3	MeOH	87 (**2Aaa**)	0
	$NaHCO_3$	MeOH	87 (**2Aaa**)	0
	NaOH	^{n}PrOH	25 (**2Aac**)	67 (**3Aac**)
1Ab	TEA	MeOH	89 (**2Aba**)	0
	TEA	EtOH	82 (**2bb**)	0
	NaOH	EtOH	42 (**2bb**)	27 (**3Abb**)

From the previous studies on photolysis of triarylbromoethenes,[2a,5,6] it is reasonable to consider arylvinyl cations as a key reactive intermediate. The ipso adducts **3A** should be formed from the attack of alkoxide ions at the ipso position of the α-aryl substituent on arylvinyl cations.

p-Alkoxy groups in arylvinyl cations delocalized the charge to the aryl group. Theoretical calculations on the p-methoxyphenylvinyl cation[7] show that a significant part of the charge resides on the oxygen so that formation of the ipso adduct is attributed to such a large contribution of structure B.



Similarly, photolysis of triarylbromoethenes **1A** was examined for the effect of added bases other than alkoxide anions. As shown in Table I, bases besides NaOH did not give ipso adducts **3A** but only enol ethers **2A** which were formed by vinylic substitution of alcohol. This result means that alkoxide anions can interact with the ipso position but an alcohol molecule is not strong enough to interact with the ipso position. Photolysis with NaOH produced

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Scheme III

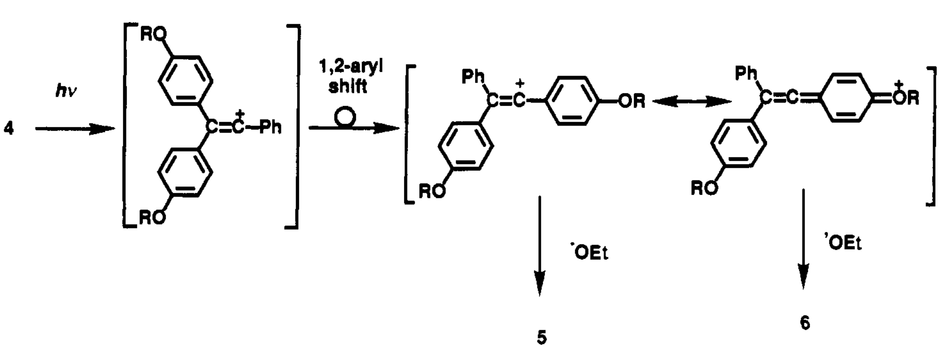


Table II. Photolysis of Arylvinyl Bromides **4** in NaOEt–EtOH

vinyl bromide	irradiation time, h	products, %	
		5	**6**
4a	3	49	40
	0.5	43	35
4b	3	20	58

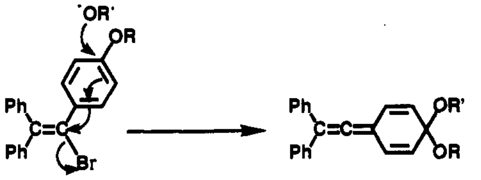
Table III. Effect of a Para Substituent on Ipso Substitution

vinyl bromide	$\sigma^+(Y)$[a]	products, %	
		2A	**3A**
1Aa (Y = MeO)	−0.78	14 (**2Aab**)	73 (**3Aab**)
1Ab (Y = EtO)	−0.82	0	88 (**3Abb**)
1Ac (Y = MeS)	−0.6	65 (**2Aeb**)[b]	0
1Ad (Y = PhO)	−0.5	82 (**2Afb**)	0

[a] Values of σ^+: Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*; Plenum Press: New York, 1984; Part A, p 183. Issacs, N. S. *Physical Organic Chemistry*; London Scientific & Technical: Harlow, 1987; p 134. [b] In addition, 14% of 1-(*p*-(methylthio)phenyl)-2,2-diphenylethene was formed.

ipso adducts **3A** together with enol ethers **2A**. Judging from formation of alkoxide ion-incorporated products (ipso adducts), it is considered that sodium alkoxide is generated as a nucleophile by proton exchange between NaOH and an alcohol.

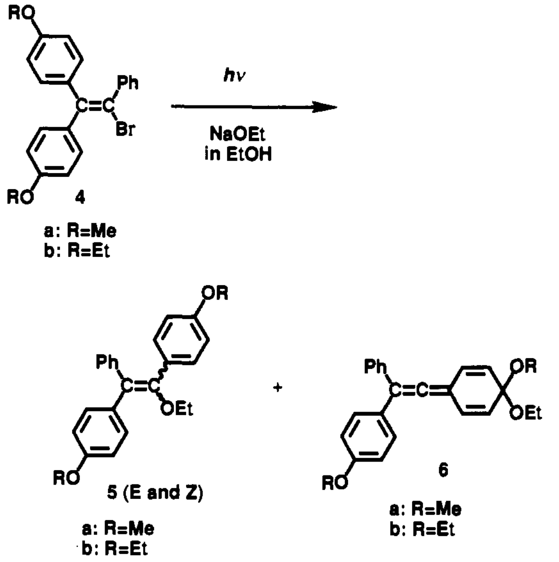
Ipso substitution under photolytic conditions proceeds under basic conditions containing strong bases such as alkoxide anions. On account of the basic conditions there is a possibility that a direct ipso substitution either by nucleophilic attack or by S_{RN} reaction without forming vinyl cations[8] operates on formation of ipso adducts **3A**.



(3)

On the other hand, 1,2-aryl shift on arylvinyl cations[2] has been extensively studied in solvolysis[9] and in photolysis[6b,10] and is one of the characteristic behaviors of vinyl cations. Therefore, occurrence of the 1,2-aryl shift is useful as a probe for examining the intervention of vinyl cations.

