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Drastic Base Dependence of Products in Photolysis of 1-(p-Methoxyphenyl)-2,2-diphenylvinyl Bromide. ipso Substitution by Alkoxide Ions

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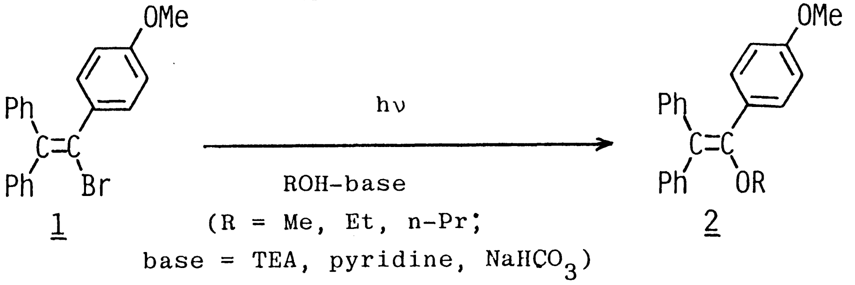
Addition of alkoxide ions resulted in ipso substitution in the photolysis of an alcohol solution of 1-(p-methoxyphenyl)-2,2-diphenylvinyl bromide, whereas addition of triethylamine, pyridine, or $NaHCO_3$ led to vinylic substitution.

Vinyl cations are very important intermediates in nucleophilic substitution of arylvinyl derivatives.1) Recently we found2) that arylvinyl cations are generated by photolysis of arylvinyl halides and they behave similarly to solvolytically generated vinyl cations. Although the nucleophilic substitution of vinyl cations occurs at the sp carbon of the double bond,1) there are, to the best of our knowledge, no examples of ipso substitution of arylvinyl cations. Very recently, we revealed that the photochemical double cyanation of arylvinyl bromides proceeded with ipso substitution of the vinyl cations followed by nucleophilic substitution.3) This successful ipso substitution by cyanide ion led us to apply the photolysis of arylvinyl bromides in the presence of strong bases. Herein we wish to report a drastic base dependence of products in the photochemical nucleophilic substitution of 1-(p-methoxyphenyl)-2,2-diphenylvinyl bromide in alcohols.

A solution of 1-(p-methoxyphenyl)-2,2-diphenylvinyl bromide (1) (2 mmol) in an alcohol (MeOH, EtOH, or n-PrOH, 100 ml)-CH_2Cl_2 (20 ml) was irradiated in the presence of triethylamine (TEA), pyridine, or $NaHCO_3$ (20 mmol) with a Pyrex-filtered high-pressure Hg lamp (100 W) under N_2 atmosphere for 3 h. After workup of the reaction mixture, 1-alkoxy-1-(p-methoxyphenyl)-2,2-diphenylethene (2, R = Me, Et, or n-Pr)4) was obtained in a high yield (≈90%). Similarly to the previous photolyses,2) 1-(p-methoxyphenyl)-2,2-diphenylvinyl cation generated by the photolysis of 1 reacts with alcohols to afford 2.



In contrast to the above photolysis, the photolysis of 1 in the presence of sodium alkoxides (10 eq) in the corresponding alcohols led to the formation of new products, 3-alkoxy-3-methoxy-6-(2',2'-diphenylvinylidene)-1,4-cyclohexadienes (3), together with 1-alkoxy-1-(p-methoxyphenyl)-2,2-diphenylethenes (2) and 1-alkoxy-1-(p-alkoxyphenyl)-2,2-diphenylethenes (4).[5)] The results are given in Table 1. The new products 3 decomposed easily on silica gel or alumina, and hydrolyzed under acidic conditions. Although 3 could not be isolated purely from the reaction mixture even in the cases of runs 2 and 3, the structural elucidation of 3 could be done by ^{1}H NMR and by alcoholysis to the corresponding vinyl ethers 2 and 4.

