so as not to confuse the manganate(V) ester intermediate with soluble (colloidal) manganese dioxide since the UV–visible spectrum of soluble (colloidal) manganese dioxide appears similar to those of the manganate(V) intermediate 1 if compared at $\lambda > 300$ nm. The manganate(V) intermediate can be distinguished from soluble (colloidal) manganese dioxide by the following criteria: (1) spectra of the manganate(V) esters have a clear absorption maximum at ca. 280 nm[6-8] while soluble (colloidal) manganese dioxide shows no maximum in its spectrum;[1] (2) plots of log A vs log λ ($\lambda > 300$ nm) for colloidal manganese dioxide give a straight line with a slope near to -4 as expected from Raileigh's Law ($A = C/\lambda^4$)[13] for colloidal solutions,[14] while the plots for the manganate(V) ester intermediates give the line with a slope steeper than -5;[10,11] (3) soluble (colloidal) manganese dioxide often shows an increase in absorbance at all wavelength on standing due to flocculation, while the manganate(V) intermediate shows decrease in absorbance due to the decomposition reaction.[1,12]

From these criteria, it appears that the manganese species observed during the reaction of permanganate ion with alkynes in dichloromethane[15] or with trimethylamine[16] in aqueous phosphate buffers are mainly colloidal manganese dioxide. In those cases, the decomposition rates of initially formed manganate(V) intermediates may be faster than those of the formation because of the instability of the intermediate itself or the high reducing power of the reductant used in excess. However, the manganese species observed during the permanganate oxidation of alcohols in dichloromethane with a quaternary ammonium salt appears to be also a manganate(V) compound.[17]

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Photocatalyzed and Electrocatalyzed Reduction of *vic*-Dibromides and Activated Ketones Using Ruthenium(I) Tris(bipyridine) as Electron-Transfer Mediator

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Effective photosensitized reduction of *vic*-dibromo and keto compounds occurs in acetonitrile solutions that include ruthenium(II) tris(bipyridine) (Ru(bpy)$_3^{2+}$) as photosensitizer and triethylamine (TEA) as electron donor. (*R*,*S*)-1,1′-(1,2-Dibromo-1,2-ethanediyl)bis(benzene) (**1**) and (*R*,*R*:*S*,*S*)-1,1′-(1,2-dibromo-1,2-ethanediyl)bis(benzene) (**2**) are debrominated to a mixture of (*E*)- (**5**) and (*Z*)-1,1′-(1,2-ethenediyl)bis(benzene) (**6**); $\phi = 0.34$ for **1** and $\phi = 0.24$ for **2**. Ethyl α,β-dibromobenzenepropionate (**3**) and (α,β-dibromo-α,β-dihydro-1-propenyl)benzene (**4**) are debrominated to (*E*)-ethyl α,β-didehydrobenzenepropionic acid (**7**), $\phi = 1.87$, and (*E*)-1-propenylbenzene (**8**), $\phi = 0.08$. The mixture of **5** and **6** formed upon debromination of **1** and **2** undergoes isomerization in the reaction medium to **6** through an energy-transfer mechanism. Debromination of the substrates occurs through the photosensitized formation of Ru(bpy)$_3^+$ ($E° = -1.33$ V vs SCE), which acts as an electron-transfer mediator in the process. The rates of the debromination processes are controlled by the primary reduction of the dibromo compounds by Ru(bpy)$_3^+$, except for **3** as substrate, where a radical chain mechanism is suggested. Cyclic voltammetry measurements reveal that Ru(bpy)$_3^+$ acts as catalyst in the debromination processes. Similarly, activated ketones, i.e., diphenylethanedione (**9**) and ethyl α-oxobenzeneacetate (**10**) are reduced by photogenerated Ru(bpy)$_3^+$ to 2-hydroxy-1,2-diphenylethanone (**11**), $\phi = 0.025$, and ethyl α-hydroxybenzeneacetate (**12**), $\phi = 0.049$.

Organic transformations catalyzed by photochemically and electrochemically induced electron-transfer reactions are a subject of extensive recent research efforts.[1-3] Photosensitized electron-transfer reactions using sacrificial electron donors were mainly examined in aqueous media.[4,5] The resulting photoproducts were applied in H_2 evolution,[6,7] CO_2 reduction,[8,9] and hydrogenation of gaseous unsaturated organic substrates.[10] Application of photosensitized electron-transfer reactions in organic transformations is limited due to the poor solubility properties of the organic substrates in water. Several approaches that

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apply micelles,[11] microemulsions,[12] or water–oil two-phase systems[13] have been used to circumvent these difficulties. Micelles and microemulsions provide microheterogeneous hydrophobic environments for the solubilization of the organic reactants. With water–oil two-phase systems, phase transfer of the reduced photoproduct has been used to mediate the reduction of organic substrates. Alternatively, heterogeneous catalysts have been applied to effect the photoinduced hydrogenation of unsaturated organic compounds as suspensions in aqueous media.[14] In this system "in situ" generated hydrogen atoms formed on the heterogeneous catalyst mediate the subsequent hydrogenation of the water-immiscible organic substrate.

The photosensitized reduction of *N*,*N'*-dialkyl-4,4'-bipyridinium salts, V^{2+}, using various sacrificial electron donors has been extensively studied.[15,16] The resulting reduced photoproduct, *N*,*N'*-dialkyl-4,4'-bipyridinium radical cation (viologen radical), $V^{\bullet+}$, has been applied in the reduction of nitro-substituted compounds,[17] debromination of 1,2-dibromides,[13,18] and reduction of activated ketones.[19] Nevertheless, the reduction potentials of bipyridinium radical cations, −0.4 to −0.5 V vs SHE, limit their broad synthetic applicability, and more powerful electron-transfer mediators are desirable. The irreversible reduction of ruthenium(II) tris(bipyridine) ($Ru(bpy)_3^{2+}$) by triethylamine (TEA) in acetonitrile has been reported.[20] The resulting photoproduct, ruthenium(I) tris(bipyridine) ($Ru(bpy)_3^{+}$), is a powerful reductant, $E° = -1.33$ V vs SCE.[21] Thus, its application in acetonitrile as electron-transfer mediator for the reduction of organic substrates seems feasible. In this report we describe the debromination of a series of 1,2-dibromides and the reduction of activated ketones, i.e., benzil and ethyl benzoylformate, by photogenerated $Ru(bpy)_3^{+}$ and discuss various mechanistic aspects involved with these transformations.

