Photocycloadditions and Photosensitizations promoted by Electron Transfer: β-Diketonatoboron Difluorides as Electron Acceptors

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The lowest singlet excited state of dibenzoylmethanatoboron difluoride interacts with alkenes by an electron-transfer mechanism to give cycloaddition or alkene dimerization products.

The reaction of β-diketones with BF_3 affords boron difluoride complexes,[1—3] such as acetylacetonatoboron difluoride ($aaBF_2$), benzoylacetonatoboron difluoride ($baBF_2$), and dibenzoylmethanatoboron difluoride ($dmbBF_2$), that possess reduction potentials[2,4] lower than that of the parent β-diketones by *ca.* 0.5 V. Similar BF_2 complexes have been used as electron acceptors in the design of photoconducting materials.[4,5] We report that these BF_2 complexes in their singlet excited state are a new class of electron acceptors in reactions with alkenes.[6] In this paper $dmbBF_2$ is used as a model compound to describe their photocycloadditions and photosensitization.

In contrast to the lack of fluorescence emission of dbm itself, $dmbBF_2$ in dilute solution fluoresces strongly, peaking at 397 and 416 nm in acetonitrile (Φ_f 0.8);[3] it also exhibits a new and broad emission peak at 522 nm, probably from an excimer, in the high concentration range of $[dmbBF_2]$ $>10^{-2}$ M. The fluorescence intensity was quenched by a variety of alkenes with quenching rate constants, k_q, determined from Stern–Volmer plots.† The correlations of log k_q either with the reported ionization potentials (E_i) of the alkenes or with the calculated energy (ΔG°) available in the excited state electron transfer[7—9] are shown in Figure 1. Electron-poor alkenes such as acrylonitrile failed to quench fluorescence of $dbmBF_2$. The dependence of k_q values on ΔG° clearly indicates that the singlet excited state of $dbmBF_2$ interacts with alkenes by a mechanism involving some degree of single electron transfer (SET). The comparison with the theoretically calculated Rhem–Weller curve (Figure 1 upper) shows that the degree of SET participation is relatively small. As energy transfer is inconceivable, the mechanism of this interaction is a current interest in our investigation.

The photolysis of $dbmBF_2$ (5×10^{-2} M) and simple monosubstituted alkenes (5×10^{-2} M) in acetonitrile gave the diketones (**2**) cleanly with quantum yields ϕ = 0.1–0.4; obviously the primary photocycloadduct (**1**) was formed regiospecifically. The photocycloaddition occurred stereospecifically with cyclic alkenes, to give *cis*-diketones which may isomerize to the *trans*-diketones during isolation (Table 1). The diketones were isolated by simple recrystallization and/or chromatography in 65—80% yields based on consumed $dbmBF_2$; they were readily identified from spectroscopic data. In the photocycloaddition to 3,3-dimethylbut-1-ene and cycloheptene, the $k_q\tau$ obtained from the product quantum yields (0.38 and 5.13 respectively) agreed reasonably with that obtained by fluorescence quenching (0.57 and 4.84 respectively). While both dibenzoylmethane and benzoylacetone have been reported to undergo photocycloaddition with substituted styrenes,[10] they did not undergo photocycloaddition with simple alkenes under de Mayo reaction conditions[11] in our experiments. As the photocycloadditions of some β-diketones to alkenes (the de Mayo reaction)[11] are generally sluggish, the present modification is a significant improvement.

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† The lifetime of the lowest singlet excited state of $dbmBF_2$ was estimated from the fluorescence quenching with biacetyl; assuming a diffusion-controlled quenching rate constant, τ_s was calculated to be 2.7 ns.

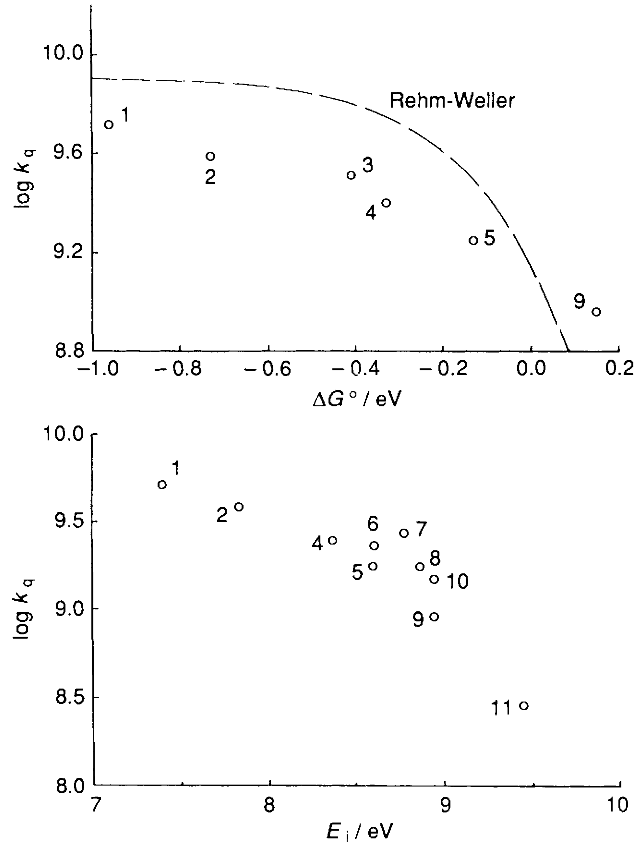
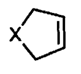
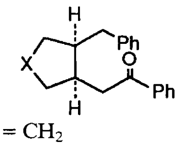
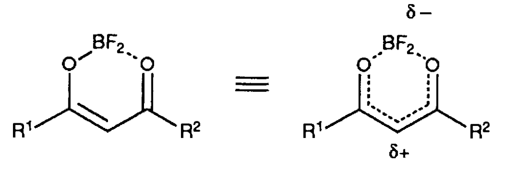