Photolysis in ethanol containing NaOEt was conducted by use of 1-bromo-2,2-bis(*p*-alkoxyphenyl)-1-phenylethenes (**4a** and **4b**) which give rise to the rearrangement of the β aryl group if the corresponding vinyl cations are generated. The results are given in Table II. Both photolyses gave ipso adducts **6** with 1,2-aryl rearranged structure. Again, the *p*-ethoxy substituent afforded better yields of ipso adducts than the *p*-methoxy substituent. Also the enol ethers **5** bear a structure with a 1,2-aryl shift. In addition, photolysis of enol ether **5a** with NaOEt in ethanol gave no ipso adducts but resulted in *E*–*Z* isomerization.

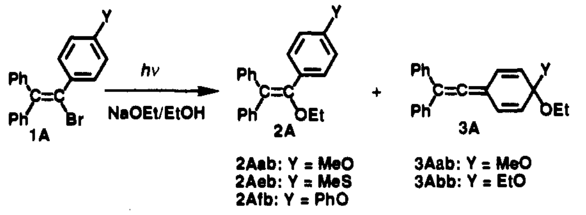


(4)

Accordingly, ipso substitution proceeds via a mechanism involving a consecutive generation of arylvinyl cations, 1,2-aryl shift, and reaction of the rearranged ion with the nucleophile as shown in Scheme III.

Effect of a Para Substituent of an α Aryl Group. The α substituent of vinyl derivatives has a strong affect on the rate of solvolysis.[2c] Highly negative ρ^+ values (ca. −4)[2b,c] and low *m* values[2c,13] in solvolysis of α-arylvinyl derivatives suggest that electron-donating groups cause charge delocalization of the aryl ring, as has been discussed about benzylic cations.[11]

Photolysis of arylvinyl bromides **1A** having other substituents at the para position was examined in order to learn the extent of electron donation required for ipso substitution. As seen from Table III, only alkoxy groups (MeO and EtO) are effective for ipso substitution and electron-donating groups such as MeS and PhO do not provide the ipso adducts.



(5)

It may be useful to use σ^+ values as the indication of the ease of the ipso substitution. According to the σ^+ value, strong elec-

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(8) (a) Cornelisse, J.; Havinga, E. *Chem. Rev.* **1975**, *75*, 353. (b) Lodder, G. *Supplement D, The Chemistry of Halides, Pseudo-Halides and Azides*; Patai, S., Rappoport, Z., Ed.; John Wiley & Sons: New York, 1983; Chapter 29. (c) van Riel, H. C. H. A.; Lodder, G.; Having, E. *J. Am. Chem. Soc.* **1981**, *103*, 7257.

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Scheme IV

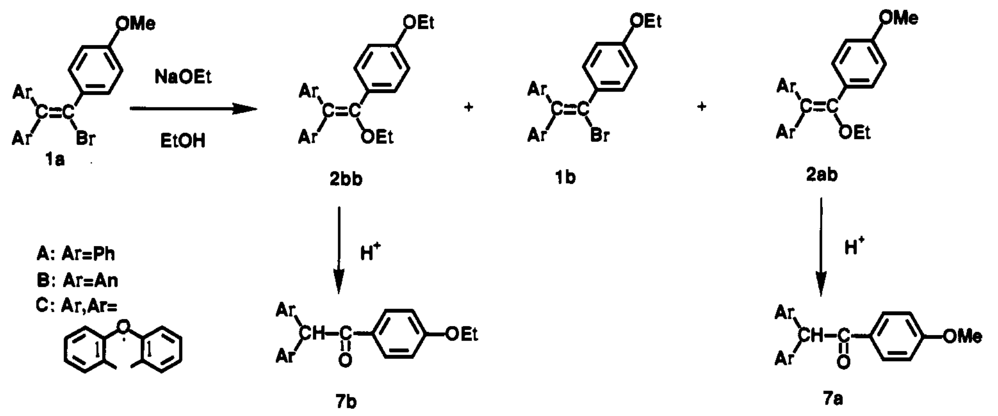


Table IV. Product Distribution After Acid Hydrolysis of the Products from Solvolysis of Arylvinyl Bromides **1a**

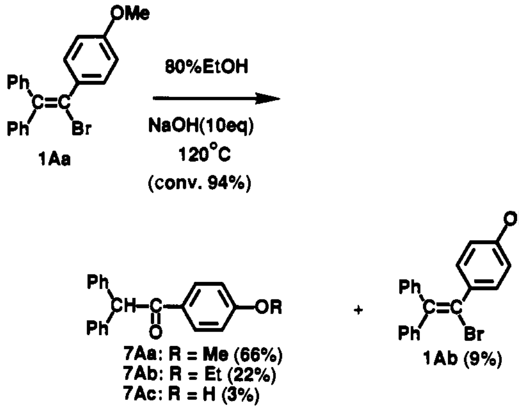
starting material	temp, °C	time, days	conv, %	products after hydrolysis, % *p*-ethoxyacetophenones **7b**	 bromoethenes **1b**	 *p*-metehoxyacetophenones **7a**
1Aa	120	2.7	60	44 (**7Ab**)	30 (**1Ab**)	26 (**7Aa**)
1Ba	120	1	80	41 (**7Bb**)	27 (**1Bb**)	22 (**7Ba**)
1Ca	130	3	78	63 (**7Cb**)	13 (**1Cb**)	24 (**7Ca**)

tron-donating groups having $\sigma^+ < -0.7$ are essential for the substitution at the ipso position of 2,2-diphenyl-1-arylvinyl cations. It is clear that arylvinyl cations need a strong electron-donating group to achieve the charge delocalization to the aryl ring and ipso substitution.

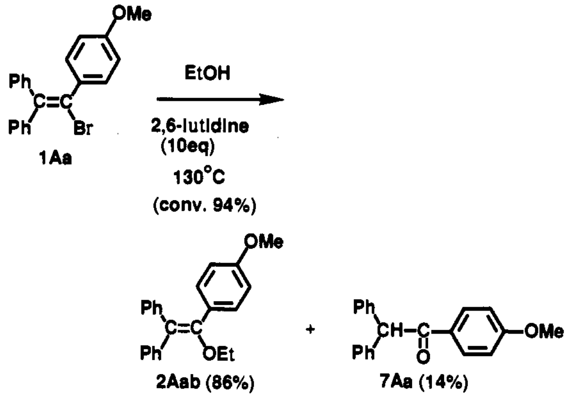
Ipso Substitution under Solvolytic Conditions. If there is not difference in nature between photogenerated vinyl cations and solvolytically generated vinyl cations, ipso substitution should be observed even in solvolysis. There is a large difference in the reaction temperature between photolysis and solvolysis. However, judging from the Lodder's identical selectivity of the photochemical and solvolytically generated ion[14] and our rearrangement experiments,[5] the behaviors of the photochemically and thermally generated vinyl cations are almost the same.