Experimental Section

Absorption spectra were recorded with a Uvikon 860 (Kontron) spectrophotometer. Liquid chromatography analyses were performed with a Merck Hitachi 655-A-11 HPLC apparatus equipped with a 655-A variable-wavelength UV detector. For all analyses $\lambda = 254$ nm was used. Gas chromatography analysis was performed with a Tracor 540 gas chromatograph equipped with an FID detector. Cyclic voltammetry experiments were performed with a BAS CV-27 instrument equipped with a BAS *x*–*y* recorder. A Pt button was used as working electrode, Ag/AgCl as reference electrode, and Pt wire as an auxiliary electrode. Samples were dissolved in acetonitrile containing tetrabutylammonium tetrafluoroborate (0.01 M) as electrolyte and purged with oxygen-free argon. Steady-state illumination was performed at room temperature in a glass cuvette (4 mL) equipped with a small magnetic stirrer and a serum stopper with a 150-W xenon arc lamp. While illuminating the 1,2-dibromides, light was filtered through a 400-nm-cutoff filter (Schott GG-400). Incident photon flux was determined by Reinecke salt actinometry[22] to be 3×10^{-3} einstein$\cdot^{-1}\cdot$min^{-1}. In the activated ketone reduction experiments, light was filtered through a 455-nm-cutoff filter, and the incident photon flux was 1.6×10^{-3} einstein$\cdot^{-1}\cdot$min^{-1}.

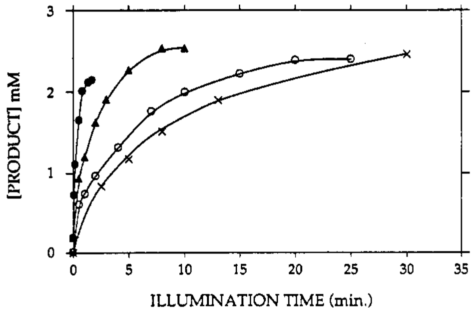

Figure 1. Rates of product formation in the photosensitized debrominations of (▲) *meso*-dibromodihydrostilbene (1), (○) *d*,*l*-dibromodihydrostilbene (2), (●) ethyl dibromocinnamate (3), and (×) dibromodihydromethylstyrene (4). In all experiments $[Ru(bpy)_3^{2+}] = 7 \times 10^{-5}$ M, $[TEA] = 2.5 \times 10^{-3}$ M, and $[\text{substrate}] = 2.5 \times 10^{-3}$ M.

Laser flash photolysis experiments were performed on a DL 200 (Molectron) dye laser pumped by a UV-14 nitrogen laser (Molectron). Unless otherwise stated, chemicals were obtained from Aldrich or Sigma. *meso*-Dibromodihydrostilbene[23] and *d*,*l*-dibromodihydrostilbene[24] were prepared according to published procedures. Ethyl dibromocinnamate and dibromodihydromethylstyrene were prepared by bromination of the respective alkenes in CCl_4.

Photoreduction of Dibromides. All systems were composed of an acetonitrile solution (4 mL) that included $Ru(bpy)_3Cl_2$ (7×10^{-5} Me) as photosensitizer, TEA (2.5×10^{-3} M) as sacrificial electron donor, and one of the following substrates (2.5×10^{-3} M): *meso*-dibromodihydrostilbene, *d*,*l*-dibromodihydrostilbene, ethyldibromocinnamate, or dibromodihydromethylstyrene. The samples, placed in a glass cuvette, were deaerated by evacuation followed by oxygen-free argon flushing. The deaerated system was illuminated, and the rate of product formation was followed by sampling the reaction solution, 20 μL, by liquid chromatography, using a Lichrospher 100 RP-18, 5-μm (25 cm) column. The following eluents were used for the various substrates: for *meso*-dibromodihydrostilbene and *d*,*l*-dibromodihydrostilbene, 85% CH_3OH–15% H_2O; for ethyl dibromocinnamate, 60% CH_3CN–40% H_2O; for dibromodihydromethylstyrene, 53% CH_3CN–47% H_2O. Flow rate was 1 mL·min^{-1} in all cases. In all experiments concentration of the dibromo substrates is high enough to maintain a plateau value for the observed quantum yield.

Photoreduction of Activated Ketones. The systems were composed of an acetonitrile solution (4 mL) that included $Ru(bpy)_3Cl_2$ (7×10^{-5} M), TEA (2.5×10^{-3} M), and 2.5×10^{-3} M of the substrates: benzil or ethyl benzoylformate. The samples were treated and illuminated as described for the dibromides. The rate of benzoin formation was followed by liquid chromatography using the mixture 60% CH_3CN–40% H_2O as eluent. The rate of ethyl mandelate formation was followed by gas chromatography using a Carbowax 20M (20%) on Chromosorb W (2 m) column. Oven temperature was 140 °C, and N_2 flow rate was 30 mL·min^{-1}. The concentrations of the activated ketones in these systems are

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Table I. Quantum Efficiencies and Kinetic Parameters in the Debromination Reactions

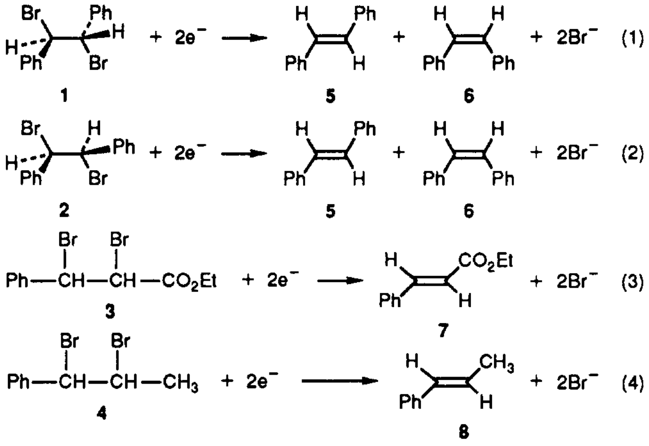
substrate	ϕ_{max}[a]	init rate,[b] M·min^{-1}	k_{obs},[c] s^{-1}
1[d]	0.34	1.03 × 10^{-3}	9.33 × 10^{4}
2[d]	0.24	0.73 × 10^{-3}	3.94 × 10^{4}
3	1.87	5.61 × 10^{-3}	5.33 × 10^{4}
4	0.08	0.23 × 10^{-3}	7.80 × 10^{4}

[a] Initial quantum yield. [b] Determined by steady-state illumination. [c] Determined by laser flash photolysis. [d] Quantum efficiencies for formation of the mixture of cis + trans isomers.

high enough to establish maximum values for the quantum yield.

