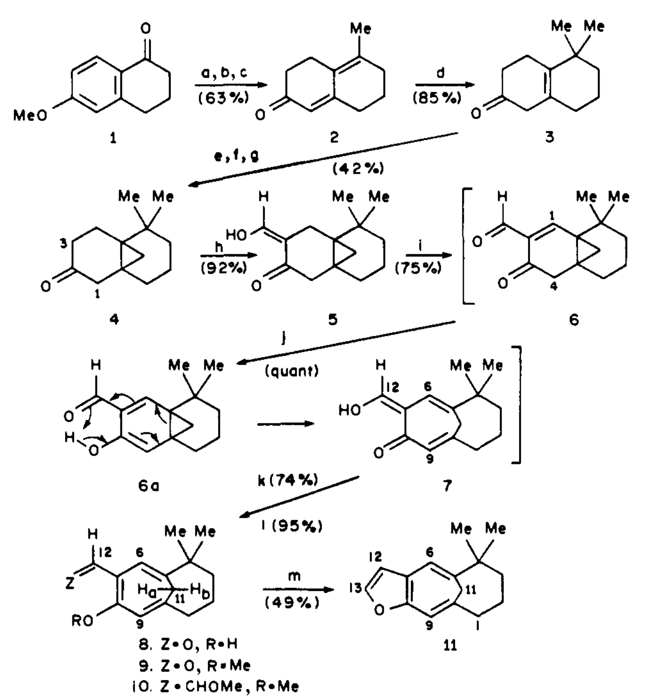
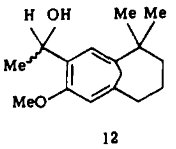
Scheme I[a]



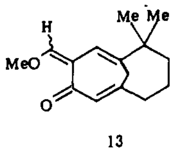
[a] (a) MeLi, Et_2O, THF; (b) Na, NH_3, EtOH; (c) HCl, H_2O, Et_2O; (d) Me_2CuLi, Et_2O; (e) $NaBH_4$, EtOH; (f) Zn(Cu), CH_2I_2, Et_2O; (g) H_2CrO_4, H_2SO_4, Me_2CO; (h) HCO_2Et, NaOMe, C_6H_6; (i) DDQ, C_6H_6; (j) HCl, H_2O, EtOAc; (k) MeI, K_2CO_3, DMF; (l) $Ph_3P^+CH_2OMe$, Cl^-, KO-*t*-Am, $CH_3C_6H_5$; (m) HCl, H_2O, Et_2O.

ketone **5.** Other, less sterically demanding enol and enolate reactions (various bases plus Me_3SiCl;[10] various bases plus PhSeCl[11]) led to mixtures of C-1–C-3 regioisomeric products. Ketone **5** was smoothly dehydrogenated at room temperature with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)[12] in benzene to give the acid labile enone **6:** ν_{max} 1695, 1680, 1600 cm^{-1}; δ 9.8 (s, CHO), 8.2 (s, H-1), 2.7 (AB, H-4, $J_{AB} = 18$ Hz, $\Delta\nu = 13$), 1.15 (s, CH_3's), 0.5 ppm (d, H-11, $J = 4$ Hz). Enone **6** rearranged with startling ease to enol **8** [ν_{max} 1630, 1600, 1515, 1365, 1280, 1195 cm^{-1}; δ 9.4 (s, H-12), 6.0, 5.8 (s, H-6, H-9), 3.05 (d, H-11b, $J = 10$ Hz), 1.25, 1.1 ppm (s, CH_3's)] upon treatment with a trace of acid or elution though silica gel. This remarkably facile ring expansion[13] was attended by dramatic changes in the NMR spectrum highlighted by the appearance of a distinctive doublet at 3.05 ppm attributable to the deshielded methano bridge endo proton (**8**, H-11b, $J = 10$ Hz)[2] and the concomitant disappearance of the shielded cyclopropane protons of enone **6** (δ 0.5 ppm).[14]

Alkylation of the hydroxy aldehyde **8** with methyl iodide-potassium carbonate in dimethylformamide yielded the enol ether **9:** mp 127-129 °C; ν_{max} 1650, 1615, 1390, 1275, 1145 cm^{-1}; δ 10.3 (s, H-12), 6.3, 5.8 (s, H-6, H-9), 3.8 (s, CH_3O), 3.1 (d, H-11b, $J = 10$ Hz), 1.25, 1.0 ppm (CH_3's)]. This structure was confirmed both by the ^{13}C NMR spectrum (aldehyde CO doublet at 191 ppm) and by addition of methyllithium to give the secondary alcohol **12** [CH_3 doublet at 1.3 ppm ($J = 6$ Hz), broad carbinyl H quartet at 5.0 ppm]. The isomeric enol ether **13** was evidently not present to an appreciable extent.