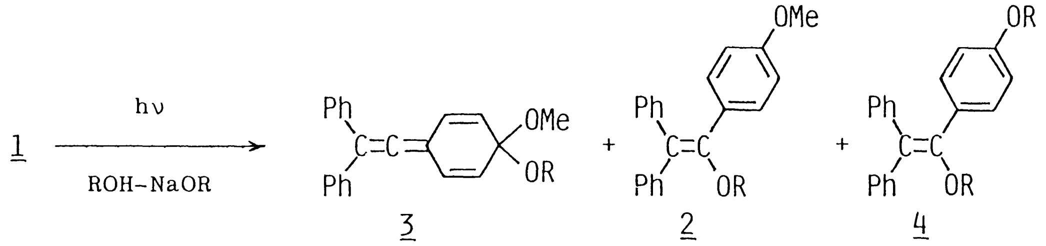


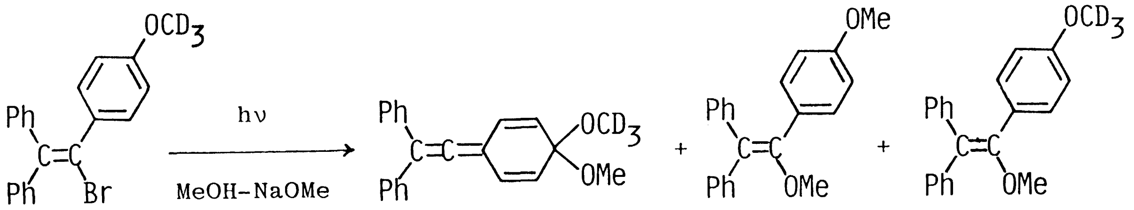
Table 1. Photolysis of 1 in NaOR-ROH[a)]

Run	Base	Solvent	Products / % yield[b)]	
			3	2 + 4
1	NaOMe	MeOH	47	38
2	NaOEt	EtOH	73	14
3	NaOPr-n	n-PrOH	74	18
4	NaOPr-i	i-PrOH	38	57

a) Photolysis was carried out as follows. A solution of 1 (2 mmol) in ROH (100 ml)-CH_2Cl_2 (20 ml) was irradiated in the presence of NaOR (20 mmol) with a Pyrex-filtered Hg lamp (100 W) under N_2 atmosphere at 0 °C for 3 h.
b) Yields were determined by ^{1}H NMR using hexamethylbenzene as an internal reference after workup.

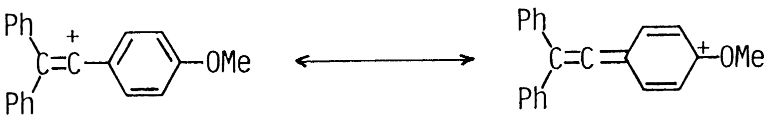
Vinylidenecyclohexadienes 3 showed a characteristic pattern of olefinic protons (AB system) in the ^{1}H NMR, δ 5.8-5.9 (d, J = 10 Hz) and 6.4-6.5 (d, J = 10 Hz), and a higher field resonance of methoxyl group (δ 3.2). These chemical shifts and the coupling constants (J) are similar to those of analogous compounds, 4,4-dimethoxycyclohexa-2,5-dienone[6)] and 3,6-diethoxy-3,6-dimethoxycyclohexa-1,4-diene.[7)] Methanolysis of 3 (R = Me) containing vinyl ether 2 (R = Me) at room temperature for 12 h resulted in exclusive formation of 2 (R = Me). Finally, 3 was identified in connection with the isolated 3,3-diethoxy-6-(2',2'-diphenylvinylidene)-1,4-cyclohexadiene.[8)]

Higher yields of 3 with NaOEt and NaOPr-n than with NaOMe led us to check the partial decomposition of 3 (R = Me) under the photolytic conditions. Due to the difficulty in isolation of 3 (R = Me), we turned to the examination of the vinyl ethers 2 and 4 resulting from the photolysis of 1-(p-methoxy-d_3-phenyl)-2,2-diphenylvinyl bromide (5). The photolysis of 5 in NaOMe-MeOH resulted in the formation of 6-(2',2'-diphenylvinylidene)-3-methoxy-3-methoxy-d_3-phenyl)-2,2-hexadiene (6) (40%), 1-methoxy-1-(p-methoxyphenyl)-2,2-diphenylethene (7) (12%), and 1-methoxy-1-(p-methoxy-d_3-phenyl)-2,2-diphenylethene (8) (26%). Since the rates of decomposition of 6 to the vinyl ethers 7 and 8[8] should be similar to each other, the result obtained above means that ca 63% [= (24/38)×100] of the vinyl ethers 7 and 8 formed arose from 6. Accordingly, ipso substitution on the ring takes place preferentially even in the case of NaOMe. Exception was the case of a bulky NaOPr-i.