Thus, solvolysis of 1-bromo-1-(*p*-methoxyphenyl)ethenes **1a** was conducted in ethanol containing 10 equiv mol of NaOEt at 120–130 °C for 1–3 days. The products were *p*-ethoxyphenyl-substituted enol ether **2bb**, *p*-ethoxyphenyl-substituted bromoethene **1b**, and *p*-methoxyphenyl-substituted enol ether **2ab**, respectively. Interestingly, ipso-substituted products were formed as major products. The product compositions were determined in detail by ^{1}H NMR spectra after acid hydrolysis of the enol ethers were compared to the corresponding acetophenone derivatives (**7a** and **7b**) (Table IV).

Surprisingly, the formation of the ipso-substituted products significantly exceeds that of the normally vinylic-substituted products. This may be attributed to a high nucleophilicity of ethoxide anion as compared in a similar manner to the photochemical results. In addition, it is also expected that ipso substitution is dependent on the solvent system. Then, the reaction of triarylbromoethene **1Aa** was carried out in 80% EtOH in the presence of 10 equiv mol of NaOH. Although the proportion of the ipso-substituted products decreased, 34% yield of the ipso products was formed. Noteworthy is that the reaction condition is a typical solvolytic condition which has been used extensively in solvolysis of vinyl systems.[2] However, the solvolysis of triarylbromoethene **1Aa** in EtOH containing 2,6-lutidine gave no ipso-substituted products but normal solvolysis products **2Aab** and **7Aa**. These results suggest that a basic nucleophile favors the ipso attack rather than the vinylic attack.



(6)



(7)

Ipso Substitution in Arylvinyl Cations. There are several favors affecting the reaction of vinyl cations: substituent, leaving group, solvent, and nucleophile.[2] Among these factors, para substituent and nucleophile play a significant role in ipso substitution of arylvinyl cations.

The para substituent should be a strong electron-donating group such as an alkoxy group, but a phenoxy group is not enough to cause the ipso substitution. That is, a strong charge delocalization is required for the ipso substitution of arylvinyl cations and, in addition, only a basic, ionic nucleophile (i.e., a hard nucleophile)

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Table V. Acid Hydrolysis of Photoproducts

photolysis	photoproducts	alcoholysis ROH	hydrolysis products **7A-R^1**	 **7A-R^2**
1Aa with NaOEt	**2Aab + 2Abb + 3Aab**	EtOH	38.5% (R^1 = Me)	61.5% (R^2 = Et)
1Aa with NaO^{n}Pr	**2Aac + 2Acc + 3Aac**	MeOH	41% (R^1 = Me)	59% (R^2 = ^{n}Pr)
1Aa with NaO^{i}Pr	**2Aad + 2Add + 3Aad**	MeOH	52% (R^1 = Me)	48% (R^2 = ^{i}Pr)
1Ab with NaOMe	**2Aba + 2Aaa + 3Aab**	MeOH	23% (R^1 = Me)	77% (R^2 = Et)

attack on the ipso position. Therefore, a nucleophile attacking the ipso position should be an alkoxide anion, not an alcohol molecule.

These results are explained by the HSAB principle.[15] The plus charge of the arylvinyl cation is delocalized by the strong electron-donating group at the para position, and, as a result, the arylvinyl cation behaves as an ambident cation. A hard nucleophile favors the attack of the ipso position where the plus charge is most populated. Furthermore, in a simple, parent *p*-methoxyphenylvinyl cation the plus charge populates largely at the ipso position compared with that at the vinylic position, while the coefficient of LUMO is larger at the vinylic position than at the ipso position.[7] Therefore, it is considered that the ipso substitution is a charge-controlled reaction.

There is another possibility that we cannot discard: the case which forms unstable ipso adducts. If the nucleophile attacks at the ipso position but forms a weak bond compared with the original MeO–C bond, the ipso adduct releases the new substituent (Nu) and ipso substitution cannot be observed.

The β substituent also affects the reaction of vinyl cations. A vacant p orbital of triarylvinyl cations lies on the plane of the double bond and is very close to the *ortho* hydrogens of β aryl groups. Such a bulky β substituent partially covers the vinylic position and hinders vinylic substitution,[2c,16] so that ipso substitution becomes preferable.[17]

There is no significant difference in the nature of arylvinyl cations between the methods for the generation, photolysis and solvolysis.[5,14] There is only the difference in the product. In the photolysis ipso adducts attacking on the ipso position are directly observed, but in solvolysis only vinyl compounds are formed. However, even in solvolysis the products are derived from the ipso adducts and suggest the existence of ipso substitution.

The scope of ipso substitution in arylvinyl cations is restricted rather than that of the corresponding saturated systems, i.e., benzylic cations. In destabilized benzylic cations,[1] ipso substitution has been observed in the cases where the para substituent is represented by MeO, MeS, and even hydrogen and the nucleophile is represented by amines and alcohols. This is attributable to the structural reason. In benzylic cations, electron-withdrawing groups can be introduced on the α position and induce enhancement of the charge delocalization to the aryl ring. However, on account of this impossibility of introducing the electron-withdrawing group at the α position, enhancement of the charge delocalization cannot be achieved in arylvinyl cations. Also the carbon–carbon double bond is not electron-withdrawing enough to destabilize arylvinyl cations because an α-phenylvinyl cation lies unstably between the benzylic cation and the α-phenylethyl cation.[12]

Experimental Section

Melting points are uncorrected. NMR spectra were taken on HITACHI R 600, BRUKER AC-250, and JEOL GSX 400. IR spectra were obtained with a HITACHI 270-30. Mass spectra were obtained with a SHIMADZU GCMS-7000.