12



13

Aldehyde **9** condensed readily with methoxymethylenetriphenylphosphorane in toluene[15] to give the bis enol ether **10.** Treatment with aqueous HCl in ethyl ether slowly gave rise to the furan **11:** δ 7.2, 6.45 (d, H-12, H-13, $J = 2$ Hz), 6.2 (s, H-6, H-9), 3.1 (d, H-11b, $J = 10$ Hz), 2.3 (m, H-1), 1.3, 1.0 ppm (s, CH_3's). The ^1H and ^{13}C NMR spectra of **11** were in complete agreement with those of dihydrospiniferin-1.[2]

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(13) The ring cleavage is a thermally allowed disrotatory electrocyclic reaction. It may also be viewed as a retro-Michael reaction in which case the proton transfer depicted in **6**a may play an important role. We have not yet examined the influence of base on enone **6.** Analogy with sigmatropic rearrangements would suggest that the enolate rearrangement would likewise be facile. (Steigerwald, M. L.; Goddard, W. A., III; Evans, D. A. *J. Am. Chem. Soc.* **1979,** *101,* 1994–97. Ireland, R. E.; Mueller, R. H.; Willard, A. K. *Ibid.* **1976,** *98,* 2868–2877.) The oxalo derivative of enone **6** ($COCO_2Et$ instead of CHO) undergoes comparable ring expansion upon base treatment.

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(16) National Science Foundation Predoctoral Fellow, 1979–1982.

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Electron-Transfer Photooxygenation. 4. Photooxygenation of *trans*-Stilbene Sensitized by Methylene Blue[1]

Sir:

Methylene Blue (MB) and other dyes are widely used as sensitizers of photooxygenations.[2] Usually, excited singlet oxygen ($^1O_2$) is produced by energy transfer from triplet dye to oxygen and reacts with acceptor (A) to give the product (AO_2).

In 1969, Rio and Berthelot[3] reported a very slow photooxygenation of *trans*-stilbene (TS) sensitized by MB to give 2 mol of benzaldehyde. These authors assumed that the reaction involved $^1O_2$. Other $^1O_2$ sensitizers, however, including Rose Bengal (RB), failed to sensitize the reaction.[3] The alcohol used to dissolve the RB was thought to cause this inefficiency.[3] However, it is difficult to understand this explanation because the lifetime of $^1O_2$ is not shortened sufficiently in methanol to account for these results.[4]

We have previously shown that the cyanoaromatic-sensitized photooxidation of TS to benzaldehyde in MeCN occurs

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Table I. Inhibition of Photosensitized Oxidations by 0.1 M *trans*-Stilbene (TS)

sensitizer	acceptor[a]	concn, M	% inhibition rel to rxn in absence of TS
MB	limonene	0.020	40 ± 10[b]
MB	tetramethylethylene	0.024	43 ± 5[c]
MB	rubrene	4×10^{-6}	48 ± 5[d]
RB	limonene	0.020	15 ± 10[b]
RB	rubrene	4×10^{-6}	15 ± 10[d]

[a] The effect of the $^1O_2$ acceptors on the amount of TS oxidation was difficult to determine because the acceptors are oxidized much more rapidly than TS under the conditions, so that they are almost completely oxidized before any appreciable amount of the TS was consumed. [b] Determined by loss of limonene; see ref 8. [c] Determined by appearance of $^1O_2$ product: see ref 8. [d] Determined by loss of fluorescence: see ref 19, 20.

via an electron-transfer mechanism.[1,5-7] The fluorescence of these sensitizers is quenched by stilbene at rates predicted for an electron-transfer process.[5] We now report that the major pathway of the MB-sensitized photooxygenation of TS in MeCN does *not* involve $^1O_2$, but may involve an electron transfer from stilbene to singlet excited MB.

