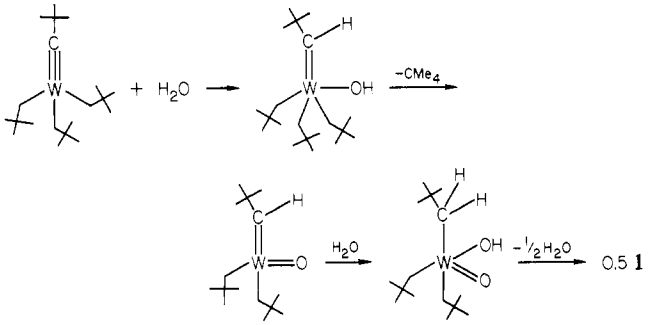
Scheme I. Proposed Mechanism of Hydrolysis of $W(CCMe_3)(CH_2CMe_3)_3$



insoluble and as yet uncharacterized white powder. However, if the water contains 1 equiv of NaOH, a colorless solution is obtained. If tetraethylammonium hydroxide is used instead of NaOH a granular white tetraethylammonium salt is formed, which is soluble in both water and dichloromethane. IR, NMR, and FD mass spectral data all suggest that this species is $[NEt_4][WO_3(CH_2CMe_3)]$ (**2**; eq 2).[7] This complex does not darken

$$W(CCMe_3)(OCMe_3)_3 + NEt_4OH \rightarrow \underset{\mathbf{2}}{[NEt_4][WO_3(CH_2CMe_3)]} \quad (2)$$

at increased temperatures and has a melting point of 164 °C in air. It is stable in water at pH 7, but appears to be more readily hydrolyzed by aqueous acid or base than **1**. The organic product of hydrolysis of **2** by 1 N NaOH at 25 °C overnight was shown to be neopentane (1.0 (±0.1) equiv in ether layer by GLC).

$W_2O_3(CH_2CMe_3)_6$ and $[WO_3(CH_2CMe_3)]^-$ can be added to the short list of d^0 complexes containing only oxo and alkyl ligands, i.e., $V(O)(CH_2SiMe_3)_3$,[8] ReO_2Me_3,[9] ReO_3Me,[10] and alkyl molybdates such as $[MoO_3Me]^-$ (observed in solution[11]). Preliminary results suggest that other tungsten(VI) alkylidyne complexes do not hydrolyze in as controlled a fashion as neopentylidyne complexes. For example, neither $W(CEt)(CH_2CMe_3)_3$[12] nor $W(CEt)(OCMe_3)_3$[13] hydrolyzes smoothly to give compounds analogous to **1** and **2**, respectively. However, $W(CPh)(OCMe_3)_3$[14] does appear to yield $[Et_4N][WO_3(CH_2Ph)]$.

The most surprising result is that **1** and **2** are so stable thermally, as well as to hydrolysis. This is likely to be a general property of such compounds since the V[8] and Re[9,10] complexes above are also reportedly stable to air and water, and $[MoO_3R]^-$ reportedly[11] hydrolyzes relatively slowly at pH 7.

We are attempting to prepare **1** and **2** by more direct routes that do not involve neopentylidyne precursors. Preparation of analogous compounds containing other hydrocarbon ligands and analogous compounds containing molybdenum has also been undertaken. We are especially interested in reactions of the alkyl ligand that are relevant to catalysis by molybdenum or tungsten oxides.

Acknowledgment. R.R.S. thanks the National Science Foundation for supporting this research (Grant CHE 81-21282), I.J. thanks the Bantrell Foundation for a postdoctoral fellowship, and S.F.P. thanks the Dow Central Research Department for a predoctoral fellowship. We also thank Dr. Catherine Costello and Dr. Henrianna Pang for obtaining FD mass spectra (NIH Grant RR317 to K. Biemann).

Registry No. 1, 87615-70-1; **2**, 87615-69-8; $W(CCMe_3)(CH_2CMe_3)_3$, 68490-69-7; $W_2O_3(CH_2CMe_3)_4(CD_2CMe_3)_2$, 87615-71-2; $W(O)(CH_2CMe_3)_3Cl$, 75846-05-8; $W(CCMe_3)(OCMe_3)_3$, 78234-36-3; NEt_4OH, 77-98-5.