Results and Discussion

Photoinduced Debromination of 1,2-Dibromides. The photosensitized debromination of (*R*,*S*)-1,1′-(1,2-dibromo-1,2-ethanediyl)bis(benzene) (*meso*-dibromodihydrostilbene) (1), (*R*,*R*:*S*,*S*)-1,1′-(1,2-dibromo-1,2-ethanediyl)bis(benzene) (*d*,*l*-dibromodihydrostilbene) (2), ethyl α,β-dibromobenzenepropionate (ethyl dibromocinnamate), (3), and (α,β-dibromo-α,β-dihydro-1-propenyl)benzene (dibromodihydromethylstyrene) (4) was examined in acetonitrile with Ru(bpy)$_3^{2+}$ as photosensitizer and triethylamine (TEA) as electron donor. Illumination of an acetonitrile solution (λ > 400 nm) that includes Ru(bpy)$_3^{2+}$ and TEA in the presence of one of the dibromides 1–4 results in debromination of the organic substrate. Debromination of 1 and 2 leads to (*E*)-1,1′-(1,2-ethenediyl)bis(benzene) (*trans*-stilbene) (5) and (*Z*)-1,1′-(1,2-ethenediyl)bis(benzene) (*cis*-stilbene) (6) (eqs 1 and 2). Debromination of 3 and 4 leads to (*E*)-ethyl α,β-didehydrobenzenepropionate (*trans*-ethyl cinnamate) (7) (eq 3) and (*E*)-1-propenylbenzene (*trans*-methylstyrene) (8) (eq 4), respectively, and no cis isomer is detected for these substrates. Figure 1 shows the rate of debromination of the different substrates upon illumination. For all of the systems debromination proceeds to 80–100% conversion efficiencies. Control experiments reveal that all components are required to effect the debromination processes, and exclusion of Ru(bpy)$_3^{2+}$, TEA, or the light source prohibits the reactions. Table I summarizes the quantum yields for the debromination of the various substrates, the initial reaction rates, and the time required to accomplish the maximum conversion efficiency for the different substrates. It is evident that the photosensitized debromination reactions of the different substrates proceed effectively: for 3 the maximum rate for debromination is observed and the quantum efficiency exceeds the value of 1 (ϕ = 1.87), implying that a radical chain mechanism is operative in this debromination process. It is also concluded that debromination of *meso*-dibromodihydrostilbene (1) is faster than that of the *d*,*l* isomer (2). The slowest reaction occurs with 4 as substrate.



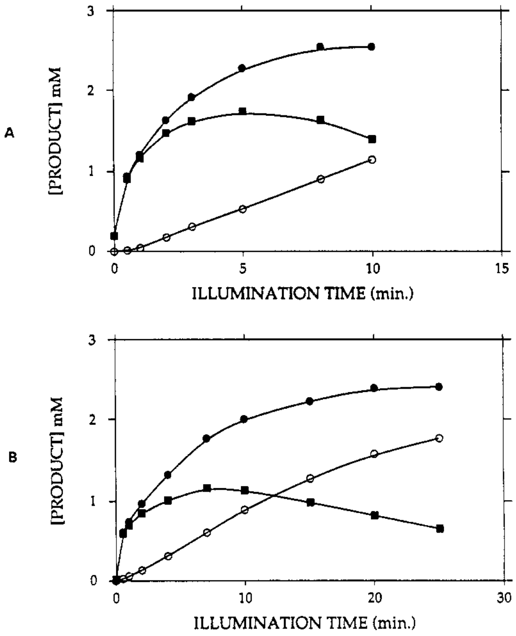


Figure 2. Rates of product formation in the photosensitized reduction of (A) *meso*-dibromodihydrostilbene (1) (B) *d*,*l*-dibromodihydrostilbene (2). In both experiments [Ru(bpy)$_3^{2+}$] = 7 × 10^{-5} M, [TEA] = 2.5 × 10^{-3} M, and [substrate] = 2.5 × 10^{-3} M. Products: (■) *trans*-stilbene (5); (○) *cis*-stilbene (6); (●) *trans*- + *cis*-stilbene.

The formation of the mixture of the isomers *trans*- and *cis*-stilbene upon debromination of 1 and 2 has been further explored. Figure 2 shows the concentration profiles of the trans and cis isomers as a function of illumination time of the systems that include 1 and 2 as substrates. It is evident that the [trans]/[cis] ratio changes even after debromination is completed. Furthermore, for both dibromo compounds 1 and 2, *trans*-stilbene (5) is the major product at early stages of illumination, while *cis*-stilbene (6) is the major product after long illumination times. The systems reach a steady-state equilibrium that corresponds to [cis]/[trans] = 15.7. The concentration profiles of *trans*-stilbene in the two systems as a function of illumination time show that the trans isomer reaches a maximum value and as illumination proceeds, its concentration declines at the expense of the cis isomer formation. These results suggest that determination of *meso*- (1) or *d*,*l*-dibromodihydrostilbene (2) leads to *trans*-stilbene (5). This primary product undergoes, however, a secondary photoinduced isomerization to *cis*-stilbene (6) in the reaction medium. Indeed, illumination of *trans*-stilbene (5) in acetonitrile in the presence of Ru(bpy)$_3^{2+}$ without any electron donor results in isomerization to *cis*-stilbene (6), and a similar steady-state [trans]/[cis] equilibrium is established as in the debromination system. The photosensitized isomerization of *trans*-stilbene by Ru(bpy)$_3^{2+}$ has been previously reported[25,26] to occur through an energy-transfer quenching mechanism of excited Ru(bpy)$_3^{2+}$. Thus, we conclude that debromination of 1 and 2 yields *trans*-stilbene as primary product and that the cis isomer