In agreement with the report of Rio and Bertholet,[3] MB slowly sensitizes the photooxygenation of TS to benzaldehyde in oxygen-saturated MeCN.[8] Using RB instead of MB gives only traces of benzaldehyde under similar conditions. Clearly the reaction cannot simply be a $^1O_2$ reaction, since both dyes are sensitizers of $^1O_2$.[2] TS also quenches the weak fluorescence of MB at 689 nm in MeCN. The quenching follows Stern-Volmer kinetics,[9] with $k_q\tau_s = 10.2 \pm 0.5$ M^{-1}.[10] The fluorescence lifetime of $^1MB^*$ (τ_s) was determined to be 1.1 ± 0.1 ns,[11,12] which indicates that $k_q = 9.5 \times 10^9$ M^{-1} s^{-1}.

Using the treatment of Rehm and Weller,[13] the rate constant for the above process ($\Delta G = -3.7$ kcal/mol) is calculated to be $k_q = 7 \times 10^9$ M^{-1} s^{-1}. The agreement between the measured and theoretical value for k_q supports the suggestion that this reaction is an electron-transfer process.

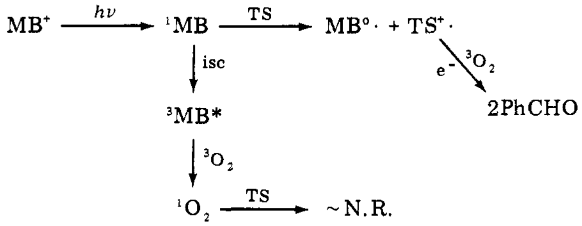
At [TS] = 0.1 M, ~50% of the MB fluorescence is quenched. The much stronger fluorescence of RB at 580 nm[15] is not quenched measureably by TS at concentrations up to 0.1 M. (The quenching of ^1RB by TS via electron transfer would be strongly endothermic). Thus the efficiency of TS in quenching dye fluorescence parallels the sensitizing efficiency of the dyes in the photooxygenation, as would be required by an electron-transfer mechanism.

If TS quenches $^1MB^*$, intersystem crossing, and thus the formation of both ^3MB and $^1O_2$, should also be quenched; 0.1 M TS should quench ~50% of the MB (but not RB) sensitized photooxygenations of substrates that react with $^1O_2$. As well-documented $^1O_2$ acceptors, we chose *d*-limonene, tetramethylethylene (TME), and rubrene.[16-18] The results are shown in Table I. With MB as sensitizer, 0.1 M TS leads to quenching of the photooxygenation of the $^1O_2$ acceptors to an extent of 44 ± 10%, which is well explained by quenching of $^1MB^*$. Since no quenching of $^1RB^*$ by stilbene was detected, the mechanism for the 15 ± 10% quenching in the RB-sensitized photooxygenations is not clear.

We have recently found that the lifetime of $^1O_2$ is ~10 times longer in CD_3CN than in CH_3CN.[20] If the mechanism of TS photooxygenation involves $^1O_2$, production of benzaldehyde (C_6H_5CHO) would be expected to be faster in the deuterated solvent.[21] The ratio of the amount of C_6H_5CHO formed in CD_3CN relative to that in CH_3CN[8] was 1.16 ± 0.2 for the MB-sensitized reaction, well below the increase expected for a $^1O_2$ reaction.

Further evidence that the MB-sensitized photooxidation of TS is not a $^1O_2$ reaction comes from a comparison of the effect of oxygen concentration on the reaction and that on a known $^1O_2$ reaction under identical conditions. The relative rates of formation of PhCHO from the TS-MB photooxidation were determined in O_2 and in air-saturated solutions.[8] The formation was ~4.5 times faster in O_2 than in air, which indicates that the TS reaction is directly dependent on $[O_2]$. The relative rates of oxidation of the $^1O_2$ acceptor TME were determined under identical conditions.[8] The rates were the same under both air and O_2, as expected.[2]

