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PHOTOLYSIS OF THE VINYL BROMIDE 9-(α-BROMOBENZYLIDENE)FLUORENE IN METHANOL. EFFECT OF WAVELENGTH OF IRRADIATION, SODIUM METHOXIDE AND OXYGEN.

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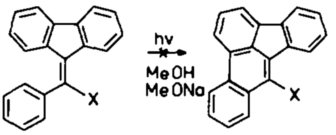
Abstract.

A quantitative study of the photosolvolysis of 9-(α-bromobenzylidene)fluorene (1̲) in methanol reveals that the wavelength of irradiation, the presence of sodium methoxide and the presence of oxygen strongly influence the product distribution and the quantum yields of the reaction.

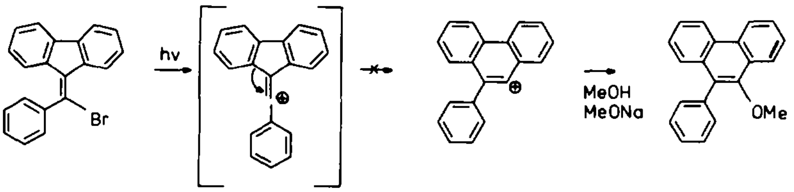
Introduction

Irradiation of vinyl bromides in appropriate media affords both products of reductive debromination and nucleophilic substitution.[1] The products of nucleophilic photo-substitution are presumably formed via trapping of photogenerated vinyl cations by the solvent or by the added nucleophile[2-4]. Studies of nucleophilic capture ratios with triarylvinyl bromides in our laboratory have shown that the cations involved are identical with the ions involved in thermal nucleophilic substitution reactions[4].
β-Aryl rearrangement studies with triarylvinyl bromides also show similar behaviour of photochemically and thermally generated ions[5].

Investigations into the ease of photogeneration of vinyl cations from triarylvinyl bromides as a function of the structure of the substrate and of the reaction conditions are hampered by the multitude of other reaction pathways of those systems. In addition to the heterolytic C-Br bond cleavage reactions (substitution and rearrangement-substitution) and the homolytic bond cleavage reaction (reductive debromination), E/Z isomerization as well as cyclization of the stilbene-like 1,2-diaryl moiety of both starting material and C-Br bond cleavage products to strongly light absorbing phenanthrenes occur. As part of a systematic quantitative study of the influence of α-substituents on the photochemistry of vinyl halides in nucleophilic media we therefore studied the photomethanolysis of α-aryl-β,β-fluorenylidene vinyl bromides, where neither electrocyclization of starting material and of cleavage products (equation 1) nor β-aryl migration (equation 2) are expected to occur.



X = Br, OMe, H (eq. 1)



(eq. 2)

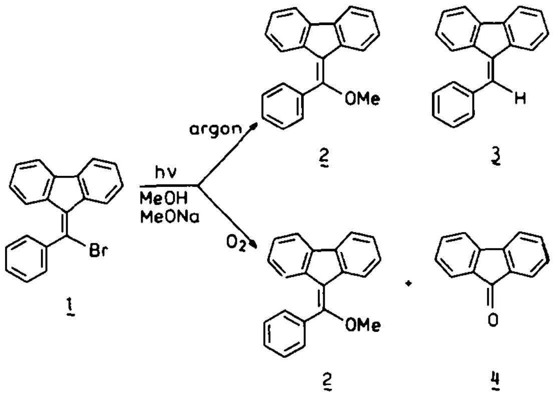
Scholz et al. have reported that irradiation of a variety of 9-benzylidenefluorenes does not yield cyclization products[6].

β-Aryl migration across the C=C double bond would have to occur via an unfavourable sterically constrained situation where the migrating C-atom has its p-orbital orthogonal to the p-orbital of the migration terminus.

In this paper we wish to report the results of our study of the photochemical behaviour of 9-(α-bromobenzylidene)fluorene (1) in methanol and in methanol/sodium methoxide.