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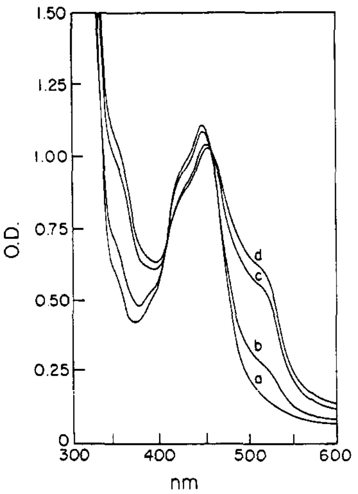
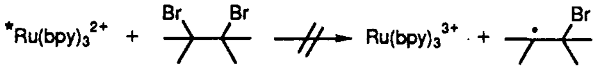


Figure 3. Absorption spectra of $Ru(bpy)_3^+$ obtained at time intervals of illumination of 7×10^{-5} M $Ru(bpy)_3^{2+}$ and 2.5×10^{-3} M TEA in CH_3CN under argon.

originates from a secondary photochemically induced energy-transfer isomerization process.

Mechanistic Aspects for the Debromination Reactions. *vic*-Dibromides can act as electron-transfer quenchers of excited photosensitizers such as zinc(II) *meso*-tetraphenylporphyrins.[27] Fluorescence quenching studies of $Ru(bpy)_3^{2+}$ reveal that none of the substrates 1–4 acts as a quencher of the excited $Ru(bpy)_3^{2+}$. Thus, debromination of the *vic*-dibromides through oxidative quenching of $Ru(bpy)_3^{2+}$ (eq 5) can be eliminated. In turn,



(5)

illumination of an acetonitrile solution of $Ru(bpy)_3^{2+}$ that includes TEA results in the reductive irreversible quenching of the photosensitizer and formation of $Ru(bpy)_3^+$ (eq 6). Figure 3 shows the formation of $Ru(bpy)_3^+$

$$Ru(bpy)_3^{2+} + TEA \xrightarrow{h\nu} Ru(bpy)_3^+ + TEA^{\bullet +} \quad (6)$$

upon illumination of the photosensitizer in the presence of TEA. Addition of any of the substrates 1–4 to a solution that includes photogenerated $Ru(bpy)_3^+$ results in the oxidation of $Ru(bpy)_3^+$ to $Ru(bpy)_3^{2+}$. Also, steady-state illumination of the photosensitizer $Ru(bpy)_3^{2+}$ with TEA in the presence of any of the dibromides 1–4 does not yield the absorption spectrum of $Ru(bpy)_3^+$, implying that the $Ru(bpy)_3^{2+}$ is regenerated under continuous illumination. These results clearly demonstrate that the primary step in the debromination reactions involves the reduction of the dibromides by $Ru(bpy)_3^+$ (eq 7). The subsequent

$$Ru(bpy)_3^+ + R_1CHBrCHBrR_2 \xrightarrow{k_{obs}} Ru(bpy)_3^{2+} + R_1\dot{C}HCHBrR_2 + Br^- \quad (7)$$

$$Ru(bpy)_3^+ + R_1\dot{C}HCHBrR_2 \rightarrow Ru(bpy)_3^{2+} + R_1CH{=}CHR_2 + Br^- \quad (8)$$

$$(CH_3CH_2)_2N^{\bullet +}CH_2CH_3 + R_1\dot{C}HCHBrR_2 \rightarrow (CH_3CH_2)_2N^+{=}CHCH_3Br^- + R_1CH{=}CHR_2 + H^+ \quad (9)$$

reduction of the radical that yields the debrominated olefin product can proceed through a second electron transfer from $Ru(bpy)_3^+$ (eq 8) or, alternatively, by the reduction of the radical by $TEA^{\bullet +}$ (eq 9) (formed in the primary quenching process (eq 6)). The latter oxidized photoproduct is known to be a powerful reductant.[28]

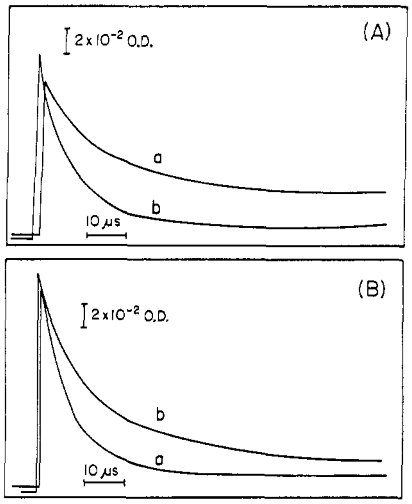


Figure 4. Transient decay of $Ru(bpy)_3^+$ followed at 510 nm (λ_{exc} = 450 nm). In all experiments $[Ru(bpy)_3^{2+}] = 7 \times 10^{-5}$ M and $[TEA] = 2.5 \times 10^{-3}$ M in CH_3CN. (A) (a) no substrate added; (b) in the presence of 2.5×10^{-3} M dibromodihydromethylstyrene (4). (B) (a) in the presence of 2.5×10^{-3} M *meso*-dibromodihydrostilbene (1), (b) in the presence of 2.5×10^{-3} M *d,l*-dibromodihydrostilbene (2).

