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Solvent Effects on Photoreactions of Dibenzoylmethanatoboron Difluoride (DBMBF₂) with Cyclic Dienes

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Abstract: The pattern of the photoreactions of DBMBF₂ with a cyclic diene is highly dependent on solvent nature, giving mainly the dimers of dienes in polar solvents but cycloadduct in non-polar solvents. The quantum yields of the adduct (Φ_A) correlate smoothly with an empirical polarity constant (E_T^N) in spite of exciplex formations with aromatic solvents.

Photolysis of DBMBF₂ and 1,3-cyclohexadiene (CHD) in acetonitrile caused rapid diene dimerization[1] via a CHD·+ initiated chain process by sensitized electron transfer to give mostly [4+2] *cis-endo*-dimer 3CN, minor *cis-exo*-dimer 3CX and traces of [2+2] dimers 4; 1,3-cyclooctadiene (1,3-COD) gave only [2+2] dimers 5 in low yields.[1] However, cycloadducts 1 and 2 were not formed in detectable amounts from both photoreactions in acetonitrile. We have reported that in benzene, toluene or *p*-xylene the photoreaction changed its product pattern giving good yields of 1 and 2 with much less amounts of dimers.[1] This remarkable inversion of product % has been ascribed to the formation of exciplexes, with these benzenes,[1b,2] that undergo dual pathways to give both types of the products. We wish to show that such dramatic changes are part of the susceptibility of these photoreactions to solvent effects that can be quantitatively correlated to solvent polarity parameters. It demonstrates that a critical choice of solvents can improve the quantum yields of either product type significantly.
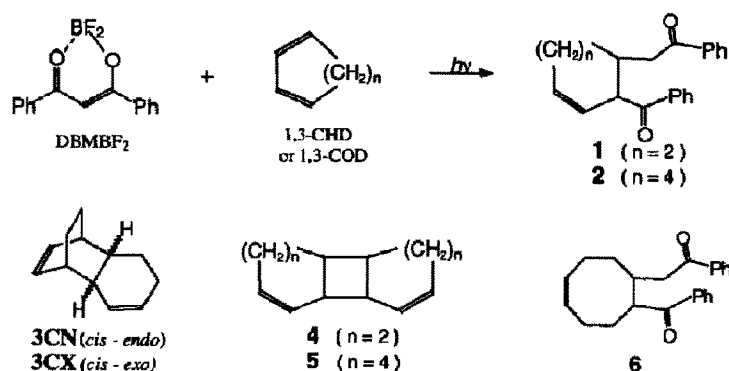
The photoreaction of DBMBF₂ with CHD in various solvents of decreasing polarity (Figure 1), ranging from acetonitrile to benzenes, was carried out in groups to give comparable amounts of products that facilitate the accuracy of analysis. The quantum yields of the total dimers varied from 0.15 to 0.007 mostly
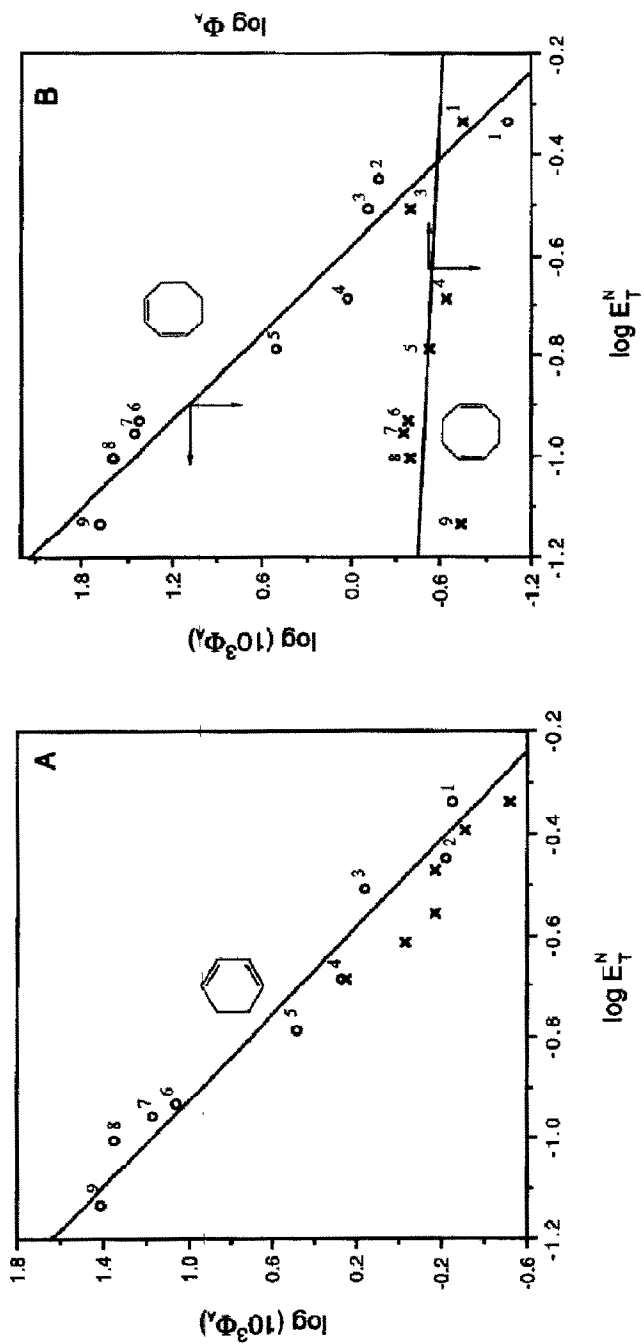
Figure 1. Plots of $\log(10^3\Phi_A) = \alpha \log E_T^N + \log c$ for the Photocycloaddition of DBMBF$_2$ with Cyclic Dienes in CH$_3$CN (1), Acetone (2), CH$_2$Cl$_2$ (3), THF (4), Dioxane (5), Ether (6), Benzene (7), Toluene (8), p-Xylene (9):