(7) ^1H NMR (CD_2Cl_2) δ 3.35 (q, 8, NCH_2CH_3), 1.68 (s, 2, J_{HW} = 15 Hz, CH_2CMe_3), 1.34 (t, 12, NCH_2CH_3), 1.02 (s, 9, CH_2CMe_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 54.67 (CH_2CMe_3), 52.84 (NCH_2CH_3), 33.60 (CMe_3), 31.68 (CMe_3), 7.82 (NCH_2CH_3); IR (Nujol) 980 (vs), 925 (vs), 800 (s), 690 (vs), 655 cm^{-1} (vs). The $[[NEt_4]_2[WO_3(CH_2CMe_3)]]^+$ ion was observed in the FD mass spectrum.

(8) Mowat, W.; Shortland, A.; Yagupsky, G.; Hill, N. J.; Yagupsky, M.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1972**, 532.

(9) Mertis, K.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 1488.

(10) Beattie, I. R.; Jones, P. L. *Inorg. Chem.* **1979**, *18*, 2318.

(11) Schrauzer, G. N.; Hughes, L.; Strumpach, N. *Z. Naturforsch., B* **1982**, *37b*, 380.

(12) This complex is a yellow oil prepared by reacting $W(CEt)(OCMe_3)_3$[13] with 3 equiv of $ClMgCH_2CMe_3$ followed by a 40 °C sublimation at <0.1 μm to separate it from $ClMg(OCMe_3)$: Murray, R., unpublished results.

(13) Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291.

(14) Wengrovius, J. H.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 3932.

Nucleophilic Aromatic Substitution by Organoaluminum Reagents. Application to the Synthesis of Indoles

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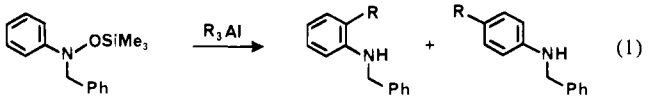
Although the electrophilic aromatic substitution represented by Friedel–Crafts reaction is undoubtedly one of the most versatile synthetic procedures for construction of C–C bonds to aromatic rings,[1] the nucleophilic counterpart has been developed only to a lesser extent due to the lack of a suitable substrate for generating electron-deficient arenes.[2-5] However, by choosing the appropriate metal reagent and substrate, it could become possible to restructure the reactivity profile of the arene from nucleophile to electrophile.[4] Disclosed herein is a new and efficient method for the nucleophilic introduction of an alkyl group such as methyl or alkynyl on the aromatic nuclei of arylhydroxylamine derivatives by organoaluminum reagents (eq 1). The produced aromatic amines



bearing the alkynyl moiety should serve as a promising building block for the elaboration of polyaromatics and fused heterocycles.[6]

The typical experimental procedure is exemplified by the alk-

(1) Friedel, C.; Crafts, J. M. *C. R. Hebd. Seances Acad. Sci.* **1877**, *84*, 1392, 1450. For reviews, see: Olah, G. A. "Friedel-Crafts and Related Reactions"; Interscience: New York, 1963–1965. Glatz, A. M. *Rev. Roum. Chim.* **1974**, *19*, 455.

(2) For reviews of classical nucleophilic aromatic substitution, see: Bunnett, J. F.; Zahler, R. E. *Chem. Rev.* **1951**, *49*, 273. Hughes, E. D.; Ingold, C. K. *Quart. Rev. (London)* **1952**, *6*, 34. Bunnett, J. F. *Ibid.* **1958**, *12*, 1. Sauer, R.; Huisgen, R. *Angew. Chem.* **1960**, *72*, 294. Ross, S. D. *Progr. Phys. Org. Chem.* **1963**, *1*, 31.

(3) Nucleophilic aromatic alkylation of anilines and its applications to natural product synthesis: Gassman, P. G.; Gruetzmacher, G.; Smith, R. H. *Tetrahedron Lett.* **1972**, 497. Johnson, C. R.; Bacon, C. C.; Kingsbury, W. D. *Ibid.* **1972**, 501. Gassman, P. G.; Gruetzmacher, G. *J. Am. Chem. Soc.* **1973**, *95*, 588. Gassman, P. G.; Drewes, H. R. *Ibid.* **1974**, *96*, 3003. Gassman, P. G.; Gruetzmacher, G. *Ibid.* **1974**, *96*, 5487. Gassman, P. G.; van Bergen, T. J.; Gilbert, D. P.; Cue, B. W. *Ibid.* **1974**, *96*, 5495. Gassman, P. G.; van Bergen, T. J.; Gruetzmacher, G. *Ibid.* **1974**, *96*, 5512.