Further evidence that $Ru(bpy)_3^+$ acts as the reductant of the dibromides is obtained from laser flash photolysis experiments and complementary cyclic voltammetry measurements. These techniques allow us to further characterize the kinetic properties of the transformations and to account for the different rates in the debromination reactions under steady-state illumination. Laser flashing of an acetonitrile solution that includes $Ru(bpy)_3^{2+}$ and TEA (λ = 450 nm) results in the trace of $Ru(bpy)_3^+$ (λ = 510 nm) due to electron-transfer quenching (eq 3). When the system is flashed in the presence of one of the dibromides 1–4, rapid decay of the photogenerated $Ru(bpy)_3^+$ is observed. For example, Figure 4A shows the decay trace of $Ru(bpy)_3^+$ in the presence of (α,β-dibromo-α,β-dihydro-1-propenyl)benzene, (dibromodihydromethylstyrene) (4). From the decay curve, the observed pseudo-first-order rate constant (k_{obs}) for the reduction of the dibromides can be calculated. Table I summarizes the observed rate constants for the reduction of the different dibromides by $Ru(bpy)_3^+$ (eq 7). Interestingly, the reduction of *d,l*-dibromodihydrostilbene (**2**) is slower than that of the meso isomer (1) (see also Figure 4B). We also see that the rates of debromination of 1, 2, and 4 under steady-state illumination coincide with the time resolved observed rate constants for the primary reduction of the dibromides by $Ru(bpy)_3^+$. That is, *meso*-dibromodihydrostilbene (1) is debrominated faster than the *d,l* isomer (2), and the latter substrate undergoes faster debromination than dibromodihydromethylstyrene (4). The same tendency is maintained in the primary reduction rate constants of these dibromides by $Ru(bpy)_3^+$ in the laser flash experiments. Only ethyl α,β-dibromobenzenepropionate (ethyl dibromocinnamate) (3) shows an inconsistency between the observed rate constant for the primary reduction step by $Ru(bpy)_3^+$ and the rate of the process under steady-state illumination. While this substrate undergoes the fastest debromination reaction under steady-state illumination, the rate constant for the

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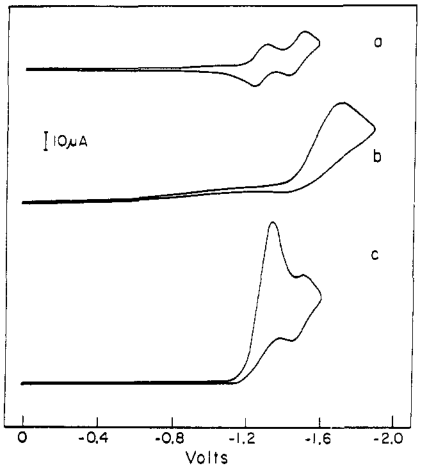

Figure 5. Cyclic voltammograms of (a) $Ru(bpy)_3^{2+}$ (1×10^{-3} M), (b) dibromodihydromethylstyrene (**4**) (2.5×10^{-3} M), and (c) $Ru(bpy)_3^{2+}$ (1×10^{-3} M) and dibromodihydromethylstyrene (**4**) (2.5×10^{-3} M). All measurements were performed in CH_3CN under argon with 0.01 M tetrabutylammonium tetrafluoroborate as electrolyte, Pt wire as working electrode, and Ag/AgCl as reference electrode. Sweep rate = 0.5 V/s.

primary reduction of this substrate by $Ru(bpy)_3^+$ is slower than that for **2**. To account for this discrepancy one should recall that **3** is the only substrate in the series that undergoes the debromination process with a quantum yield of $\phi = 1.87$. This value for the quantum yield suggests that a chain mechanism is operative in the debromination of **3**. Previous studies on the direct photosensitized reduction of 1,2-dibromides by zinc porphyrin have reported[27] high quantum yields ($\phi \gg 1$), and a radical chain mechanism has been suggested. Thus, for the debromination of **3** by $Ru(bpy)_3^+$, a modified chain mechanism is suggested. The primary step involves the reduction of **3** by $Ru(bpy)_3^+$ (eq 10). The resulting radical undergoes elimination that yields a bromine radical (eq 11) that initiates a radical chain process by abstraction of a proton from TEA (eqs 12 and 13). Thus, we conclude that the debromination

$$PhCHBrCHBrCO_2Et + Ru(bpy)_3^+ \rightarrow Ph\dot{C}HCHBrCO_2Et + Br^- + Ru(bpy)_3^{2+} \quad (10)$$

$$Ph\dot{C}HCHBrCO_2Et \rightarrow PhCH{=}CHCO_2Et + Br^\bullet \quad (11)$$

$$Br^\bullet + N(CH_2CH_3)_3 \rightarrow HBr + (CH_3CH_2)_2N\dot{C}HCH_3 \quad (12)$$

$$(CH_3CH_2)_2N\dot{C}HCH_3 + PhCHBrCHBrCO_2Et \rightarrow (CH_3CH_2)_2N^+{=}CHCH_3 + Br^- + Ph\dot{C}HCHBrCO_2Et + H^+ \quad (13)$$

of **1**, **2**, and **4** is controlled by the primary reduction step of the dibromide by $Ru(bpy)_3^+$. In turn, the rate of debromination of **3** under steady-state illumination is controlled by a radical chain mechanism initiated by the relatively slow reduction process of **3** by $Ru(bpy)_3^+$.

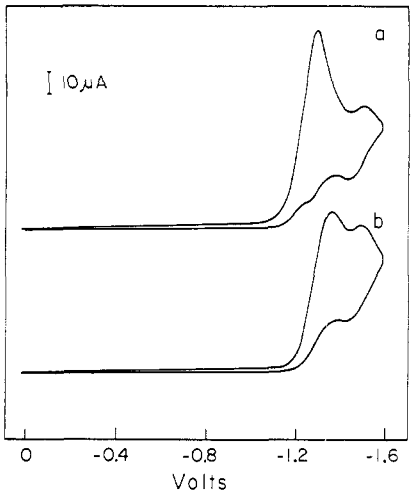

Figure 6. Cyclic voltammograms of (a) $Ru(bpy)_3^{2+}$ (1×10^{-3} M) and *meso*-dibromodihydrostilbene (**1**) (2.5×10^{-3} M) and (b) $Ru(bpy)_3^{2+}$ (1×10^{-3} M) and *d,l*-dibromodihydrostilbene (**2**) (2.5×10^{-3} M). Both experiments were performed in CH_3CN under argon with tetrabutylammonium tetrafluoroborate as electrolyte, Pt wire as working electrode, and Ag/AgCl as reference electrode. Sweep rate = 0.5 V/s.