Preparation of Triarylbromoethenes 1 and 4. Triarylbromoethenes **1Aa**,[18] **1Ab**,[19] **1Ac**,[20] **1Ba**,[18] **1Ca**,[21] **4a**,[9a] and **4b**[19] were prepared by the procedure described in the literature.

1-Bromo-1-(*p*-phenoxyphenyl)-2,2-diphenylethene (**1Ad**) was prepared by a general procedure[19] from ethyl *p*-phenoxyphenylacetate: mp 127.5–129 °C (EtOH–hexane); ^{1}H NMR (CCl$_4$) δ 6.56–7.33 (m, ArH); MS (*m/z*) 428 (M$^+$ + 2), 426 (M$^+$). Anal. Calcd for $C_{26}H_{19}OBr$: C, 73.07; H, 4.48. Found: C, 72.86; H, 4.47.

Photolysis of Triarylbromoethenes 1A in the Presence of Alkoxide Anions. In a Pyrex photoreactor was dissolved triarylbromoethene **1A** (2 mmol) with dichloromethane (20 mL), and it was diluted with an alcohol (100 mL) containing the corresponding alkoxide anion (20 mmol). A nitrogen gas was bubbled into the solution for 1 h before irradiation and during irradiation. The solution was irradiated at 0 °C for 3 h by a Pyrex-filtered high-pressure Hg lamp (100 W). The photolysis containing *tert*-butyl alcohol was carried out at room temperature. The solvent was removed in vacuo at 0 °C, and water was added. The products were extracted twice with ether, and the organic layer was washed with water and saturated NaCl solution and dried. After removal of the solvent the products were analyzed by ^{1}H NMR in CDCl$_3$ with hexamethylbenzene as an internal standard.

Only the ipso adduct, 3,3-diethoxy-6-(2,2-diphenylvinylidene)-1,4-cyclohexadiene (**3Abb**), was isolated as crystals after workup of the reaction mixture as follows. After irradiation and workup, 2 mL of hexane was added to the crude oil, and the mixture was cooled to −70 °C. The resulting pale yellow crystals were filtered and washed with a small portion of hexane. Recrystallization from hexane gave white crystals: mp 96–97 °C, ^{1}H NMR (CDCl$_3$) δ 1.21 (t, *J* = 7 Hz, 6 H, Me), 3.52 (q, *J* = 7 Hz, 4 H, CH$_2$), 5.92 (d, *J* = 10 Hz, 2 H, =CH), 6.56 (d, *J* = 10 Hz, 2 H, =CH), 7.32 (br s, 10 H, ArH); ^{13}C NMR (C_6D_6) δ 15.94 (CH$_3$), 57.16 (CH$_2$), 94.55 (quaternary sp^3 carbon), 103.34, 111.33, 125.46, 128.57, 128.90, 129.08, 136.06 (sp^2 carbons), 213.48 (C=*C*=C); IR (KBr) 3060 (w), 3030 (w), 2980 (s), 2930–2880 (s), 1910 (m, C=C=C), 1650 (m), 1600 (m), 1490 (s), 1440 (s), 1420 (m), 1390 (m), 1200 (s), 1140–1050 (vs), 980 (vs), 900 (m), 770 (s), 750 (m), 700 (vs), 630 (m); MS (*m/z*, rel intensity) 344 (M$^+$, 89), 316 (23), 301 (70), 287 (100), 260 (23), 181 (23), 164 (64). Anal. Calcd for $C_{24}H_{24}O_2$: C, 83.69; H, 7.02. Found: C, 83.22; H, 7.02.

Other ipso adducts **3Aaa–3Aad** could not be isolated because of their instability (decomposition on silica gel or alumina and hydrolysis under acidic conditions). The ipso adducts **3Aaa–3Aad** were characterized by ^{1}H NMR: 1H NMR (CDCl$_3$) **3Aaa** δ 3.24 (s, OMe), 5.89 (d, *J* = 10 Hz, =CH), 6.54 (d, *J* = 10 Hz, =CH), **3Aab** δ 1.17 (t, *J* = 7 Hz, Me), 3.17 (s, OMe), 3.50 (q, *J* = 7 Hz, OCH$_2$), 5.85 (d, *J* = 10 Hz, =CH), 6.41 (d, *J* = 7 Hz, =CH), **3Aac** δ 3.15 (s, OMe), 5.85 (d, *J* = 10 Hz, =CH), 6.44 (d, *J* = 10 Hz, =CH), **3Aad** δ 3.15 (s, OMe) (d, *J* = 10 Hz, =CH), 6.41 (d, *J* = 10 Hz, =CH). Furthermore, the ipso adducts were confirmed by alcoholysis to the corresponding enol ethers and by their acid hydrolysis to the acetophenone derivatives.

After irradiation of triarylbromoethene **1Aa** (2 mmol) in ethanol (100 mL) and dichloromethane (20 mL) containing NaOEt (20 mmol), the products obtained by the above procedure were subject to alcoholysis with ethanol (70 mL) with stirring at room temperature for 12 h. After evaporation of the solvent the ^{1}H NMR spectra showed formation of enol ethers **2Aab** and **2Abb**, and these enol ethers were used for hydrolysis without further purification. Acid hydrolysis of the crude mixture was performed by refluxing with ethanol (50 mL) containing 6 M HCl (5 mL) for 2 h. After evaporation of the solvent the products were extracted with dichloromethane, washed with water, and dried. Evaporation of the solvent gave crystals, which were shown to be a mixture of 4′-methoxy-2,2-diphenylacetophenone and 4′-ethoxy-2,2-diphenylacetophenone (see, solvolysis part) which were further separated by column chromatography and identified.

After irradiation of triarylbromoethene **1Aa** (2 mmol) in 2-propanol (100 mL) and dichloromethane (20 mL) containing NaO^{i}Pr (20 mmol), the crude products were subject to methanolysis with 70 mL of MeOH with stirring at room temperature for 12 h. After evaporation of the solvent the resulting enol ethers were hydrolyzed with ethanol (50 mL)

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containing 6 M HCl (5 mL) by reflux for 2 h. After workup of the reaction mixture, ^{1}H NMR spectra showed the formation of 4′-methoxy-2,2-diphenylacetophenone and 4′-isopropoxy-2,2-diphenylacetophenone as a mixture, which was isolated by column chromatography on silica gel.