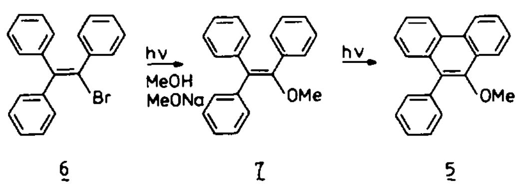
Results

Irradiation of a solution of 1 (5 x 10^{-4} M) in argon-saturated methanol and in argon-saturated methanol/sodium methoxide yields 9-(α-methoxybenzylidene)fluorene (2) and 9-benzylidenefluorene (3); in oxygen-saturated solutions the products are 2 and fluorenone (4) (equation 3).[7]



(eq. 3)

The products are photostable. Benzo[b]fluoranthene derivatives which would result from stilbene-like cyclization of 1, 2 or 3 are not formed. 9-Methoxy-10-phenyl-phenanthrene (5), which would be the product if β-aryl migration would occur, is also not found. The latter compound was independently synthesized by photolysis of 1,2,2-triphenylvinyl bromide (6) in MeOH/MeONa followed by further photocyclization of 7 in hexane (equation 4).



(eq. 4)

The quantum yields of disappearance of 1 and formation of 2, 3 and 4 were determined at 254 and 313 nm, in methanol and in methanol/0.10 M sodium methoxide and in the presence and absence of oxygen[8]. The results are shown in Table I. The influence of 2 x 10^{-2} M *trans*-piperylene on the reactions of 1 in argon-saturated methanol upon irradiation at 254 nm and 313 nm is reported in Table II.

Table I: Quantum yields of the photoreactions of 1 in methanol and methanolic sodium methoxide

λ_{irr} (nm)	[MeONa] [M]	gas[a)]	Φ_{dis}[b)] x10^3	Φ_{OMe}[c)] x10^3	Φ_H[d)] x10^3	$\Phi_{C=O}$[e)] x10^3
254	0	argon	66	35	15	-
254	0.10	argon	146	35	51	-
254	0	oxygen	62	28	-	22
254	0.10	oxygen	43	31	-	16
313	0	argon	8	5	2	-
313	0.10	argon	12	6	3	-
313	0	oxygen	9	5	-	2
313	0.10	oxygen	7	6	-	2

Table II Quantum yields of the photoreactions of 1 in methanol in the presence of *trans*-piperylene

λ_{irr} (nm)	[*trans*-piperylene] [M]	gas[a)]	Φ_{dis}[b)] x 10^3	Φ_{OMe}[c)] x 10^3	Φ_H[d)] x 10^3	$\Phi_{C=O}$[e)] x 10^3
254	0.020	argon	43	30	8	-
313	0.020	argon	9	5	1	-

All measurements were carried out at least in duplo.

[a)] gas bubbled through the solution; [b)] quantum yield of disappearance of 1;
[c)] quantum yield of formation of 2; [d)] quantum yield of formation of 3;
[e)] quantum yield of formation of 4.

Discussion

Effect of wavelength of irradiation.

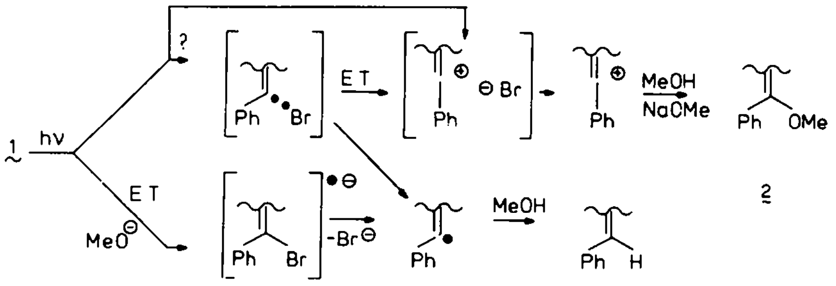
The data in Table I show that compound 1 is considerably more photoreactive upon irradiation at 254 nm than at 313 nm. The wavelength dependence[10] is most probably not caused by selective excitation at the lower wavelength of an impurity acting as a sensitizer[11] or in a charge transfer absorption band[12] of 1 with methanol or methoxide. Benzene, toluene and acetone proved to be ineffective as photosensitizers. Irradiation of extra added 2, 3 or 4 also does not bring about photochemistry of 1. The UV spectrum of 1 is insensitive to variation of solvent or addition of sodium methoxide[13]. The spectrum shows two absorption bands with λ_{max} 317 nm (ε 15500 l mol^{-1}. cm^{-1}) and λ_{max} 258 nm (ε 40500 l. mol^{-1}. cm^{-1}) . The difference in quantum yields at 313 and 254 nm is thought to be the result of different chemical reactivity of the S_1 and S_2 states. Possibly due to a large n-σ^* contribution to its electronic character the S_2 (or T_2) state apparently gives efficient C-Br bond dissociation able to compete with internal conversion to the S_1(or T_1) state. The different responses to the presence of O_2, piperylene and sodium methoxide at the two wavelengths of irradiation also indicate the involvement of two different excited states.