Further insight into the participation of $Ru(bpy)_3^+$ in the reduction of the *vic*-dibromides is obtained from cyclic voltammetric measurements. Figure 5a shows the cyclic voltammogram of $Ru(bpy)_3^{2+}$ in acetonitrile in the range 0 to −1.6 V vs Ag/AgCl. The cyclic voltammogram is composed of two reversible reduction waves at $E_{pc} = -1.32$ V and $E_{pc} = -1.52$ V that correspond to electrochemical redox reactions outlined in eqs 14 and 15, respectively. Figure 5b shows the reduction wave of (α,β-dibromo-α,β-dihydro-1-propenyl)benzene (dibromodihydromethylstyrene) (**4**) in acetonitrile. It is evident that the electrochemical reduction of **4** is an irreversible process that occurs at $E_{pc} = -1.71$ V, a value that is far more negative than the reduction potential of $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^+$. Figure 5c shows the cyclic voltammogram of $Ru(bpy)_3^{2+}$ in the presence of **4**. We see that a strong cathodic current is observed at the potential where the first reduction of $Ru(bpy)_3^{2+}$ occurs. Similarly, the reversibility of the first reduction wave is depleted. These results demonstrate that electrogenerated $Ru(bpy)_3^+$ reduces **4** (eq 7), and this results in the catalytic cathodic current wave for the reduction potential of $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^+$. Also, the reversibility of the wave is depleted since electrogenerated $Ru(bpy)_3^+$ reacts with **4** and is not available for reoxidation. Thus, we conclude that **4** exhibits a substantial overpotential toward direct electroreduction, but electrogenerated $Ru(bpy)_3^+$ acts as an electron-transfer catalyst for the reduction of **4**. Similar results are obtained for the other dibromides. Of particular interest is the comparison of the catalytic cathodic waves observed with *meso*- (**1**) and *d,l*-dibromodihydrostilbene (**2**) (Figure 6). We see that the catalytic current of $Ru(bpy)_3^+$ using *meso*-dibromodihydrostilbene (**1**) is remarkably higher than that for *d,l*-dibromodihydrostilbene (**2**). These results imply that $Ru(bpy)_3^{2+}$ is more effectively regenerated through oxidation of $Ru(bpy)_3^+$ by **1** as compared to **2** (eq 7). Thus, the cyclic voltammetry experiments reconfirm that reduction of *meso*-dibromodihydrostilbene (**1**) by $Ru(bpy)_3^+$ is faster than that of the *d,l* isomer (**2**) and are in agreement with the laser flash photolysis studies and the steady-state illumination experiments.

$$Ru(bpy)_3^{2+} + e^- \rightleftharpoons Ru(bpy)_3^+ \quad (14)$$

$$Ru(bpy)_3^+ + e^- \rightleftharpoons Ru(bpy)_3^0 \quad (15)$$

A further aspect to consider involves the steric course of the debromination of *meso*- and *d,l*-dibromodihydrostilbenes. Numerous studies involving electrochemical means or dark chemical reductions have discussed the stereoelectronic factors that control the resulting configuration of the olefin product formed upon debromination.[29,30] While the meso isomer (**1**) yields only *trans*-stilbene (**5**), debromination of *d,l*-dibromodihydro-

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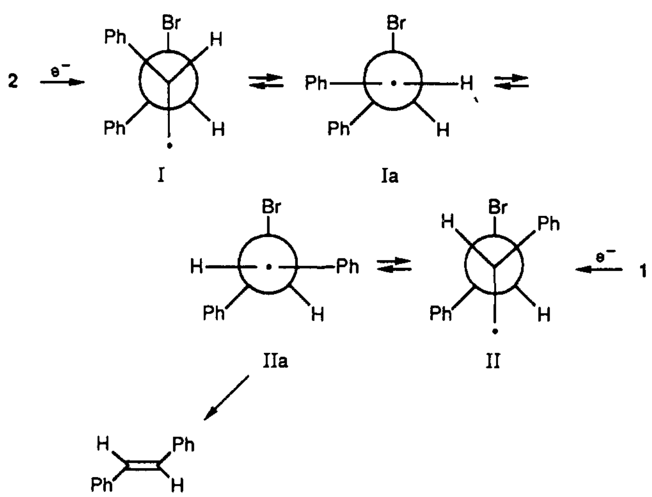
Scheme I



stilbene (2) yields *cis*-stilbene (6), *trans*-stilbene (5), or mixtures of the two products, depending on the experimental conditions.[31,32] When the process proceeds through a carbanionic intermediate formed upon a two-electron reduction of the dibromide, antiperiplanar elimination of the anion derived from 2 results in *cis*-stilbene. Reduction of the dibromide through sequential one-electron processes results in the stable benzyl radical (I, Scheme I). Internal rotation of the radical before it encounters another molecule of reductant equilibrates conformation I with the more stable anti conformation II. This conformation is equivalent to that formed upon one-electron reduction of *meso*-dibromodihydrostilbene (1). Our laser flash studies clearly indicate that debromination of the dibromides proceeds through a primary one-electron-transfer step (eq 5). Thus the configuration of the resulting olefins formed upon debromination of *meso*- and *d,l*-dibromodihydrostilbenes is expected to be *trans*-stilbene as observed experimentally.

Photoreduction of Activated Ketones. Photoreduction of ketones through excitation of the carbonyl function has been the subject of numerous reports.[33,34] The photosensitized reduction of ketones by electron transfer is however scarce.[35] In the present study the photoinduced reduction of activated ketones, i.e., diphenylethanedione (benzil) (9) and ethyl α-oxobenzeneacetate (ethyl benzoylformate) (10) through "in situ" photogeneration of $\mathrm{Ru(bpy)_3^+}$ has been examined.

