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Structural Dependence on Photoaddition of Methanol to Arylalkenes. Solvent and Additive Effects on Photoinduced Electron Transfer Reaction

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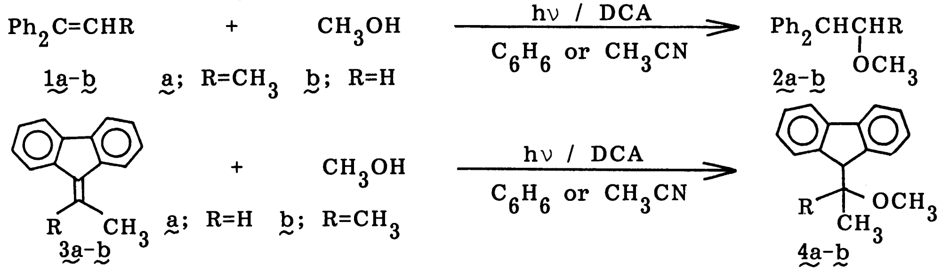
The 9,10-dicyanoanthracene(DCA)-sensitized photoaddition of methanol to arylalkenes occurred both in benzene and acetonitrile to give the corresponding anti-Markownikoff type adducts. The efficiency of the photoreaction depended on the solvents and the structures of the substrates. The geminate radical ion pair in benzene and the solvent separated radical cation in acetonitrile were proposed as key intermediates. The stereochemical feature of the photoaddition of methanol to 1,2-dihydro-4-phenylnaphthalene was also described.

Since Neunteufel and Arnold reported the photoaddition of methanol to 1,1-diphenylethene in 1973,[1)] the photoaddition of nucleophiles to electron-donating substrates via photoinduced electron transfer has been a subject of considerable interest from mechanistic and synthetic viewpoints.[1-3)] It has long been recognized that these photoreactions generally occur in polar solvents, but not in nonpolar solvents. We now report the first example of structure-dependent medium effects on the photochemical polar addition of methanol to arylalkenes. We also describe that the stereoselectivity in the photoaddition of methanol to cyclic arylalkene depends on solvent polarity.

Irradiation of a benzene solution containing 1,1-diphenyl-1-propene (1a, 0.02 mol dm^{-3}) and methanol in the presence of DCA (1×10^{-3} mol dm^{-3}) through an aqueous NH_3-$CuSO_4$ filter solution (≥ 400 nm) gave 2-methoxy-1,1-diphenylpropane (2a) as a sole product.[4,5)] This photoaddition also occurred efficiently in other aromatic solvents such as toluene and p-xylene, but occurred inefficiently in acetonitrile, diethyl ether, and ethyl acetate.

In benzene, the quantum yield (ϕ_{2a}) for the formation of 2a varied with the concentration of added CH_3OH, and a maximum quantum yield appeared at $[CH_3OH]=$



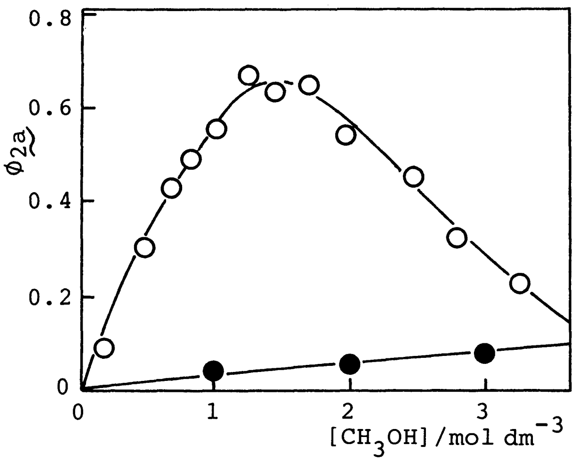


Fig.1. Plots of quantum yields for the formation of 2a at 405 nm vs. $[CH_3OH]$ in the presence of DCA: [1a]=0.02 mol dm^{-3}, -○-; in benzene. -●-; in acetonitrile.

Table 1. Photochemical Polar Addition of Methanol to Arylalkenes[a)]

Alkene	Solvent	Time/h	Conv/%	Yield/%[b)]
1a	C_6H_6	0.5	90	88
1a	CH_3CN	3.0	70	56
1b	C_6H_6	1.5	—	20
1b	CH_3CN	1.5	—	24
3a	C_6H_6	3.0	< 3	trace
3a	CH_3CN	0.5	98	94
3b	C_6H_6	3.0	58	48
3b	CH_3CN	0.5	98	88
5	C_6H_6	1.0	95	91[c)]
5	CH_3CN	2.0	99	89[c)]

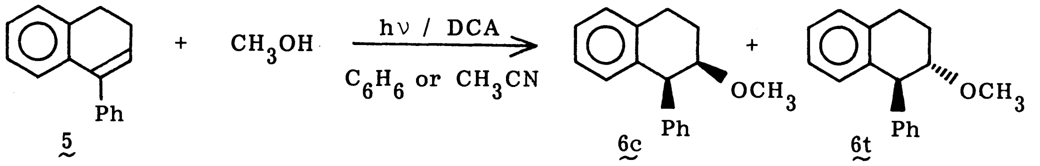
a) $[CH_3OH]$=1 mol dm^{-3} (in benzene), 5 mol dm^{-3} (in acetonitrile). b) GLC yields of the products based on the arylalkenes used. c) Total yields of 6c and 6t.