Figure 1. Plots of log k_q against the ionization potentials[7] and the calculated ΔG° ($\approx E^{ox}_{1/2} - E^{red}_{1/2} - E_s$)†[7,8] of the alkenes: 1, quadricyclene; 2, cyclohexadiene; 3, dihydropyran; 4, norbornadiene; 5, ethyl vinyl ether; 6, penta-1,3-diene; 7, octa-1,3-diene; 8, cycloheptene; 9, cyclohexene; 10, norbornene; 11, 3,3-dimethylbut-1-ene. The Rehm–Weller theoretical curve (upper) was computed according to the parameters given in ref. 7(d).

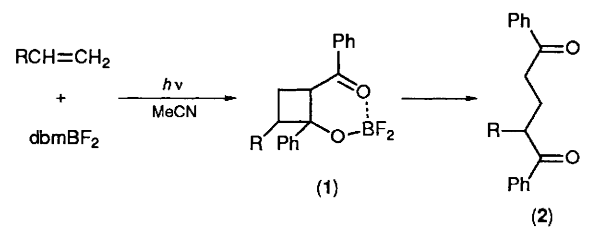
Table 1. Photocycloadditions of $dbmBF_2$ to simple alkenes in acetonitrile.[a]

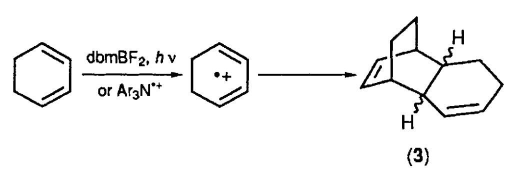
Alkene, $RCH{=}CH_2$	Product, $PhCOCHRCH_2CH_2COPh$	Irradiation time/h	% Yield[b]
Hex-1-ene	R = Bu^n	2.2	78
Hexa-1,5-diene	R = $CH_2{=}CH[CH_2]_2$	3.5	92
t-Butylethylene	R = Bu^t	3.5	69
			
Cyclopentene	X = CH_2	7.5	68[c]
Cyclohexene	X = $[CH_2]_2$	8.0	69
Cycloheptene	X = $[CH_2]_3$	10.0[e]	23
Cyclo-octene	X = $[CH_2]_4$	2.5	68
Cyclo-octa-1,5-diene	X = $-CH_2CH{=}CHCH_2-$	3.0	50
Norbornene		3.5	55[d]

[a] Solutions of $dbmBF_2$ (0.05 M) and the alkene (0.5 M) in acetonitrile were irradiated with 3500 Å Rayonet lamps. [b] The structures were determined from spectroscopic data and elemental analyses. [c] This contains 10% of the *trans*-isomer derived from isomerization during isolation. [d] The major isomer has the *endo,cis* configuration; the minor isomer (10%) is assumed to be *exo,cis*-isomer. [e] Overirradiation.



$aaBF_2$, $R^1 = R^2 = Me$
$baBF_2$, $R^1 = Ph$, $R^2 = Me$
$dbmBF_2$, $R^1 = R^2 = Ph$





A more favourable electron-transfer interaction is indicated in the photoreactions involving electron-rich alkenes. $dbmBF_2$ (and other BF_2 complexes) did photosensitize cyclohexa-1,3-diene to undergo the [4 + 2] cycloaddition [Diels–Alder type product (**3**)],[12–16] and *trans*-anethole to undergo [2 + 2] cycloaddition[17,18] to give cyclobutane derivatives. In both dimerizations, the product patterns were similar to those initiated with a triarylaminium radical or by photosensitization with singlet state 9,10-dicyanoanthracene; chain reactions propagated by cation radicals[12–14] have been demonstrated for these dimerizations previously. Furthermore, the quenching of the $dbmBF_2$ fluorescence intensity by quadricyclene (QC) and norbornadiene (NBD) was accompanied by the rearrangement of QC to NBD but not in the reverse direction. Since the singlet excited state energy of $dbmBF_2$ is far lower than those of QC and NBD,[19] the electron-transfer mechanism proposed by Roth can be invoked to explain the one-way rearrangement[20] in reaction (1) in which the reaction is exothermic ($\Delta H \geq 40$ kJ mol^{-1}).

$$(dbmBF_2)^{\bullet-}\ (QC)^{\bullet+} \underset{\times}{\rightleftarrows} (dmbBF_2)^{\bullet-}\ (NBD)^{\bullet+} \qquad (1)$$

For the SET series involving $dmbBF_2$, the photolysis pattern indicates that the transition from a cation-radical reaction type to a photocycloaddition type occurs at a donor E_i of about 8.6 eV (in the vicinity of ethyl vinyl ether and penta-1,3-diene in Figure 1), although the plot does not show a clear sign of such a change. Among other possible explanations, we propose that, while with 'electron-poor' alkenes partial SET occurs from exciplexes to yield contact ion pairs (*ca.* 3.5 Å apart), with 'electron-rich' alkenes it occurs at distances to yield solvent-separated radical ion pairs (*e.g.* >7.5 Å centre-to-centre distance).[21] In the former the proximity of radical ions facilitates the cycloaddition, but in the latter cation radicals rapidly undergo their own reactions.

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