4′-Isopropoxy-2,2-diphenylacetophenone: mp 122–123 °C (EtOH); ^{1}H NMR (CDCl$_3$) δ 1.21 (d, J = 6.0 Hz, Me), 4.47 (sept, J = 6.0 Hz, OCH), 5.89 (s, CH), 6.71–7.89 (m, ArH); ^{13}C NMR (CDCl$_3$) δ 21.94, 59.02, 70.13, 115.16, 127.03, 128.67, 129.20, 129.43, 131.35, 139.56, 162.03, 196.63. Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.24; H, 6.58.

The same procedure above was conducted in the case of photolysis of triarylbromoethene **1Aa** (2 mmol) in propanol (100 mL) and dichloromethane (20 mL) containing NaO^{n}Pr (20 mmol). 4′-Methoxy-2,2-diphenylacetophenone and 4′-propoxy-2,2-diphenylacetophenone were obtained.

4′-Propoxy-2,2-diphenylacetophenone: mp 128–130 °C (EtOH); ^{1}H NMR (CDCl$_3$) δ 0.98 (t, J = 7 Hz, Me), 1.76 (sext, J = 7 Hz, CH$_2$), 3.88 (t, J = 7 Hz, OCH$_2$), 5.98 (s, CH), 6.79–7.98 (m, ArH); ^{13}C NMR (CDCl$_3$) δ 10.40, 22.37, 58.98, 69.63, 114.22, 126.95, 128.59, 129.13, 129.58, 131.23, 139.49, 163.02, 196.54. Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.54; H, 6.58.

Enol ethers **2Aaa**, **2Aab**, **2Abb**, **2Aac**, **2Aad**, and **2Aba** were identified by comparison with authentic samples prepared from photolysis with TEA (see below). The presence of enol ethers **2Acc** and **2Add** which were derived from ipso adducts **3Aac** and **3Aad**, respectively, was confirmed by ^{1}H NMR but further study was not conducted.

Photolysis of Triarylbromoethenes 1A with Other Bases, A solution of triarylbromoethene **1A** (2 mmol) in an alcohol (100 mL) and dichloromethane (20 mL) containing a base (20 mmol) was similarly irradiated by a Pyrex-filtered high-pressure Hg lamp at 0 °C for 3 h. After removal of the solvent under reduced pressure, the products were extracted with ether and were analyzed by ^{1}H NMR by using hexamethylbenzene as an internal standard. Then, the products were separated by column chromatography on silica gel with hexane–dichloromethane as an eluent.

1-Methoxy-1-(*p*-methoxyphenyl)-2,2-diphenylethene (**2Aaa**): mp 148.5–149.5 °C (EtOH) (lit.[7] mp 145–147 °C); ^{1}H NMR (CDCl$_3$) δ 3.37 (s, OMe), 3.68 (s, OMe), 6.58–7.23 (m, ArH).

1-Ethoxy-1-(*p*-methoxyphenyl)-2,2-diphenylethene (**2Aab**): mp 108–109 °C (hexane) (lit.[18] 100–101 °C); ^{1}H NMR (CDCl$_3$) δ 1.17 (t, J = 7 Hz, Me), 3.66 (q, J = 7 Hz, CH$_2$), 3.69 (s, OMe), 6.60–7.25 (m, ArH).

1-(*p*-Methoxyphenyl)-2,2-diphenyl-1-propoxyethene (**2Aac**): mp 90–91 °C (EtOH); ^{1}H NMR (CDCl$_3$) δ 0.83 (t, J = 7 Hz, Me), 1.54 (sext, J = 7 Hz, CH$_2$), 3.54 (t, J = 7 Hz, OCH$_2$), 3.69 (s, OMe), 6.60–7.25 (m, ArH). Anal. Calcd for $C_{24}H_{24}O_2$: C, 83.69; H, 7.02. Found: C, 83.63; H, 6.92.

1-(*p*-Methoxyphenyl)-2,2-diphenyl-1-(2-propoxy)ethene (**2Aad**): mp 84–86 °C (EtOH); ^{1}H NMR (CDCl$_3$) δ 1.08 (d, J = 6 Hz, Me), 3.61 (s, OMe), 3.94 (sept, J = 6 Hz, OCH), 6.58–7.41 (m, ArH). Anal. Calcd for $C_{24}H_{24}O_2$: C, 83.69; H, 7.02. Found: C, 83.40; H, 6.95.

1-(*p*-Ethoxyphenyl)-1-methoxy-2,2-diphenylethene (**2Aba**): mp 77–79 °C (EtOH); ^{1}H NMR (CDCl$_3$) δ 1.36 (t, J = 7 Hz, Me), 3.40 (s, OMe), 3.92 (q, J = 7 Hz, OCH$_2$), 6.51–7.18 (m, ArH). Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.67; H, 6.71. Found: C, 83.54; H, 6.64.

1-Ethoxy-1-(*p*-ethoxyphenyl)-2,2-diphenylethene (**2Abb**):[7] mp 88–90 °C (hexane); ^{1}H NMR (CDCl$_3$) δ 1.19 (t, J = 7 Hz, Me), 1.36 (t, J = 7 Hz, Me), 3.67 (q, J = 7 Hz, OCH$_2$), 3.97 (q, J = 7 Hz, OCH$_2$), 6.60–7.27 (m, ArH).

Photolysis of 1-Bromo-2,2-bis(*p*-alkoxyphenyl)-1-phenylethenes 4, A solution of triarylbromoethene **4** (1 mmol) in dichloromethane (10 mL) and ethanol (90 mL) containing NaOEt (10 mmol) was irradiated at 3 °C for 3 h under a nitrogen atmosphere by use of a Pyrex-filtered Hg lamp (100 W). After irradiation the solvent was removed in vacuo, and the products were extracted with ether. The organic layer was washed with water and saturated NaCl and dried. After evaporation of the solvent the product yield was determined by ^{1}H NMR (400 MHz) by using hexamethylbenzene as an internal standard.