Scheme I



Thus, while we cannot rule out $^1O_2$ as an intermediate in a minor pathway, we can safely conclude from the overall data that *the major pathway of the MB-sensitized photooxygenation of TS to benzaldehyde does not involve* $^1O_2$. By analogy to the dicyanoanthracene-sensitized photooxygenations we have studied,[1,5-7] we suggest that the MB-sensitized photooxygenation of TS also goes by an electron-transfer mechanism (Scheme I). The exact mechanism of the formation of benzaldehyde from $MB^{0}\cdot$ and $TS^{+}\cdot$ has not been established. The electron-transfer step from $MB^{0}\cdot$ to $^3O_2$ is strongly endothermic in this case, although it is exothermic in the case of cyanoaromatics.[7] A direct reaction of $TS^{+}\cdot$ with O_2 (as suggested for the Barton chemical oxidation)[22] or a chain propagation must be considered.[23]

$$MB^{0}\cdot + {}^3O_2 \rightarrow O_2^{-}\cdot + MB^{+} \qquad \Delta E_0 = -0.67\ V^{14}$$

The interception of singlet excited dyes is not unprecedented. Recently Davidson and Tretheway[24] have shown that singlet states of RB and MB can be quenched by amines and β-carotene if sufficiently high concentrations are used.

Thus, as might be expected,[2] dye-sensitized photooxygenations cannot blindly be interpreted as $^1O_2$ reactions, especially when the reactions are slow or high substrate concentrations are used. Other reactions sensitized by Methylene Blue which could well go via the above mechanism are the photooxygenations in methanol of 2-trimethylsiloxynorbornene,[25] 1,3-dimethylindole,[26] and 2-methoxynorbornene.[27] The results from these experiments have been cited as support for a zwitterionic peroxide intermediate in $^1O_2$ chemistry;[27] however, they are equally compatible with an electron-transfer process giving substrate radical cation which can add solvent and oxygen. However, each of the substrates in the above cases may also react with singlet oxygen; the actual course of the reactions requires reinvestigation.

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(8) A GE Lucalox sodium lamp with a 500-nm cutoff filter (1.2 g of $K_2Cr_2O_7$ in 1 L of H_2O, 1 cm) was used. The tubes were photolyzed on a merry-go-round for 12 min for MB-sensitized (0.01 mg/mL) photooxygenation of stilbene (0.1 M) leading to ~1% conversion into benzaldehyde. *p*-Dimethoxybenzene, added after irradiation, was used as a GLC internal standard. The disappearance of limonene was analyzed by GLC at 60 °C. For the MB-sensitized (0.01 mg/mL) photooxygenation of TME, the hydroperoxide product was reduced by addition of excess $(C_6H_5)_3P$ and the resulting alcohol was analyzed at 50 °C by GLC.

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(11) Fluorescence lifetimes were determined by R. Brewer in the laboratory of M. F. Nicol at UCLA. Values of τ_s in both CH_3CN and CD_3CN were the same within experimental error. The apparatus used has been described in detail elsewhere.[12] For the MB determination, λ_{exc} was 620 nm, λ_{em} 677 nm. Saturation of the samples with air had no measurable effect on the fluorescence lifetime.

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(19) The disappearance of rubrene due to its reaction with $^1O_2$ was followed by monitoring its fluorescence at 546 nm (λ_{exc} 460 nm). Details of the procedure can be found in ref 20.

(20) Ogilby, P.; Foote, C. S., to be published.

(21) The actual rate enhancement for a $^1O_2$ reaction in going from CH_3CN to CD_3CN is 3–4 when 0.1 M TS is present. It seems that TS either quenches ^{3}dye or $^1O_2$ to a small extent. This would also explain the ~15% quenching of the RB-sensitized reactions in Table I.

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A New, Convenient, and Efficient Route to Dimolybdenum(II) Compounds from MoO_3

Sir:

Since the discovery and recognition of quadruple bonds between metal atoms,[1] hundreds of compounds containing $M{\equiv}M$ (M = Cr, Mo, W, Tc, Re) were prepared. Molybdenum has been the subject of the greatest and still growing number of reports about these compounds.[2] The interest in the $[Mo{\equiv}Mo]^{4+}$ unit and its derivatives stems firstly from the quadruple bonds themselves and secondly from their use as reactants in the preparation of many other interesting molybdenum compounds.[2] Nevertheless, this part of the molybdenum chemistry has been considered by many chemists as an exotic field, separated from the conventional chemistry of this element. The origin of this erroneous concept was the fact that, until now, there has not been any report of a simple synthetic procedure which describes the forming of the unit $[Mo{\equiv}Mo]^{4+}$ by reduction of molybdenum species of higher oxidation number. Almost all of the procedures which have been used involve the relatively expensive starting material, $Mo(CO)_6$.[3]

All these reactions are carried out under severe anhydrous and anaerobic conditions and do not always produce high yields of Mo_2^{4+}.