A wavelength effect similar to the one described here has recently been noted in the reductive debromination of 5-bromouracil[14] and 2-bromo-4,4-dimethyl-2-cyclohexenone[15].

In those cases the reactivity differences were ascribed to population of a reactive π,π^* state versus population of an unreactive n,π^* state.

Effect of sodium methoxide.

At both wavelengths of excitation upon addition of 0.10 M sodium methoxide the rate of disappearance of 1 and the rate of formation of the reduction product 3 strongly increase; the rate of formation of the nucleophilic substitution product 2 is barely affected. The latter effect is in accordance with the formation of a reactive intermediate vinyl cation as the rate limiting step for nucleophilic photo-substitution. The former effect is most probably caused by the nucleophile methoxide acting as an electron donor to the excited vinyl halide. As the resulting radical anion RA will easily lose bromide ion this pathway leads to vinyl radical VR which readily yields 3 (equation 5). In the field of haloaromatics there is ample evidence for the increase of reductive dehalogenation by nucleophiles via electron transfer[1a,16].



(eq. 5)

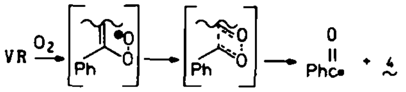
2

RA VR 3

An alternative pathway in which 3 is formed by protonation of the radical anion RA by the solvent, followed by expulsion of Br• is ruled out by the fact that upon irradiation of 1 with a high-pressure mercury lamp in MeOD/MeONa no deuterium incorporation in 3 is found.The increase in reduction product with concurrent constancy of substitution product proves that the substitution reaction does not occur via the $S_{RN}1$ mechanism[17].

Effect of oxygen.

Saturation of the solution with oxygen changes the product composition from 2 plus 3 to 2 plus 4. In methanol the amount of 4 formed is nearly equal to the amount of 3 in the argon-saturated solutions. Compound 3 is not a precursor of 4. Upon irradiation of 1 in methanol in the presence of 5.0×10^{-5} M 3 and O_2 the concentration of 3 remained constant while 4 was formed as usual. In view of their comparable rates of formation 3 and 4 may have a common precursor and 4 may be formed via oxygen scavenging of the vinyl radical VR[18,19] (equation 6).



(eq. 6)

8

Reaction of radical 8 with oxygen followed by abstraction of hydrogen from the solvent will give perbenzoic acid, abstraction of hydrogen from the solvent by 8 will give benzaldehyde. Benzaldehyde and perbenzoic acid are not found, but at 254 nm in methanol, in the presence of oxygen benzoic acid was isolated in a yield of 12% relative to fluorenone. Indeed, perbenzoic acid is known to be capable of oxidizing benzaldehyde thereby producing benzoic acid[20].

In methanol at 254 nm oxygen hardly affects the rate of disappearance of 1 and the rate of appearance of 2 . At λ 313 nm the influence of oxygen is even smaller.

The effect of *trans*-piperylene is similar to that of oxygen. These observations are indicative of very short-lived reactive excited states[21].

The pronounced effect of O_2 in methanol / sodium methoxide is in line with the photoproduction in that situation of radical anions, species known to be quenched very efficiently by O_2[22].