(4) For reviews of nucleophilic alkylation of arene–metal complexes, see: Semmelhack, M. F. *Ann. N. Y. Acad. Sci.* **1977**, *295*, 36. Jaouen, G. In "Transition Metals Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1978; p 65. Semmelhack, M. F. In "Organic Synthesis. Today and Tomorrow"; Trost, B. M., Hutchinson, C. R., Eds.; Pergamon Press: New York, 1981; p 63. See also: Semmelhack, M. F.; Zask, A. *J. Am. Chem. Soc.* **1983**, *105*, 2034.

(5) Julia, M.; Le Goffic, F.; Igolen, J.; Braillage, M. *Tetrahedron Lett.* **1969**, 1569. Ohta, T.; Machida, R.; Takeda, K.; Endo, Y.; Shudo, K.; Okamoto, T. *J. Am. Chem. Soc.* **1980**, *102*, 6385. Endo, Y.; Shudo, K.; Okamoto, T. *Ibid.* **1982**, *104*, 6393.

(6) Since the amino group can be readily replaced with other functions via diazotization, the present method offers access to a variety of disubstituted aromatics.

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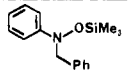
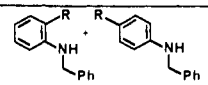
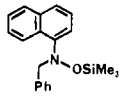
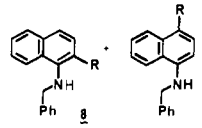
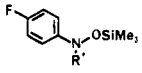
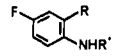
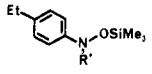
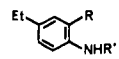
Table I. Nucleophilic Aromatic Substitution by Trialkylaluminums (R_3Al)[a]

entry	substrate	R	product[b]	yield[c] (ratio)[d]
1		Me		71 (3:2)
2		*n*-BuC≡C		77 (1:1)
3		Me_3SiC≡C		55 (1:1)
4	1	PhC≡C	2 3	68 (3.7:1)
5		Me		69 (1:1)
6		*n*-BuC≡C		83 (2.4:1)
7		Me_3SiC≡C	8	70 (1:2)
				
8	R′ = CH_2Ph	Me		42
9		*n*-BuC≡C		40
10	R′ = CHMePh	*n*-BuC≡C	7	70
11		Me_3SiC≡C		83
				
12	R′ = CH_2Ph	Me		43
13		*n*-BuC≡C		39
14	R′ = CHMePh	*n*-BuC≡C		61
15		Me_3SiC≡C		66

[a] Reaction was carried out under argon atmosphere by using 4 equiv of R_3Al at 0 °C for 30 min. [b] All products were identified by ^1H NMR and IR spectra. [c] Isolated yield after silica gel column chromatography. [d] Isolated ratio of ortho- and para-alkylated aromatic amines.

ynylation of *N*-benzyl-*N*-phenyl-*O*-(trimethylsilyl)hydroxylamine (**1**). To a solution of 1-hexyne (984 mg, 12 mmol) in toluene (10 mL) was added dropwise with stirring at 0 °C a solution of *n*-butyllithium (12 mmol, 7.3 mL of a 1.64 M *n*-hexane solution) under an argon atmosphere. After 30 min at 0 °C, anhydrous $AlBr_3$ (1.07 g, 4 mmol) dissolved in CH_2Cl_2 (20 mL)[7] was added, and the stirring was continued for an additional 30 min. A solution of trimethylsilyl ether **1** (271 mg, 1 mmol) in CH_2Cl_2 (3 mL) was then added at 0 °C and stirred there for 30 min to complete the alkylation. The reaction mixture was poured onto 5% NaOH, extracted with ether repeatedly, dried over Na_2SO_4, and concentrated in vacuo. The residual liquid was subjected to column chromatography on silica gel (ether/hexane, 1:20–1:10) to give a mixture of *N*-benzyl(1-hexynyl)aniline **2** and **3** (R = *n*-BuC≡C) (202 mg, 77% yield) in a ratio of 1:1.[8,9]