5 6 (40%) 7 (12%) 8 (26%)

In analogy with the photocyanation of arylvinyl bromides,[3] α-arylvinyl cations should be key intermediates for the ipso substitution.[9] The methoxyl group causes the charge delocalization to the aryl ring and provides a significant contribution of structure 10.[10] A highly basic (nucleophilic)



9 10

alkoxide ion could interact with the ipso position to give vinylidenecyclohexadienes 3, whereas alcohol itself was not strong enough to interact with the ipso position and reacted at the sp carbon of the double bond to give vinyl ethers 2. Since TEA, pyridine, and $NaHCO_3$ are much less basic than an alkoxide ion,[11] they can not provide any significant amount of alkoxide ion in alcohol. Therefore, the observed drastic dependence of the reaction on the added bases can be explained in terms of the basicity of the bases.

In summary, we found that the photolysis of 1-(p-methoxyphenyl)vinyl bromide 1 was affected by the added base and especially that a strong base, alkoxide ion, attacked the ipso position of the aryl ring. Further studies designed to establish the details of these ipso substitutions are now in progress.

References

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4) 2 (R = Me): mp 148.5-149.5 °C; ^{1}H NMR δ (CDCl$_3$) 3.37 (s, OMe), 3.68 (s, OMe), 6.58-7.23 (m, ArH). 2 (R = Et): mp 108-109 °C; ^{1}H NMR δ (CDCl$_3$) 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). 2 (R = n-Pr): mp 90-91 °C; ^{1}H NMR δ (CDCl$_3$) 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). As byproducts, 1-(p-methoxyphenyl)-2,2-diphenylethene and 10-alkoxy-3-methoxy-9-phenylphenanthrene were detected.

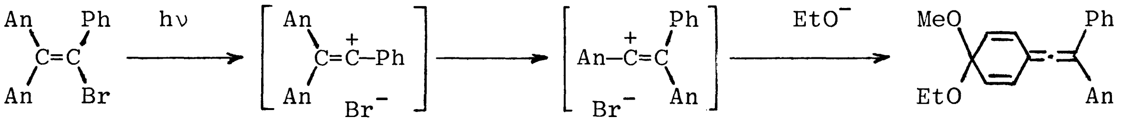
5) Although vinyl ethers 2 and 4 could not be separated from each other, these were identified by comparison with authentic samples and by acid hydrolysis to the corresponding 1-(p-alkoxyphenyl)-2,2-diphenylethanones.

6) J. A. Chudek, R. Foster, and F. J. Reid, J. Chem. Soc., Perkin Trans. 2, 1984, 287; ^{1}H NMR δ (liq. NH$_3$) 5.6 (d, J = 10 Hz, CH=) and 6.8 (d, J = 10 Hz, CH=).

7) G. M. Elgy, W. B. Jennings, and A. E. Pedler, J. Chem. Soc., Perkin Trans. 1, 1983, 1225; ^{1}H NMR δ (CDCl$_3$) 3.20 (OMe) and 5.92 (CH=CH).

8) T. Kitamura, T. Kabashima, S. Kobayashi, and H. Taniguchi, Tetrahedron Lett., in press.

9) Although a direct ipso substitution in vinyl bromide 1 may be possible, the presence of β-anisyl rearrangement in the photolysis of 2,2-bis(p-methoxyphenyl)-1-phenylvinyl bromide in EtONa-EtOH supports the intermediacy of vinyl cations in the ipso substitution.



An = p-MeOC$_6$H$_4$ 30%

10) Such a large charge delocalization was observed in solvolysis of p-methoxybenzylic system bearing two CF$_3$ groups at the α position. See, A. D. Allen, V. M. Kanagasabapathy, and T. T. Tidwell, J. Am. Chem. Soc., 108, 3470 (1986).

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