1.0-2.0 mol dm^{-3}. However, in acetonitrile ϕ_{2a} increased continuously with increasing the concentration of added methanol up to 3.0 mol dm^{-3}, but the values of ϕ_{2a} were smaller than those in benzene in this concentration range (Fig. 1).

The efficiency of the photoreaction was also affected by solvent and additive (Table 1). The addition of benzene, toluene, or p-xylene into the acetonitrile solution facilitated the formation of 2a. The formation of 2a was depressed by the addition of $Mg(ClO_4)_2$ (0.1 mol dm^{-3}) by a factor of 0.75 in acetonitrile. The DCA-sensitized photoaddition of methanol to 1,1-diphenylethene (1b) occurred in a similar fashion, but this reaction gave appreciable amounts of the dimeric products of 1b along with 2b.[4)]

On the other hand, the photoaddition of methanol to 9-alkylidenefluorenes (3a-b) occurred in benzene inefficiently under the similar conditions, but did occur efficiently in acetonitrile giving 4a-b in high yields.[5)] The addition of $Mg(ClO_4)_2$ (0.01 mol dm^{-3}) facilitated the formation of 4a by a factor of 1.5 in acetonitrile.

The photoaddition of methanol to 1,2-dihydro-4-phenylnaphthalene (5) occurred in benzene in a stereoselective manner to give 6c and 6t in a 1:3.2 ratio.[6)] However, the stereoselectivity in this photoreaction depended on the solvent polarity; in acetonitrile 6c and 6t were produced in a 3.8:1 ratio. These product ratios were independent of the reaction time. The relative quantum yield for the formation of 6c and 6t in benzene was 2.5 times higher than that in acetonitrile.



The fluorescence of DCA in acetonitrile was efficiently quenched by all the arylalkenes at nearly diffusion controlled rates (Table 2). In benzene, however, the rate constants k_q depended on the structures of the arylalkenes, though their oxidation potentials were close to each other. In the cases of 3b and 5, the weak emissions due to the exciplex formation with DCA were observed in benzene in much

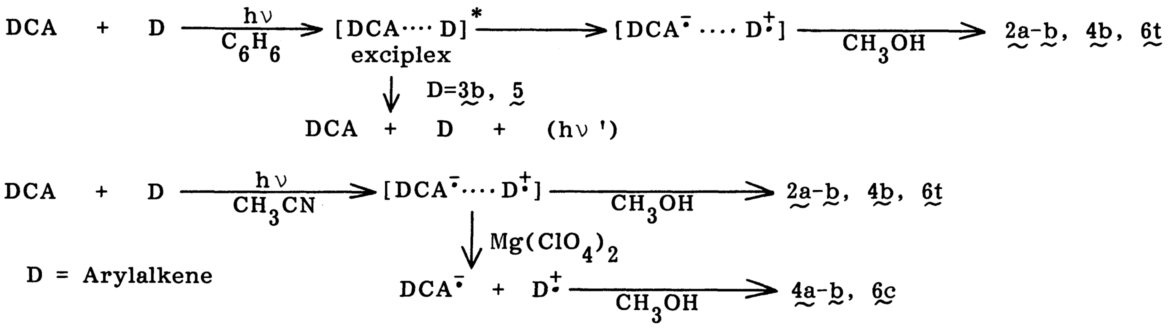
Table 2. Oxidation Potentials of Arylalkenes, Rate Constants for Fluorescence Quenching of DCA and Calculated ΔG Values for a One-Electron Transfer from the Arylalkenes to $^1DCA^*$ in Acetonitrile

Alkene	$E^{ox}_{p/2}$/V a) (Ag/Ag^+)	Solvent	$k_q\tau$ / $mol^{-1}dm^3$ s	$k_q \times 10^{-9}$ b) / $mol^{-1}dm^3$	ΔG e) / kJ mol^{-1}
1a	1.13	CH_3CN	134 (133)c)	8.32	-100.0
		C_6H_6	5 (27)d)	0.33	
1b	1.26	CH_3CN	120	7.45	-87.4
		C_6H_6	8	0.53	
3a	1.11	CH_3CN	106 (110)c)	6.58	-101.9
		C_6H_6	47 (49)d)	4.41	
3b	1.05	CH_3CN	148	9.19	-107.7
		C_6H_6	70	4.61	
5	1.01	CH_3CN	183	11.37	-111.5
		C_6H_6	80	5.26	

a) Oxidation potentials of arylalkenes in acetonitrile. b) Rate constants for fluorescence quenching in aerated solutions; τ(air)=16.1 ns (acetonitrile), τ(air)=15.2 ns (benzene). c) Values in the presence of $Mg(ClO_4)_2$ ($[Mg(ClO_4)_2]$= 0.2 mol dm^{-3}). d) Values in the presence of CH_3OH($[CH_3OH]$=1.0 mol dm^{-3}). e) Ref. 9.