Several examples are listed in Table I. The characteristic features of the reaction follow. (1) As indicated in Table I, the reaction appears general with respect to the structural types of arylhydroxylamine derivatives, which can be readily accessible from a wide variety of nitro compounds in 50–65% overall yield by the following sequence: (i) reduction of nitroarenes with zinc and aqueous NH_4Cl in EtOH;[10] (ii) alkylation using benzyl bromide and K_2CO_3 in degassed MeOH;[11] (iii) silylation with trimethylsilyl chloride and NEt_3 in CH_2Cl_2. (2) The high oxygenophilic aluminum reagent is capable of cleaving the N–O bond heterolytically to yield the discrete anilenium ion,[12] which is readily susceptible toward nucleophilic attack of trialkylaluminum at either the ortho or para position.[9,13] It should be noted that the novel aryl–alkynyl coupling described here cannot be attained by the ordinary Friedel–Crafts process.[1] (3) Any double alkylation products were not detected in the present reaction. This represents another distinct advantage over the classical Friedel–Crafts reaction. (4) The choice of trimethylsilyl ethers is essential for obtaining C-alkylation products almost exclusively. Attempted alkylation of *N*-benzyl-*N*-phenyl-*O*-allylhydroxylamine[14] with Me_3Al resulted in formation of N-methylation product, *N*-benzyl-*N*-methylaniline, predominantly. (5) Para-substituted arylhydroxylamines yielded the desired ortho alkylation products contaminated with considerable amounts of imine resulting from the facile elimination of benzylic proton (entries 8, 9, 12, and 13). However, the use of the 1-phenetyl group as substituent effected the clean alkylation to furnish 2,4-disubstituted anilines as sole isolable products (entries 10, 11, 14, and 15).

The availability of aromatic amines bearing the ortho alkynyl moiety[9] allowed the development of a convenient access to indole synthesis.[15] Thus, treatment of *N*-benzyl(2-(trimethylsilyl)-ethynyl)aniline (**4**) with CuI (0.5 equiv) and $CaCO_3$ (1 equiv) in DMF at 120 °C for 2 h[16] led to smooth cyclization and concurrent elimination of the trimethylsilyl group to furnish 1-benzylindole (**5**) in 73% yield. No trace of the intermediate 1-benzyl-2-(trimethylsilyl)indole could be detected. Deprotection of **5** with Na/NH_3[17] gave rise to indole (**6**) in 80% yield. Other *o*-alkynylanilines **2** (R = *n*-BuC≡C), **7** (R = Me_3SiC≡C), and **8** (R = *n*-BuC≡C), when subjected to the same conditions,

(7) Anhydrous $AlBr_3$ is the reagent of choice for preparation of trialkynylaluminums, and anhydrous $AlCl_3$ did not give the reproducible results presumably because of its low solubility in nonpolar solvents. For preparation of trialkynylaluminums from the corresponding alkynyllithiums and $AlCl_3$, see: Negishi, E.; Baba, S. *J. Am. Chem. Soc.* **1975**, *97*, 7385.

(8) An independent synthesis of **2** and **3** (R = *n*-BuC≡C, Me_3SiC≡C, and PhC≡C) via an alternative route (Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467) aided our analysis.

(9) The ortho- and para-alkylated anilines can be separated without any difficulty by the ordinary isolation procedures, since they have quite different R_f values (e.g., R_f 0.59 and 0.33 (ether/hexane, 1:9) for **2** and **3** (R = *n*-BuC≡C), respectively).

(10) Kamm, O. *Org. Synth.* **1941**, *1*, 445.

(11) The molecular oxygen should be removed from the reaction system in the alkylation step, since arylhydroxylamines are easily transformed to the corresponding nitrosoarenes by molecular oxygen in the presence of base.

(12) For chemistry of anilenium ions, see: Gassman, P. G.; Campbell, G. A.; Frederick, R. C. *J. Am. Chem. Soc.* **1972**, *94*, 3884. Gassman, P. G.; Campbell, G. A. *Ibid.* **1972**, *94*, 3891, and references cited therein.

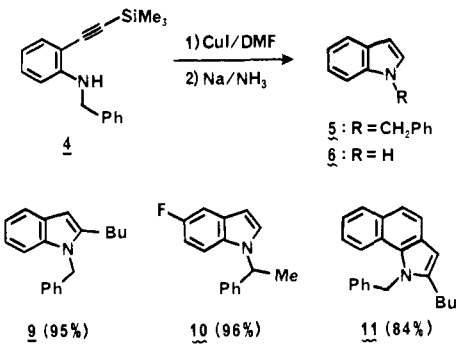
(13) Treatment of **1** with Et_3Al or *i*-Bu_3Al under the similar conditions gave *N*-benzylaniline as a major product.