The formation of ipso adducts was confirmed by the presence of the characteristic olefinic protons. Furthermore, in the case of photolysis of triarylbromoethenes **4b** with NaOEt in ethanol ^{13}C NMR and IR spectra supported the structure of ipso adduct **6b**.

3-Ethoxy-3-methoxy-6-[2-(*p*-methoxyphenyl)-2-phenylvinylidene]-1,4-cyclohexadiene (**6a**): ^{1}H NMR (CDCl$_3$) δ 1.18 (t, J = 7 Hz, Me), 3.22 (s, OMe), 3.50 (q, J = 7 Hz, OCH$_2$), 5.84 (d, J = 10 Hz, =CH), 6.49 (d, J = 10 Hz, =CH).

3,3-Diethoxy-6-[2-(*p*-ethoxyphenyl)-2-phenylvinylidene]-1,4-cyclohexadiene (**6b**): ^{1}H NMR (CDCl$_3$) δ 1.20 (t, Me), 3.52 (q, CH$_2$), 5.90 (d, J = 10 Hz, =CH), 6.51 (d, J = 10 Hz, =CH); ^{13}C NMR (CDCl$_3$) δ 211.17 (C=*C*=C); IR 1910 cm^{-1} (C=C=C).

The structures of enol ethers **5a** and **5b**, respectively, were determined by separation with column chromatography on silica gel and by acid hydrolysis to the corresponding ketones. To the crude photoproducts were added 2 M HCl (10 mL) and ethanol (30 mL), and the solution was refluxed for 12 h. The solvent was evaporated, and the products were extracted with ether. The organic layer was washed with water and saturated NaCl and dried. After evaporation of the solvent, ^{1}H NMR spectrum of the crude product indicated the formation of 2,2-diaryl-4′-alkoxyacetophenones as the sole product.

2-(*p*-Methoxyphenyl)-2-phenyl-4′-methoxyacetophenone:[9a] ^{1}H NMR (CDCl$_3$) δ 3.60 (s, OMe), 3.64 (s, OMe), 5.83 (s, CH), 6.70–7.89 (m, ArH); ^{13}C NMR (CDCl$_3$) δ 55.11, 55.33, 58.19, 113.74, 114.08, 126.88, 128.56, 129.02, 129.80, 130.13, 131.20, 131.48, 139.83, 158.59, 163.33, 196.86.

2-(*p*-Ethoxyphenyl)-2-phenyl-4′-ethoxyacetophenone: mp 98–99 °C (MeOH); ^{1}H NMR (CDCl$_3$) δ 1.34 (t, J = 7 Hz, Me), 1.36 (t, J = 7 Hz, Me). 3.94 (q. J = 7 Hz, CH$_2$), 3.99 (q, J = 7 Hz, CH$_2$), 5.91 (s, CH), 6.73–8.04 (m, ArH); ^{13}C NMR (CDCl$_3$) δ 14.87, 15.09, 58.43, 63.58, 63.93, 114.47, 114.91, 127.13, 128.82, 129.34, 129.93, 130.41, 131.50, 131.67, 140.23, 158.26, 163.06, 197.18; IR (KBr) 1678 cm^{-1} (C=O). Anal. Calcd for $C_{24}H_{24}O_3$: C, 79.97; H, 6.71. Found: C, 79.93; H, 6.60.

Photolysis of enol ether **5a** (1 mmol) in ethanol (100 mL) and dichloromethane (20 mL) containing NaOEt (10 mmol) was carried out in a similar manner described above for 4 h. After the same workup of the reaction mixture, ^{1}H NMR spectrum of the crude product showed an absence of ipso adduct **6a** and was identical with that of *E*- and *Z*-isomers of enol ethers **6a**.

Photolysis of Triarylbromoethenes (1Ac and 1Ad), A solution of triarylbromoethene **1Ac** or **1Ad** (2 mmol) in ethanol (100 mL) and dichloromethane (20 mL) containing NaOEt (20 mmol) was irradiated for 3 h at 0 °C by use of a Pyrex-filtered Hg lamp (100 W). The solvent was removed in vacuo at 0 °C, and the products were extracted with ether. The organic layer was washed with water and saturated NaCl and dried. After evaporation of the solvent the product yields were determined by ^{1}H NMR using hexamethylbenzene as an internal standard. The products were isolated by column chromatography on silica gel with hexane–dichloromethane as an eluent.

1-Ethoxy-1-(*p*-(methylthio)phenyl)-2,2-diphenylethene (**2Aeb**): mp 88–89 °C (EtOH); ^{1}H NMR (CDCl$_3$) δ 1.16 (t, J = 7 Hz, Me), 2.31 (s, SMe), 3.65 (q, J = 7 Hz, CH$_2$), 6.73–7.29 (m, ArH); ^{13}C NMR (CDCl$_3$) δ 15.23, 15.27, 66.07, 125.50, 125.72, 126.14, 126.49, 127.88, 127.91, 129.93, 130.59, 131.46, 132.47, 138.47, 141.26, 141.52, 151.91. Anal. Calcd for $C_{23}H_{22}OS$: C, 79.73; H, 6.40. Found: C, 79.89; H, 6.26.

1-(*p*-(Methylthio)phenyl)-2,2-diphenylethene:[20] mp 110–112 °C; ^{1}H NMR (CDCl$_3$) δ 2.39 (s, SMe), 6.89 (s, =CH), 6.95 (s, ArH), 7.27 (br s, ArH).

1-Ethoxy-1-(*p*-phenoxyphenyl)-2,2-diphenylethene (**2Afb**): mp 104–105 °C (EtOH); ^{1}H NMR (CDCl$_3$) δ 1.20 (t, J = 7 Hz, Me), 3.69 (q, J = 7 Hz, CH$_2$), 6.77–7.31 (m, ArH); ^{13}C NMR (CDCl$_3$) δ 15.09, 65.99, 117.84, 119.16, 123.48, 125.35, 125.96, 126.36, 127.73, 127.80, 129.70, 129.83, 130.61, 131.39, 131.64, 141.11, 141.51, 151.79, 156.64, 156.89. Anal. Calcd for $C_{28}H_{24}O_2$: C, 85.68; H, 6.16. Found: C, 85.28; H, 6.11.