(A), Φ_A of **1** in pure solvent (o) and in binary mixture of CH$_3$CN and THF (x);
(B), Φ_A of **2** (o) and **6** (x) in pure solvent.

due to the decrease of 3CN while those of [2+2] dimers relatively remain invariable between 0.004-0.007. As the formation of [4+2] dimers 3, via radical chain process,[3] is sensitive to conditions, these data fluctuate and are not amenable to do correlations. The quantum yield of cycloaddition (Φ_A) correlates with the normalized solvent polarity parameter E_T^N-values[4] according to log $(10^3\Phi_A)$ = log c + αlog (E_T^N) as shown in Figure 1, to give a reasonable correlation of α = -2.3. The quantum yield of 1 in binary mixtures of varying proportions of acetonitrile in THF was also determined under similar conditions, and plotted in Figure 1A using composite E_T^N-values; the slope of α = -2.3 indicated that the response of excited state solutes to the solvent polarity changes is real and attested to the reasonableness of the correlation. In Figure 1B, the solvent effects on adducts 2 and 6, i. e., the photocycloaddition to 1,3- and 1,5-COD,[5] are expressed; in contrast to the invariable quantum yields of the latter formation, the slope of the former is fair sized, α = -3.4. The yield of 2, though insignificant in acetonitrile even under extended irradiation, becomes very high in ether or benzene. It should be also added that if log($10^3\Phi_A$) is plotted against E_T^N values, there appeared to be a break point in the linear correlation at about E_T^N = 0.2; this point is still far from aromatic solvents.

The successful correlations in Figures 1 indicated that the quantum yield of photoaddition is a simple function of solvent polarity parameters, in spite of the fact that more than one intermediacy of singlet excited DBMBF$_2$ and its excimer[6] or aromatic exciplexes[2] could be involved depending on solvent. In non-aromatic solvents, at [DBMBF$_2$] $\geq$ 0.03 M, more than 90 % of the singlet excited state is in the excimer form,[6] through which the primary reactions should occur. This conclusion is also supported by the observation of quantum yield increases for 1 and 2 along the increases in [DBMBF$_2$] = 0.01-0.07 M. We suggest that all these excited intermediates converge on a common precursor which responds to solvent polarity and partitions to adduct (1 or 2) and others; this species is assumed to be the non-fluorescing (undetected) exciplex *(DBMBF$_2$-CHD) through whole range of solvents (see Scheme 1). The exciplex interactions with solvent is most likely

Scheme 1:

A = DBMBF$_2$ R = Benzenes   D = Dienes
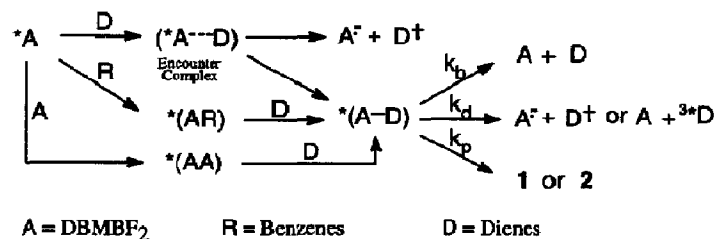
reflected in its partitions measured by the coefficient $k_p/(k_p+k_b+k_d)$, where CHD$^{\cdot+}$ is regulated from the CT contribution to the exciplex. In the reactions of exciplex substitution, it is believed that a triplex may be involved; such a possibility was reported[7] previously.

The efficient formation of [4+2] dimers 3 in polar acetonitrile implies a long range electron transfer to generate CHD$^{\cdot+}$ in the encounter stage;[8] it is known that this leads to dimers 3CN/ 3CX in the ratio of 4 ~ 5

to 1.[3,7] Further approaches of the reactants should collapse to exciplex *(DBMBF$_2$-CHD) as assumed generally.[8] The ratio of *endo/exo* [4+2] dimers also drastically changes from 8 : 1 to 0.2 : 1 with the decrease of either the solvent polarity or the [CHD] in 1.0 ~ 0.01 M. Under these variations, the quantum yield of 3CX parallels that of [2+2] dimers 4. We[1b] and others[9] have shown that these dimers, 4 and also 3CX, are formed from triplet state 1,3-CHD. The triplet CHD should be generated by the mutation of exciplex *[DBMBF$_2$-CHD] (Scheme 1) since singlet excited DBMBF$_2$ is completely scavenged at [CHD] > 0.01 M and does not have the chance to undergo intersystem crossing. We continue to search for other examples of allied solvent effects among the photocycloadditions to other electron rich olefins, and to study the quantitative aspects of the effects.

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6.   Chow, Y. L.; Cheng, X. E.; Johansson, C. I. *J. Photochem. Photobiol. A*: **1991**, *57*, 247. Our group found that the rate constant (k_m) is 2×10^{10} M^{-1}s^{-1} for the formation of DBMBF$_2$ excimer (*AA), and that *AA lifetime (τ_{AA}) is about 15 ns in aerated CH$_3$CN. The ratio of [*AA]/[*A] at steady-state could hence be estimated by [*AA]/[*A] = $k_m\tau_{AA}$[A].

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