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Solvent effects on photocycloadditions of dibenzoylmethanatoboron difluoride with enol ethers

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Abstract

The photolysis of dibenzoylmethanatoboron difluoride ($DBMBF_2$) in the presence of vinyl ethers in acetonitrile gave dimers of the latter from acid catalysis or electron transfer sensitization, but, in contrast, gave cycloaddition products in an efficient reaction in less polar solvents such as tetrahydrofuran (THF) and benzene.

Keywords: Solvent effects; Photocycloaddition; Dibenzoylmethanatoboron difluoride; Enol ethers

1. Introduction

Dibenzoylmethanatoboron difluoride ($DBMBF_2$) photolytically adds efficiently by the [2+2] mode to simple olefins [1] and α,β-unsaturated carbonyl compounds [2] to give good yields of 1,5-diketones after hydrolysis–ring opening steps. It also sensitizes cyclohexadiene and anethole [3] to undergo cation radical dimerizations mediated by electron transfer. In spite of these facile photoreactions, it fails to give any cycloadduct in the presence of ethyl vinyl ether (**1a**) and 3,4-dihydro-2H-pyran (**4**) under similar conditions, although the fluorescence intensity of $DBMBF_2$ is efficiently quenched with rate constants of 0.7×10^{10} and 1.3×10^{10} M^{-1} s^{-1} respectively [4]. We wish to report that the product pattern shifts dramatically and that the cycloaddition product dominates in ethers and aromatic solvents. As the correct choice of solvent is critical to afford enhanced product yields, we seek rapid publication of this preliminary note.

2. Experimental details

2.1. General conditions

For both photoreaction and fluorescence quenching studies, the solvents and purification procedures were the same as those used previously [1–3]. Tetrahydrofuran (THF) (BDH, analytical reagent) was freshly distilled in the presence of sodium and benzophenone (to generate the ketyl radical) under nitrogen. Ethyl vinyl ether (Eastman), isobutyl vinyl ether (Aldrich) and 3,4-dihydro-2H-pyran (Aldrich) were distilled before use. Phenyl vinyl ether was prepared according to the literature [5] from 2-bromoethyl phenyl ether (Aldrich). Fluorescence quenching was carried out on a Perkin–Elmer MPF44B spectrophotometer.

2.2. Preparative photocyloaddition of $DBMBF_2$ to the vinyl ethers

A typical reaction is described below. An ether solution (30 ml) of $DBMBF_2$ (0.018 M) and a vinyl ether (0.2–0.5 M) was mixed and sealed under nitrogen in several Pyrex test tubes (110×13 mm), which were placed in a 'Merry-go-round' mounted in a Rayonet photoreactor equipped with RPR 350 nm lamps. For preparative runs, the irradiation was interrupted when the conversion of $DBMBF_2$ on gas chromatography (GC) reached more than 50%. The photolyzate was concentrated in vacuo and then mixed with hexane–ether (2:1) to precipitate and remove $DBMBF_2$. The crude product was taken directly for chromatography on silica gel, with hexanes containing 6–10 vol.% ethyl acetate as eluent. The isolated products showed nuclear magnetic resonance (NMR), IR, mass spectrometry (MS) and analytical data compatible with the assigned structures. For quantum yield determination, a mixture of benzophenone (0.05 M) and benzhydrol (0.10 M) in benzene was used as actinometric solution (3 ml); the quantum yield was assumed to be 0.74 [4].

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3. Results and discussion

In acetonitrile, the photolysis of $DBMBF_2$ and vinyl ether **1** gave dimers of **1** with trace amounts of adduct **2**; in ether or benzene as solvent, **2** became either the major (**2a** and **2c**) or the exclusive (**2b**) product. In the reaction with **1a**, an unstable dimer X was shown to be formed by an acid-catalyzed (or BF_3-catalyzed) dark reaction, but could not be obtained pure. Indeed, in the presence of pyridine to tie-up the acid, a similar photoreaction failed to give X. The photoreaction with **1c** in acetonitrile gave the known photodimers **3** in good efficiency ($\Phi = 0.1$); the dimer **3** decreased as the solvent shifted to lower polarity and eventually was superseded by **2c** in ether or benzene. The quantum yields are summarized, together with the respective solvent polarities in Table 1. Similar photolysis in the presence of 3,4-dihydro-2H-pyran (**4**) did not give the corresponding adduct in a variety of solvents, but gave two acid-catalyzed dimers of **4**, the major one of which was **5** on the basis of the one proton singlet at 6.68 ppm; this compound was isolated previously [7]. The minor product gradually changed to **5** during isolation. On the basis of mechanistic considerations, the unstable dimer X from **1a** could be deduced to possess a structure analogous to **5**. The structures of the cycloadducts **2** were assigned using their spectroscopic data, in particular by the presence of double doublets at about 4.7 ppm (**2a**, **2b**) and 5.65 ppm (**2c**) for H_a. The coupling pattern and chemical shifts ruled out the structure from the alternative addition, which should have a plane of symmetry, and give simpler ^1H and ^{13}C NMR spectra.