longer wavelength region than the emission of DCA and the isoemissive points appeared at 520 and 510 nm, respectively. The fluorescence of DCA was not quenched by $Mg(ClO_4)_2$ in acetonitrile. The rate constants for the fluorescence quenching by the arylalkenes were not affected by the addition of $Mg(ClO_4)_2$ in an appreciable amount.

All the above results may be explained on the basis of the mechanism shown in Scheme 1. A striking feature of the photoreactions is that the mechanistic and reactivity characteristics depend on the structures of the arylalkenes. In the case of the arylalkenes 1a-b,7) the photoaddition occurs through a geminate radical ion pair $[D^{+\cdot} \cdots DCA^{-\cdot}]$ (D; arylalkene) which is generated most probably in benzene or other aromatic solvents. In this intermediate, the cationic center may be localized on the olefinic part owing to a distortion of the coplanarity of the double bond with the aromatic rings. The attack of methanol on the intermediate leads to the formation of 2a-b. The mechanism is supported by the fact that the efficiency of the formation of 2a-b was suppressed by the addition of $Mg(ClO_4)_2$, which facilitates the dissociation of the geminate radical ion pair to the solvent separated radical ions.8)



Scheme 1.

On the other hand, the conformationally more rigid arylalkenes **3a-b** give stable emissive or nonemissive exciplexes in benzene because of their constrained planar structures. But, these stable exciplexes are not attacked by methanol. For these alkenes, the photoaddition occurs via a solvent separated radical cation ($D^{+\cdot}$) which can be generated efficiently in acetonitrile to give **4a-b**. That the addition of $Mg(ClO_4)_2$ to the reaction media facilitates the formation of the methanol-addition products, supports this mechanism.$^{8)}$

The cyclic arylalkene **5** is attacked in benzene by methanol to give **6t**, a cis-addition product, in a stereoselective manner. On the other hand, in acetonitrile the trans-addition product **6c** is produced preferentially. Probably, the former reaction proceeds via the radical ion pair and the latter reaction via the solvent separated radical cation.

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4) Any dimeric products were not obtained from the photoreactions of **1a**, **3a-b**, and **5**. However, in the case of the photoreaction of **1b** the appreciable amounts of dimeric products, 1,1,2,2-tetraphenylcyclobutane and 1,1,4-triphenyl-1,2,3,4-tetrahydronaphthalene, are produced; cf. Ref. 3.

5) **2a**: oil; ^1H NMR ($CDCl_3$) δ1.08 (3H, d, J=6.0 Hz), 3.23 (3H, s), 3.87 (1H, d, J=8.5 Hz), 4.01 (1H, dq), 7.1-7.4 (10H, m). **4a**: oil; 0.58 (3H, d, J=6.4 Hz), 3.57 (3H, s), 4.06 (1H, dq, J=4.0, 6.4 Hz), 4.33 (1H, d), 7.2-7.8 (8H, m). **4b**: mp 61.5-62.5 °C. δ1.05 (6H, s), 3.45 (3H, s), 4.17 (1H, s), 7.1-7.7 (8H, m).

6) The authentic sample of **6c** was prepared by the catalytic hydrogenation of 1,2-dihydro-3-methoxy-4-phenylnaphthalene on Pd-charcoal in a high yield. **6c**: oil; ^1H NMR ($CDCl_3$, 270 MHz) δ1.82-1.93 (1H, m), 1.95-2.03 (1H, m), 2.86 (1H, dt, J=8.1, 17.3 Hz), 3.07 (1H, dt, 6.1, 17.3 Hz), 3.34 (3H, s), 3.70 (1H, ddd, J=3.3, 4.8, 9.0 Hz), 4.35 (1H, d, J=4.8 Hz), 6.90 (1H, d, J=7.7 Hz), 7.02-7.35 (8H, m). **6t**: mp 44-45 °C; δ1.85 (1H, ddt, J=6.1, 6.7, 13.5 Hz), 2.04 (1H, dddd, J=2.5, 6.1, 8.5, 13.5 Hz), 2.84 (1H, dt), 2.98 (1H, ddd, J=6.1, 8.5, 13.7 Hz), 3.33 (3H, s), 3.64 (1H, ddd, J=2.5, 5.2, 6.7 Hz), 4.18 (1H, d, J=5.2 Hz), 6.84 (1H, d, J=8.1 Hz), 7.00-7.29 (8H, m).

7) Molecular models of **1a-b** and **5** indicate that two aryl groups cannot be coplanar to each other by steric hindrance.

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