Solvolysis of Triarylbromoethenes 1a in Ethanol with NaOEt, To a pressure bottle (100 mL) was placed triarylbromoethene **1a** (1.2 mmol) and ethanol (60 mL) containing NaOEt (12 mmol). The bottle was heated in a oil bath at the temperature and the time given in Table V. After evaporation of the solvent the products were extracted with ether, and organic layer was washed with water and saturated NaCl and dried. The solvent was removed, and the residue was analyzed by ^{1}H NMR (400 MHz). In the case of solvolysis of triarylbromoethene **1Aa**, the ^{1}H NMR showed the formation of ipso-substituted products **2Aa** and **1Ab**, but it was found that the NMR spectrum was not suited for the quantitative analysis because of partial overlapping of the methoxy and ethoxy signals. Then, to simplify the ^{1}H NMR spectrum enol ethers **2ab** and **2bb** were hydrolyzed to the corresponding 2,2-diaryl-4′-alkoxyacetophenones **7a** and **7b**. To the crude solvolysis products were added 6 M HCl (5 mL) and ethanol (50 mL), and the mixture was refluxed for 2 h. After evaporation of the solvent, the products were extracted with ether, and the organic layer was washed with water and saturated NaCl, and dried. After evaporation of the solvent, the yields of the products were determined by ^{1}H NMR (400 MHz) by using hexamethylbenzene as an internal standard. Furthermore, the products were separated by column chromatography on silica gel with dichloromethane–hexane as an eluent.

4′-Ethoxy-2,2-diphenylacetophenone (**7Ab**): mp 146–148 °C (EtOH); ^{1}H NMR (CDCl$_3$) δ 1.39 (t, J = 7 Hz, Me), 4.05 (q, J = 7 Hz, CH$_2$),

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5.99 (s, CH), 6.77–8.05 (m, ArH); IR (Nujol) 1668 cm^{-1} (C=O); MS (*m/z*) 167 (7, Ph_2CH^+), 165 (11), 149 (100, $EtOC_6H_4CO^+$), 135 (11), 121 (34). Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.52; H, 6.37. Found: C, 83.79; H, 6.37.

1-Bromo-1-(*p*-ethoxyphenyl)-2,2-diphenylethene (**1Ab**) was identified by comparison with an authentic sample: mp 94–96 °C (EtOH) (lit.[19] mp 95 °C); ^1H NMR ($CDCl_3$) δ 1.36 (t, J = 7 Hz, Me), 3.95 (q, J = 7 Hz, CH_2), 6.58–7.33 (m, ArH).

4′-Methoxy-2,2-diphenylacetophenone (**7Aa**)[18] was identified by comparison with an authentic sample.

4′-Ethoxy-2,2-bis(*p*-methoxyphenyl)acetophenone (**7Bb**) oil; ^1H NMR ($CDCl_3$) δ 1.34 (t, J = 7 Hz, Me), 3.67 (s, Me), 3.96 (q, J = 7 Hz, CH_2), 5.79 (s, CH), 6.68–7.96 (m, ArH); ^{13}C NMR ($CDCl_3$) δ 14.20, 54.66, 56.89, 63.29, 113.67, 113.83, 129.25, 129.72, 130.83, 131.64, 158.17, 162.40, 196.79; IR (Nujol) 1678 cm^{-1} (C=O); MS (*m/z*) 227 (100 An_2CH^+), 149 (41, $EtOC_6H_4CO^+$), 121 (18).

9-(*p*-Ethoxybenzoyl)xanthene (**7Cb**): mp 131–133 °C (EtOH); ^1H NMR ($CDCl_3$) δ 1.37 (t, J = 7 Hz, Me), 4.01 (q, J = 7 Hz, CH_2), 5.74 (s, CH), 6.74–8.00 (m, ArH); IR (Nujol) 1666 cm^{-1} (C=O). MS (*m/z*) 181 (100, xanthylium), 149 (94, $EtOC_6H_4CO^+$), 121 (34). Anal. Calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 80.19; H, 5.44.

1-Bromo-1-(*p*-ethoxyphenyl)-2,2-bis(*p*-methoxyphenyl)ethene (**1Bb**) was identified by comparison with an authentic sample: mp 77–80 °C (EtOH) (lit.[19] mp 76 °C); ^1H NMR ($CDCl_3$) δ 1.36 (t, J = 7 Hz, Me), 3.68 (s, Me), 3.80 (s, Me), 3.96 (q, J = 7 Hz, CH_2), 6.49–7.35 (m, ArH); MS (*m/z*) 440 (28, $M^+ + 2$), 438 (28, M^+), 359 (100, $M^+ - Br$).

9-[Bromo(*p*-ethoxyphenyl)methylene]xanthene (**1Cb**): mp 120–122 °C (benzene–EtOH); ^1H NMR ($CDCl_3$) δ 1.41 (t, J = 7 Hz, Me), 4.02 (q, J = 7 Hz, CH_2), 6.69–8.37 (m, ArH); MS (*m/z*) 394 (37, $M^+ + 2$), 392 (37, M^+), 313 (100, $M^+ - Br$). Anal. Calcd for $C_{22}H_{17}O_2Br$: C, 67.19; H, 4.36. Found: C, 67.24; H, 4.32.

4′-Methoxy-2,2-bis(*p*-methoxyphenyl)acetophenone (**7Ba**)[18] and 9-(*p*-anisoyl)xanthene (**7Ca**)[21] were identified by comparison with authentic samples.