Two minor products were also obtained, namely cage product **6** when **1a** and **1b** were used, and threo and erythro isomers of **7** when the reaction was carried out in THF. The structure of the former was confirmed by its simple ^1H and ^{13}C NMR pattern, e.g. only four ^{13}C aromatic signals indicate that the two phenyl rings are identical. The long-range couplings for four alkyl protons with well-defined patterns suggest a rigid cage structure for **6**. The coupling product **7** can be assumed to arise from H-atom transfer and radical coupling of the carbonyl group, but it is obviously not formed from triplet reactions: the radical ion pair $THF^{\cdot +}$ $-DBMBF_2^{\cdot -}$ is believed to be the precursor, giving **7** through hydrogen transfer and coupling.

Table 1
Product quantum yields in different solvents

Solvent	ϵ [a]	$\Phi_{2b} \times 100$ [b]	$\Phi_{2c} \times 100$	$\Phi_3 \times 100$
CH_3CN	35.9	0.32	0.22	10.4
CH_2Cl_2	8.93	1.26	–	–
THF	7.58	0.96	1.69	0.29
Dioxan	2.21	1.52	4.44	0.66
Et_2O	4.20	2.52	8.83	1.40
Benzene	2.27	4.37	10.7	1.11
Toluene	2.38	4.90	13.0	–
p-Xylene	2.27	4.15	16.2	1.87

[a] ϵ is the solvent dielectric constant [6].

[b] The solution contains 2,6-lutidine (1.14×10^{-3} M) in order to neutralize the generated acid.

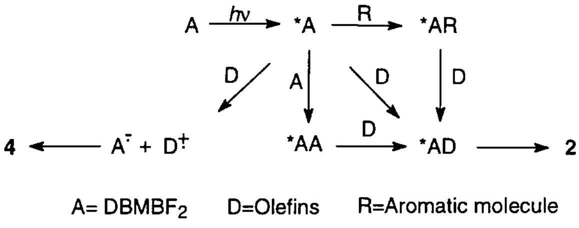
Table 2
Stern–Volmer constant (K_{sv}) from fluorescence quenching and quantum yield study in THF [a]

Substrate	K_{sv}^m	K_{sv}^{ex}	K_{sv}^y	Φ/Φ_0
1a	2.4	21.0	–	1–1.7
1b	2.2	18.1	8.0 [b], 14.5 [c], 18.7 [c]	1–1.5
1c	3.3	15.6	8.6 [b], 12.9 [c]	–
5	4.5	122.0	–	–

[a] K_{sv}^m measured with $[DBMBF_2] = 5 \times 10^{-6}$ M at 398 and 416 nm; K_{sv}^{ex} determined as shown in Fig. 1; K_{sv}^y determined according to $1/\Phi = 1/\alpha + 1/\alpha K_{sv}^y$ [1]; Φ_0 is the quantum yield of **2** at $[DBMBF_2] = 0.01$ M and Φ those at 0.03, 0.05 and 0.07 M; here [**1**] = 0.3 M fixed in the Φ/Φ_0 study.

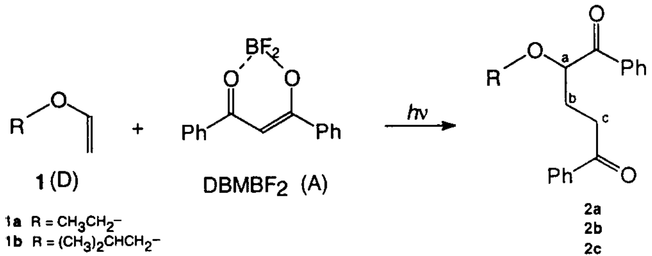
[b] $[DBMBF_2] = 0.03$ M.

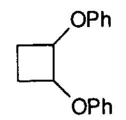
[c] $[DBMBF_2] = 0.2$ M.



Scheme 1.

As shown in Table 1, the quantum yields of the adducts and dimers, regardless of their mechanistic origin, vary in the opposite direction, within experimental error, to the polarity changes, including benzene derivatives. Singlet excited $DBMBF_2$ has a short lifetime (e.g. 0.27 ns in CH_3CN) and forms a relatively long-lived excimer ($\tau = 50$ ns in CH_3CN) or exciplexes with benzenes ($\tau = 5$–10 ns) [8]; they are expected to play primary roles in the reaction sequence. In non-aromatic solvents, both $*DBMBF_2$ and the excimer $*(DBMBF_2)_2$ [8] must be reacting species, as supported by two lines of evidence (Table 2). Firstly, the quantum yields of **2a** and **2b** increase with increasing $DBMBF_2$ concentration in the 0.01–0.07 M region; the excimer concentration is proportional to $[DBMBF_2]$ (Scheme 1). Secondly, the Stern–Volmer constant (K_{sv}^y), determined from the quantum yields of **2b** and **2c** (from $1/\Phi = 1/\alpha + 1/\alpha K_{sv}^y$ [**1**]), is higher at higher concentrations of $DBMBF_2$, and approaches the value of K_{sv}^{ex} for the excimer reaction determined from fluorescence quenching, as shown in Fig. 1, according to the known equation [9] $(I_0/I_{ex})/(I_0/I)_m = 1 + K_{sv}^{ex}$ [**1**] at $[DBMBF_2] = 0.20$ M. At $[DBMBF_2] = 5 \times 10^{-6}$ M, the quenching constant of