Attempts to reduce Mo(VI) in aqueous media by strong reducing agents invariably yielded only Mo(III) species which could not be reduced any further by any conventional method.

This report shows, for the first time, a simple way to convert MoO_3 into $[Mo{\equiv}Mo]^{4+}$ derivatives, by using conventional reduction methods in aqueous media. This synthesis consists of three steps, two of which have already been known in the literature for many years. The first step is the electrolytic reduction of Mo(VI) in HCl to $MoCl_6^{3-}$.[5] The second, described by Nyholm et al. in 1969,[6] was the condensation reaction of $MoCl_6^{3-}$ to produce the triply bridged dinuclear $Mo_2Cl_9^{3-}$ by evaporation of the aqueous HCl solution of $MoCl_6^{3-}$ to near dryness.

We report now that $Mo_2Cl_9^{3-}$ and $Mo_2Br_9^{3-}$ can be reduced quantitatively by an amalgamated zinc column (Jones reductor) to the dimolybdenum(II) $[Mo{\equiv}Mo]^{4+}$ species and that compounds derived from this species, such as $Mo_2(O_2CCH_3)_4$,[7] $K_4Mo_2Cl_8 \cdot 2H_2O$,[8] and $K_4Mo_2(SO_4)_4 \cdot 2H_2O$,[9] can be obtained.

MoO_3 (2 g) was dissolved in 50 mL of HCl (12 M).[5] This solution was reduced electrolytically to $MoCl_6^{3-}$ in a cell using a platinum cathode and a graphite rod anode separated by a porous clay compartment.[10] The red solution of $MoCl_6^{3-}$ was then evaporated to near dryness with a rotating evaporator, 80 mL of HCl (0.6 M) was added, and the solution was passed through an ice-cooled Jones-reductor column (15 × 1 cm) into a solution containing sodium acetate (5 g) in 30 mL of H_2O. The heavy yellow precipitate of $Mo_2(O_2CCH_3)_4$ was collected, washed with water, acetone, and ether, and dried under vacuum: yield, 2.37 g (80%). When the sodium acetate was omitted, a deep red solution of Mo_2^{4+} was obtained from the reductor. By passing gaseous HCl into this solution at −10 °C, followed by the addition of KCl, the salt $K_4Mo_2Cl_8 \cdot 2H_2O$ was precipitated. The red compound was filtered, rinsed with alcohol and ether, and dried under vacuum: average yield, 55%. When this experimental procedure was carried out without external cooling, the temperature of the solution increased by the dissolution of the gaseous HCl, and $Mo_2Cl_8^{4-}$ was oxidized to $Mo_2Cl_8H^{3-}$.[11] Addition of CsCl to the resulting deep yellow solution precipitated $Cs_3Mo_2Cl_8H$: average yield, 90%. When 50 mL of H_2SO_4 (0.5 M) was added instead of HCl (0.6 M) to the almost dry $H_3Mo_2Cl_9$ and passed through the reductor into 40 mL of H_2SO_4 (2 M) containing K_2SO_4 (2 g), $K_4Mo_2(SO_4)_4 \cdot 2H_2O$ was obtained: average yield, 60%. It was found that other Mo(III) species are reducible to Mo_2^{4+}. These species, $Mo_2X_8H^{3-}$ (X = Br, Cl)[12] and $Mo_2(HPO_4)_4^{2-}$ [14] do not, however, open new synthetic routes to Mo_2^{4+} since they themselves are prepared by oxidation of Mo_2^{4+}.[11,13]

The fact that $Mo_2X_9^{3-}$, $Mo_2X_8H^{3-}$ (X = Cl, Br) and $Mo_2(HPO_4)_4^{2-}$ are reduced to Mo_2^{4+} unlike other Mo(III) species in aqueous solution raises the question of the factors which determine the reducibility of Mo(III) species. All known molybdenum(III) species in aqueous solutions are listed in Table I, with their Mo–Mo distance and reduction behavior. The information in Table I indicates that it is essential that the starting material should have a dinuclear nature but the MoMo

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