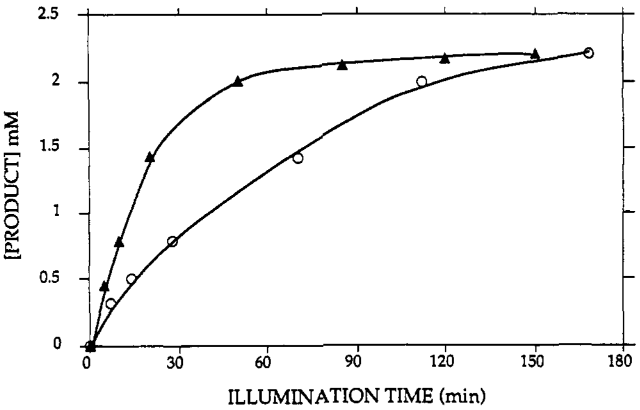


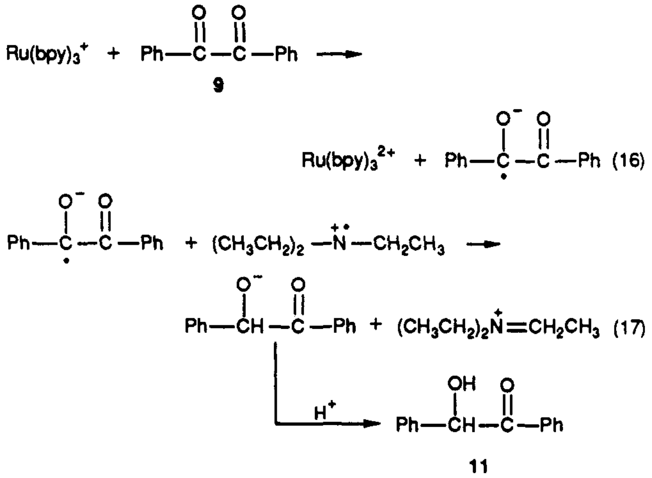
Figure 7. Rates of product formation in the photosensitized reduction of (○) benzil (10) to benzoin (11) and (▲) ethyl benzoylformate (12) to ethyl mandelate (13). In both experiments $[\mathrm{Ru(bpy)_3^{2+}}] = 7 \times 10^{-5}$ M, [TEA] = 2.5×10^{-3} M, and [substrate] = 2.5×10^{-3} M.

Table II. Quantum Efficiencies and Kinetic Parameters Involved in the Reduction of Ketones

substrate	ϕ_{max}[a]	init rate,[b] M·min^{-1}	illum time for max conv, min	TN[c](Ru(bpy)$_3^{2+}$
9	0.025	3.6×10^{-5}	170	35.5
10	0.049	7.9×10^{-5}	150	32.2

[a] Initial quantum yield. [b] Determined by steady-state illumination. [c] Turnover number of $\mathrm{Ru(bpy)_3^{2+}}$: defined as (moles of product)/(moles of $\mathrm{Ru(bpy)_3^{2+}}$).

The electrochemistry of benzil has been extensively explored.[36,37] In an acetonitrile solution benzil undergoes two successive, almost indistinguishable, one-electron-reduction processes $E_{1/2}(1) = -1.169$ V vs SCE and $E_{1/2}(2) = -1.251$ V. Thus, photogenerated $\mathrm{Ru(bpy)_3^+}$, $E° = -1.33$ V vs SCE, is thermodynamically capable of reducing benzil. Indeed, illumination of an acetonitrile solution (λ > 455 nm) that includes $\mathrm{Ru(bpy)_3^{2+}}$ as photosensitizer, triethylamine (TEA) as electron donor, and proton source in the presence of benzil results in the formation of 2-hydroxy-1,2-diphenylethanone (benzoin) (11) (eqs 16 and 17). The rate of formation of 11 upon illumination is



$$\mathrm{Ru(bpy)_3^+} + \underset{\mathbf{9}}{\mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}Ph}} \longrightarrow \mathrm{Ru(bpy)_3^{2+}} + \mathrm{Ph{-}\underset{\bullet}{\overset{\overset{O^-}{|}}{C}}{-}\overset{\overset{O}{\|}}{C}{-}Ph} \quad (16)$$

$$\mathrm{Ph{-}\underset{\bullet}{\overset{\overset{O^-}{|}}{C}}{-}\overset{\overset{O}{\|}}{C}{-}Ph} + \mathrm{(CH_3CH_2)_2{-}\overset{+\bullet}{N}{-}CH_2CH_3} \longrightarrow \mathrm{Ph{-}\overset{\overset{O^-}{|}}{CH}{-}\overset{\overset{O}{\|}}{C}{-}Ph} + \mathrm{(CH_3CH_2)_2\overset{+}{N}{=}CH_2CH_3} \quad (17)$$

$$\xrightarrow{H^+} \underset{\mathbf{11}}{\mathrm{Ph{-}\overset{\overset{OH}{|}}{CH}{-}\overset{\overset{O}{\|}}{C}{-}Ph}}$$

displayed in Figure 7. The initial quantum yield for the formation of 11 is $\phi = 0.025$. Control experiments reveal that all of the components are essential to effect the reduction of benzil. Exclusion of either TEA, $\mathrm{Ru(bpy)_3^{2+}}$, or the light source prohibits the reduction of 9. Also, the addition of benzil to a solution that includes photogenerated $\mathrm{Ru(bpy)_3^+}$ regenerates $\mathrm{Ru(bpy)_3^{2+}}$ (Figure 3), implying that 9 is reduced by $\mathrm{Ru(bpy)_3^+}$. The electrochemical characteristics of benzil as compared to those of $\mathrm{Ru(bpy)_3^+}$ together with the complementary spectroscopic experiments allow us to formulate the sequential reduction route of benzil to 11 (eqs 16 and 17). In the primary step photogenerated $\mathrm{Ru(bpy)_3^+}$ reduces 9 by a one-electron-transfer process (eq 16). The resulting radical anion undergoes further reduction by the oxidized electron donor, triethylamine radical cation ($\mathrm{TEA^{\bullet+}}$) (eq 17). Table II summarizes the turnover number of $\mathrm{Ru(bpy)_3^{2+}}$ and the initial rate of 9 reduction. It is evident that the photosensitizer

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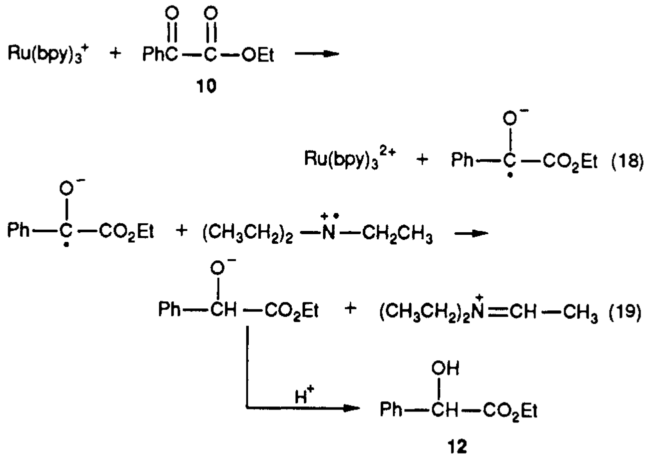
is effectively recycled in the photosensitized reduction of benzil.