(14) Prepared from *N*-allyl-*N*-benzylaniline by MCPBA oxidation followed by Meisenheimer rearrangement in 87% yield.

(15) Recent indole syntheses: Ito, Y.; Kobayashi, K.; Saegusa, T. *J. Am. Chem. Soc.* **1977**, *99*, 3532. Mori, M.; Chiba, K.; Ban, Y. *Tetrahedron Lett.* **1977**, 1037. Hegedus, L. S; Allen, G. F.; Bozell, J. J.; Waterman, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 5800. Beugelmans, R.; Roussi, G. *J. Chem. Soc., Chem. Commun.* **1979**, 950. Trost, B. M.; Reiffen, M.; Crimmin, M. *J. Am. Chem. Soc.* **1979**, *101*, 257. Bard, R. R.; Bunnett, J. F. *J. Org. Chem.* **1980**, *45*, 1546. Kozikowski, A. P.; Greco, M. N. *J. Am. Chem. Soc.* **1980**, *102*, 1165. Houlihan, W. J.; Parrino, V. A.; Uike, Y. *J. Org. Chem.* **1981**, *46*, 4511. Wender, P. A.; White, A. W. *Tetrahedron Lett.* **1981**, *22*, 1475. Adam, G.; Andrieux, J.; Plat, M. *Ibid.* **1981**, *22*, 3181. Ueno, Y.; Chino, K.; Okawara, M. *Ibid.* **1982**, *23*, 2575.

(16) Castro, C. E.; Gaughan, E. J.; Owsley, D. C. *J. Org. Chem.* **1966**, *31*, 4071. Addition of $CaCO_3$ improved the yield of the reaction.

(17) Julia, M.; Manoury, P.; Igolen, J. *C. R. Hebd. Seances Acad. Sci.* **1960**, *251*, 394.



produced functionalized indoles **9**, **10**, and **11**, respectively, in excellent yields.

Acknowledgment. This work was supported by the Ministry of Education, Japanese Government (Grant-In-Aids 58110005).

Registry No. 1, 87587-23-3; **2** (R = Me), 5405-13-0; **2** (R = C≡CBu), 87587-24-4; **2** (R = C≡CSiMe$_3$), 87587-25-5; **2** (R = C≡CPh), 87587-26-6; **3** (R = Me), 5405-15-2; **3** (R = C≡CBu), 87587-27-7; **3** (R = C≡CSiMe$_3$), 87587-28-8; **3** (R = C≡CPh), 87587-29-9; **5**, 3377-71-7; **6**, 120-72-9; **7** (R = Me; R′ = CH_2Ph), 87587-30-2; **7** (R = C≡CBu; R′ = CH_2Ph), 87587-31-3; **7** (R = C≡CBu; R′ = CHMePh), 87587-32-4; **7** (R = C≡CSiMe$_3$; R′ = CHMePh), 87587-33-5; **8** (R = Me), 87587-34-6; **8** (R = C≡CBu), 87587-35-7; **8** (R = C≡CSiMe$_3$), 87587-36-8; **9**, 87587-40-4; **10**, 87587-41-5; **11**, 87587-42-6; Me_3Al, 75-24-1; $(BuC{\equiv}C)_3Al$, 45234-85-3; $(Me_3SiC{\equiv}C)_3Al$, 87587-48-2; $(PhC{\equiv}C)_3Al$, 47461-44-9; *N*-benzyl-4-methyl-1-naphthalenamine, 87587-37-9; *N*-benzyl-4-(1-hexynyl)-1-naphthalenamine, 87587-38-0; *N*-benzyl-4-(trimethylsilylethynyl)-1-naphthalenamine, 87587-39-1; *N*-benzyl-*N*-(trimethylsilyloxy)-1-naphthalenamine, 87587-43-7; *N*-benzyl-4-fluoro-*N*-(trimethylsilyloxy)aniline, 87587-44-8; 4-fluoro-*N*-(1-phenethyl)-*N*-(trimethylsilyloxy)aniline, 87587-45-9; *N*-(benzyl)-4-ethyl-*N*-(trimethylsilyloxy)aniline, 87587-46-0; 4-ethyl-*N*-(1-phenethyl)-*N*-(trimethylsilyloxy)aniline, 87587-47-1.