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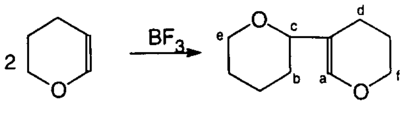

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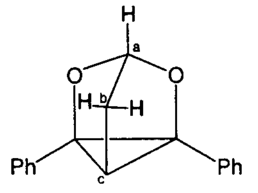

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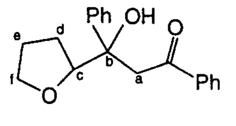

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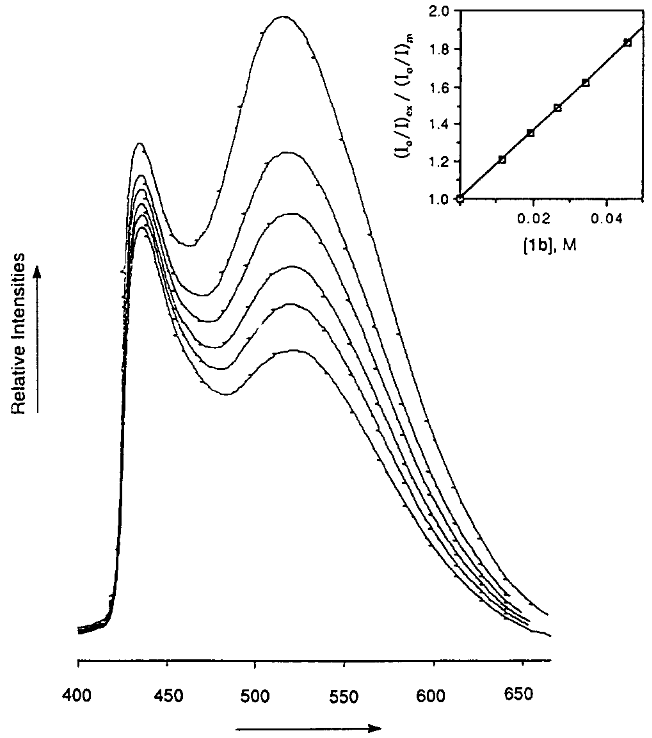

Fig. 1. Quenching of DBMBF$_2$ (0.2 M) fluorescence in THF (λ_{ex}=365 nm) by **1b** (less than 0.046 M); $(I_0/I)_{ex}$ is measured at 528 nm, the excimer fluorescence maximum, and $(I_0/I)_m$ at 446 nm, the monomer peak. The inset is the Stern–Volmer plot of $(I_0/I)_{ex}/(I_0/I)_m$ vs. [**1b**].

the *DBMBF$_2$ monomer fluorescence at 398 and 418 nm was determined to give K_{sv}^{m} by the standard Stern–Volmer equation $I_0/I = 1 + K_{sv}^{m}$ [D] (Table 2). We are investigating whether the DBMBF$_2$ photocycloaddition also occurs from the excited monomer as observed with simple olefins [1].

In view of the continuous variation of the quantum yields with the solvent polarity, adducts **2** should be derived from a common precursor which is responding to excited state solute–solvent interactions. It is proposed that both excimer *(AA) and exciplexes *(AR) undergo substitution [9] to give a non-fluorescent common precursor *(AD) (see Scheme 1) which partitions to **2** and ground state substrates; the latter probably occurs by back electron transfer of radical ion pairs. We believe that benzene acts as a mediator to raise the lower singly occupied molecular orbital (SOMO) level of *(AR), which is now placed in closer proximity to the highest occupied molecular orbital (HOMO) of **1**, and thus facilitates the substitutive interaction; such a process may conceivably involve a triplex [10] *(ARD) as an intermediate. In acetonitrile, electron transfer in the encounter stage should dominate the quenching process to form the solvent-separated radical ion pair ($A^{\cdot -}\cdots D^{\cdot +}$) [11], the back electron transfer of which must contribute heavily in the photoreaction involving **4** to quench the net reaction. The quantitative effects of the exciplex–excimer on the quantum yields are now being investigated. Since efforts to increase the yields of **6** have not been rewarded by changing the conditions, its mechanism of formation remains obscure.

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