Photoinduced reduction of ethyl benzoylformate (**10**) proceeds similarly through photogeneration of $\mathrm{Ru(bpy)_3^+}$ that acts as electron-transfer mediator. Illumination of an acetonitrile solution that includes $\mathrm{Ru(bpy)_3^{2+}}$ as photosensitizer, triethylamine as electron donor, and **10** as substrate results in the formation of ethyl α-hydroxy benzeneacetate (ethyl mandelate) (**12**). Figure 7 shows the rate of formation of **12** as a function of illumination time. The initial quantum yield of **12** formation corresponds to $\phi = 0.049$. Control experiments reveal that the photosensitizer and TEA are essential components to effect the reduction of the substrate. Exclusion of either $\mathrm{Ru(bpy)_3^{2+}}$, TEA, or the illumination prohibits the process. Cyclic voltammetry measurements imply that $\mathrm{Ru(bpy)_3^+}$ acts as a primary electron-transfer catalyst for the reduction of **10** (eq 18). The substrate **10** exhibits a reversible one-electron-reduction wave at $E_{1/2} = -1.32$ V. The cyclic voltammogram of $\mathrm{Ru(bpy)_3^{2+}}$ in the presence of **10** shows a catalytic cathodic current at the first reduction wave of $\mathrm{Ru(bpy)_3^{2+}}$. These results imply that electrogenerated $\mathrm{Ru(bpy)_3^+}$ mediates the reduction of **10** (eq 18). The resulting radical anion formed in the photosensitized process is subsequently reduced by $\mathrm{TEA^{\bullet+}}$ and yields **12** (eq 19). Table II summarizes the initial rate of **10** reduction and the turnover number of the photosensitizer in the system. The value of the turnover number implies that the photosensitizer is effectively recycled in the reduction process of **10**.



$$\mathrm{Ru(bpy)_3^+} + \mathrm{PhC(=O)-C(=O)-OEt}\ (\mathbf{10}) \longrightarrow \mathrm{Ru(bpy)_3^{2+}} + \mathrm{Ph-\dot{C}(O^-)-CO_2Et} \quad (18)$$

$$\mathrm{Ph-\dot{C}(O^-)-CO_2Et} + \mathrm{(CH_3CH_2)_2\overset{\bullet+}{N}-CH_2CH_3} \longrightarrow \mathrm{Ph-CH(O^-)-CO_2Et} + \mathrm{(CH_3CH_2)_2\overset{+}{N}{=}CH-CH_3} \quad (19)$$

$$\mathrm{Ph-CH(O^-)-CO_2Et} \xrightarrow{H^+} \mathrm{Ph-CH(OH)-CO_2Et}\ (\mathbf{12})$$

Conclusions

We have demonstrated that photosensitized electron-transfer reactions in organic solvents (acetonitrile) initiated by visible light provide a means to effect debromination of *vic*-dibromides and reduction of activated carbonyl functions. Photogenerated $\mathrm{Ru(bpy)_3^+}$ acts in these transformations as an electron-transfer mediator. The complementary electrochemical studies reveal that electroreduction of *vic*-dibromides and of **10** is accompanied by kinetic limitations. Electrogenerated $\mathrm{Ru(bpy)_3^+}$ acts as an electron-transfer catalyst that effects these processes. Thus, photochemically or electrochemically induced generation of $\mathrm{Ru(bpy)_3^+}$ provides a route for the reduction of organic substrates through electron-transfer catalysis.

Acknowledgment. This research project was supported by the Bundesministerium für Forschung and Technologie (BMFT), West Germany.

Registry No. **1**, 13440-24-9; (±)-**2**, 13027-48-0; **3**, 5464-70-0; **4**, 1196-45-8; **5**, 103-30-0; **6**, 645-49-8; **7**, 4192-77-2; **8**, 873-66-5; **9**, 134-81-6; **10**, 1603-79-8; (±)-**11**, 579-44-2; (±)-**12**, 4358-88-7; $\mathrm{Ru(bpy)_3Cl_2}$, 14323-06-9; $\mathrm{(CH_3CH_2)_2NCH_2CH_3}$, 121-44-8; $\mathrm{Ru(bpy)^+}$, 56977-24-3.

Base-Catalyzed Reactions of Anthrones with Dienophiles[1]

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Anthrone in the presence of an amine functions as a reactive diene in [4 + 2] cycloadditions. Dienophiles which differ in reactivity over a range of ca. 10^5 give products at 25 °C. Thus *N*-methylmaleimide (NMM) gives cycloadduct within minutes in various solvents containing catalytic triethylamine. The reaction of dimethyl fumarate is slower, and a convenient rate with methyl acrylate requires the use of the dienophile as solvent or a primary amine catalyst. The reactions take a different course in methanol solvent, ultimately leading to Michael adduct. Cycloadducts are detected at short reaction times and are shown to be viable precursors to Michael adducts. A 5-alkoxy group on naphthacene directs Diels–Alder reaction mainly to the unsubstituted central ring. The analogous reaction with naphthacen-5-one and amine catalyst affords the bridgehead hydroxyl product. Dithranol (1,8-dihydroxyanthrone) reacts more rapidly than anthrone and exhibits a strong tendency to give Michael adduct. Possible intramolecular protonation of a carbanion (enolate) intermediate was ruled out by the use of deuterated substrate. The product with NMM is deuterated stereoselectively trans to the anthracenyl ring, implying sterically controlled intermolecular reaction. Similar stereoselectivity was observed for the conversion of anthrone–NMM cycloadduct to Michael adduct in MeOD cosolvent. Cycloadducts may be formed either by stepwise (Michael + aldol) reactions, or by oxyanion accelerated concerted Diels–Alder reactions. Arguments favoring the latter mechanism are presented. The reaction is discussed in the context of other base-induced and base-catalyzed cycloadditions of 1-oxido and 2-oxido 1,3-dienes.

Introduction

Diels–Alder reactions are generally viewed as concerted asynchronous processes,[2] although a body of literature ascribes stepwise mechanisms to certain formal [4 + 2] cycloadditions. In particular, the synthetically valuable cycloadditions[3-13] of enolates derived from α,β-unsaturated

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