The results presented here show that ionic versus radical behaviour of photo-excited vinyl halides is not only determined by the structure of the substrate but also by the reaction conditions such as the wavelength of irradiation and the presence of nucleophiles which can act as electron donors.

References and notes

1. For reviews see:
   a) G. Lodder, in S. Patai and Z. Rappoport (eds.), The Chemistry of Halides, Pseudohalides and Azides, Wiley, Chichester, 1605 (1983);
   b) P.J. Kropp, Acc. Chem. Res., 17, 131 (1984).
2. T. Kitamura, S. Kobayashi and H. Taniguchi, J. Org. Chem., 47, 2323 (1982).
3. P.J. Kropp, S.A. McNeely and R.D. Davis, J. Am. Chem. Soc., 105, 6907 (1983).
4. F.I.M. van Ginkel, J. Cornelisse and G. Lodder, manuscript in preparation.
5. T. Kitamura, S.Kobayashi, H. Taniguchi, C.Y. Fiakpui, C.C. Lee and Z. Rappoport, J. Org. Chem., 49, 3167 (1984).
6. M. Scholz, F. Dietz and M. Mühlstädt, Tetrahedron Letters, 2835 (1970).
7. The reaction mixtures were separated by means of preparative HPLC. The products were identified on the basis of ^{1}H NMR, UV, IR and MS data and by comparison of their retention times and spectral data with those of independently synthesized samples.
8. The variations in the concentration of starting material and products as a function of the time of irradiation were followed by quantitative HPLC. For actinometry the rate of the photolysis of 3-nitroanisole in an aqueous 0.1 M NaOH solution$^{9)}$ was used.
9. R.O. de Jongh, thesis Leiden (1965).
10. For a review of wavelength dependent photoreactions, see N.J. Turro, V. Ramamurthy, W. Cherry and W. Farneth, Chem. Rev., 78, 125 (1978).
11. P. Suppan, S. Huber and E. Haselbach, Helv. Chim. Acta, 66, 2597 (1983).
12. G. Jones II and W.G. Becker, J. Am. Chem. Soc., 105, 1276 (1983).
13. The U.V. spectrum of 1 was measured in methanol, methanol/0.10 M sodium methoxide, acetonitril and hexane. No significant changes in λ_{max} and ε_{max} were observed.
14. B.J. Swanson, J.C. Kutzer and T.H. Koch, J. Am. Chem. Soc., 103, 1274 (1981).
15. H. Hombrecker and P. Margaretha, Helv. Chim. Acta, 65, 2313 (1982).
16. R.S. Davidson, J.W. Goodin and G. Kemp, Adv. Phys. Org. Chem., 20, 191 (1984).
17. J.F. Bunnett, X. Creary and J.E. Sundberg, J. Org. Chem., 41, 1707 (1976).
18. J.Y. Pack, M.C. Heaven and D. Gutman, Chem. Phys. Letters, 104, 469 (1984).
19. A referee has suggested that the peroxy radical shown in equation 6 might abstract a hydrogen atom from the solvent. The resulting hydroperoxide is expected to absorb also at $\lambda > 300$ nm; upon excitation the O-O band will be cleaved. The ensuing radical, which is stabilized by resonance, may react with oxygen at C-9. Abstraction of a hydrogen atom from the solvent then gives rise to 9-benzoyl-9-hydroperoxyfluorene which might undergo an intramolecular [2+2] cycloaddition of the carbonyl group and the hydroxy group, yielding a hydroxydioxetane derivative. Fluorenone and benzoic acid will then be produced via the well-known dioxetane cleavage reaction.
20. J.A. Howard, "Homogeneous Liquid-Phase Autoxidations", Chapter 12 in "Free Radicals" (J.K. Kochi, ed.), Volume II, Wiley-Interscience, New York, 1973.
21. Using the Stern-Volmer equation and the numbers $\Phi_o = 0.066$, $\Phi = 0.043$, $k = 10^{10}\ s^{-1}mol^{-1}$ and [*trans*-piperylene] = 0.020 mol.l^{-1}, τ is calculated to be 2.5×10^{-9}s.
22. R.A. Rossi and J.F. Bunnett, J. Org. Chem., 38, 1407 (1973).