Photoreduction of Methylviologen Sensitized by Dihydroxytin(IV) Uroporphyrin

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Photocatalytic reduction of methylviologen (MV^{2+}) using porphyrins[1-13] or phthalocyanines[14-16] as sensitizers has been reported by several workers. In the presence of suitable catalyst[1-3] $MV^{+\cdot}$ reduces water to H_2 at the expense of a sacrificial electron donor. Central to efficient electron transfer and charge separation is the nature of the MV^{2+}–metalloporphyrin complex.

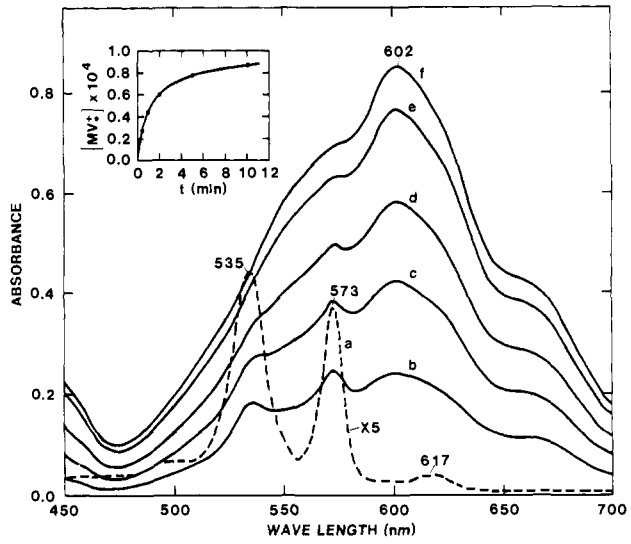

Figure 1. Absorption spectral changes upon irradiation of an aqueous solution of $Sn(OH)_2UroP$ I (1.5×10^{-5} M), MV^{2+} (5.1×10^{-3} M), and EDTA (0.27 M) (a) before irradiation (×5), (b) 30 s, (c) 1 min, (d) 2 min, (e) 5 min, and (f) 10 min total irradiation time. The weak band at 617 nm is from a small amount of the chlorin (see ref 11) formed when the sample was previously deaerated, irradiated to generate over 5 times as much $MV^{2+\cdot}$ as porphyrin in the system, aerated to remove the $MV^{+\cdot}$ generated, and then deaerated again. Inset: Plot of $[MV^{+\cdot}]$ vs. irradiation time. Total power on sample is about 0.4 W (see text).

With metalloporphyrins that have their water solubility conferred by positively charged substituents on the macrocycle, electrostatic repulsion of MV^{2+} prevents close approach and π–π complex formation; electron transfer is slow, but the repulsive interaction in the encounter complex allows reduced acceptor ($MV^{+\cdot}$) to diffuse away before the back reaction can occur. The result is quantum yields for $MV^{+\cdot}$ production ($\phi = 2\phi_{H_2}$) as high as 0.75.[1,2,17,18]

On the other hand for negatively charged substituents, strong electrostatic attraction of the viologen dication results in a tight ground-state complex with the metalloporphyrin. Efficient electron transfer occurs in the complex, but rapid back reaction prevents charge separation and significant production of reduced viologen.[2,8]

The uroporphyrins in alkaline aqueous solutions are an extreme example of the latter category.[19] With eight negatively charged carboxylate groups on the porphyrin ring, MV^{2+} forms a very tight ($\log K \geq 6$) ground-state complex.[19-23] The complex most likely has the pyridinium rings of MV^{2+} flat against and in π–π interaction with the porphyrin π system. Unfortunately, as for the negatively charged meso-substituted porphyrins that have been previously investigated, the π–π complex is photochemically much less active than the repulsive encounter complexes.[1,2,8,17,18]

In contrast with the H_2, Cu, Zn, Pd, Ag, V(IV)O, and other metallouroporphyrins for which we have observed tight π–π complexes and no reduction of MV^{2+}, dihydroxytin(IV) uroporphyrin I ($Sn(OH)_2UroP$) is an efficient photosensitizer of viologen reduction. Figure 1 shows the result of irradiation of a solution containing ethylenediaminetetraacetic acid as an electron

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