Solvolysis of 1-Bromo-1-(*p*-methoxyphenyl)-2,2-diphenylethene (1Aa) in 80% EtOH with NaOH. A mixture of triarylbromoethene **1Aa** (438 mg, 1 mmol) and 80% EtOH (v/v) (60 mL) containing NaOH (12 mmol) was heated at 120 °C for 65 h in a pressure bottle. After evaporation of the solvent the crude products were hydrolyzed with a solution of 6 M HCl (5 mL) and ethanol (50 mL). After reflux for 2 h, the solvent was evaporated, and the products were extracted three times with ether. The organic layer was washed with water and saturated NaCl and dried. The solvent was removed, and the residue was analyzed by ^1H NMR (400 MHz). Then, the residue was dissolved in a mixture of ether and benzene. The organic layer was extracted with aqueous NaOH, and the alkaline extract was acidified and again extracted with ether. The ethereal layer was washed with water and saturated NaCl and dried. Evaporation of the ether yielded a crystalline 4′-hydroxy-2,2-diphenylacetophenone (**7Ac**) (43 mg): mp 179–181 °C (lit.[22] mp 180–182 °C); ^1H NMR ($CDCl_3$) δ 4.80 (br s, OH), 5.97 (s, CH), 6.76 (d, J = 9 Hz, ArH), 7.26 (s, ArH), 7.93 (d, J = 9 Hz, ArH).

The former organic layer was washed with water and saturated NaCl and dried. After evaporation of the solvent, the residue was submitted to column chromatography on silica gel. Gradient elution with dichloromethane and hexane gave **1Ab**, **1Aa**, **7Ab**, and **7Aa**, in turn.

Solvolysis of 1-Bromo-1-(*p*-methoxyphenyl)-2,2-diphenylethene (1Aa) in Ethanol with 2,6-Lutidine. A mixture of triarylbromoethene **1Aa** (438 mg, 1.2 mmol), 2,6-lutidine (1.4 mL, 12 mmol), and ethanol (60 mL) was heated at 130 °C for 48 h in a pressure bottle. After evaporation of the solvent, the products were extracted with ether, and the organic layer was washed with water and saturated NaCl and dried. The solvent was evaporated, and the products were analyzed by ^1H NMR (400 MHz) by using hexamethylbenzene as an internal standard.

Registry No, **1Aa**, 25354-48-7; **1Ab**, 121410-90-0; **1Ac**, 133776-70-2; **1Ad**, 135043-32-2; **1Ba**, 25354-46-5; **1Bb**, 135043-37-7; **1Ca**, 87712-58-1; **1Cb**, 135043-38-8; **2Aaa**, 122127-41-7; **2Aab**, 122127-42-8; **2Aac**, 122127-43-9; **2Aad**, 122127-48-4; **2Aba**, 121410-92-2; **2Abb**, 121410-93-3; **2Acc**, 122127-49-5; **2Add**, 122127-50-8; **2Aeb**, 135043-33-3; **2Afb**, 135043-34-4; **3Aaa**, 122127-44-0; **3Aab**, 122127-45-1; **3Aac**, 122127-46-2; **3Aad**, 122127-47-3; **3Abb**, 121410-91-1; **4a**, 41038-34-0; **4b**, 60883-74-1; (*E*)-**5a**, 128421-76-1; (*Z*)-**5a**, 128421-77-2; (*E*)-**5b**, 128421-73-8; (*Z*)-**5b**, 128421-74-9; **6a**, 122127-54-2; **6b**, 128421-72-7; **7Aa**, 1889-74-3; **7Ab**, 128191-31-1; **7Ba**, 61161-13-5; **7Bb**, 135043-35-5; **7Ca**, 87712-61-6; **7Cb**, 135043-36-6; TEA, 121-44-8; NaOMe, 124-41-4; NaOEt, 141-52-6; NaOPr, 6819-41-6; NaO-*i*-Pr, 683-60-3; KO-*t*-Bu, 865-47-4; *t*-BuOH, 75-65-0; K_2CO_3, 584-08-7; $NaHCO_3$, 144-55-8; NaOH, 1310-73-2; MeOH, 67-56-1; EtOH, 64-17-5; PrOH, 71-23-8; *i*-PrOH, 67-63-0; 2,6-lutidine, 108-48-5; pyridine, 110-86-1; 1-(*p*-(methylthio)phenyl)-2,2-diphenylethene, 133776-80-4.

HCN Dimers: Iminoacetonitrile and *N*-Cyanomethanimine

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Abstract: Iminoacetonitrile (**1**) has been prepared by two methods: (i) thermal decomposition of the tosylhydrazone salts **13** at 200 °C and (ii) Ar matrix photolysis of azidoacetonitrile (**15**). Ab initio calculations indicate that **1Z** is of slightly lower energy than **1E**, and this is confirmed by the IR spectra with use of the thermal methods. **1E**/**1Z** undergo photochemical interconversion, giving a ca. 3:1 photostationary *E*:*Z* ratio. **1E** and **1Z** are fully characterized by their gas-phase, matrix, and thin-film IR spectra, which are in excellent agreement with ab initio calculations, by ^1H and ^{13}C NMR spectroscopy in solution, and by mass spectrometry. **1** polymerizes in solution above −40 °C; pyrolysis produces HCN, and matrix photolysis produces HNC and van der Waals complexes containing HNC. *N-tert*-Butyliminoacetonitrile thermally fragments to *tert*-butyl isocyanide and HCN. *N*-Cyanomethanimine (**3**) has also been prepared by two methods: (i) pyrolysis of trimethylenetetrazole (**20**) at 500–800 °C and (ii) pyrolysis of ditetrazolopyrazine **22** at 600–850 °C. Both methods are extremely clean. **3** is fully characterized by its IR spectrum in agreement with ab initio calculations and, in conjunction with other work, by its mass and millimeter-wave spectra. **3** is thermodynamically stable in the gas phase up to ca. 800 °C at low pressure and short contact times but polymerizes in the solid state above −100 °C.

Introduction

The covalent dimers of HCN are of considerable interest as potential interstellar and prebiotic molecules. Both HCN and HNC are widely distributed in interstellar clouds.[2] HCN, $(CN)_2$, and cyanoacetylene have been detected in the atmosphere of Titan[3] and HCN and the CN radical on comets.[4] HCN is widely

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