donor, MV^{2+}, and Sn(OH)$_2$UroP. Dichlorotin(IV) uroporphyrin I was purchased from Porphyrin Products and further purified and converted to the dihydroxy complex by chromatography on a G-50-40 Sephadex column. [We have been able to make the halogen complexes (SnCl$_2$UroP and SnBr$_2$UroP) in water only in 5 M acid (HCl or HBr).][24]

Upon irradiation of this system a rapid buildup of MV$^{+\cdot}$ is detected by its broad absorption with maximum near 602 nm ($\epsilon_{602} = 1.0 \times 10^4$ M^{-1} cm^{-1}) as illustrated in Figure 1. The sample was irradiated with white light from a 25-W tungsten (Tensor) lamp using an ultraviolet sharp-cut filter (Corning, CS3-75) to eliminate UV light below 380 nm. Under similar conditions Cu-, Ag-, Zn-, Pd-, and V(IV)OUroP and the free base[13] give no reduced viologen.

The quantum yield ϕ for production of MV$^{+\cdot}$ was measured with a band-pass filter (Oriel S-60) (524–565 nm) and a 200-W quartz-iodide lamp source and power meter (Spectra Physics, Model 404). A solution containing EDTA (0.2 M), Sn(OH)$_2$UroP (2.4×10^{-5} M), and MV^{2+} (0.011 M) at pH 9 gave a quantum yield of 0.42 ± 0.1. This value is at least an order of magnitude higher than for other anionic porphyrins[18] and is similar to high quantum yields found for cationic porphyrins such as zinc tetrakis(*N*-methylpyridyl)porphyrin (ZnTMPyP) for which ϕ = 0.75.[18]

As shown in the inset in Figure 1, MV$^{+\cdot}$ reaches a steady-state concentration of about 0.9×10^{-4} M. This is close to the steady-state concentration of 1×10^{-4} M measured by McLendon and Miller[1] for ZnTMPyP under similar conditions. The saturation effect is partly due to screening by the strong absorption of MV$^{+\cdot}$ in the region of the metalloporphyrin absorption bands.[8] The quantum yields quoted are calculated from the maximum rate of MV$^{+\cdot}$ generation at early times before screening is significant.

The quantum yield is a strong function of solution conditions. For example, the MV$^{+\cdot}$ concentration at saturation ranges from 2.5×10^{-6} M at pH 3.2 to 3.5×10^{-4} M at pH 13.1. Therefore, the quantum yield of 0.42 at pH 9 is clearly not obtained at optimum pH. For the donor triethanolamine (0.01 M) at pH 10.2, the concentration of MV$^{+\cdot}$ reached under steady-state conditions is about 50% higher than with EDTA at the same pH and 0.3 M. No photodecomposition of the porphyrin is observed with TEA, whereas some porphyrin decomposition is noted at EDTA concentrations below 0.2 M and at acid pH.

The high activity of the tin uroporphyrin system when compared with other anionic metalloporphyrins can be understood in terms of the electrostatic and steric interactions of the porphyrin and acceptor. Strong axial ligation of hydroxides blocks formation of the tight π–π complex usually favored by the electrostatic, hydrophobic, and charge-transfer forces. Addition of MV^{2+} to a solution of Sn(OH)$_2$UroP produces only subtle changes in the absorption spectrum of the porphyrin. These changes are not typical of the π–π complex for which the Soret band shifts and large absorbance changes in the Soret and visible bands are noted.[8,19-23] Shifts in Raman lines are observed also, and they indicate the porphyrin ring acts as an acceptor in the ground-state complex.[20-23]

That the axial ligands block π–π complex formation is further supported by the failure of Sn(OH)$_2$UroP to aggregate under solution conditions for which other uroporphyrins aggregate as evidenced by characteristic changes in their absorption spectra. At room temperature in 0.1 M NaOH (pH 14) uroporphyrins are monomeric up to about 0.01 M.[19-23,25-27] Upon addition of salt (5 M) most metallouroporphyrins dimerize resulting is large spectral changes, especially in the Soret.[19-23,25-27] In contrast, the absorption spectrum of Sn(OH)$_2$UroP is unchanged by addition of NaCl. Neutralization of the carboxylates by protonation at acid pH normally also results in spectral changes characteristic of π–π aggregation, but not in the case of Sn(OH)$_2$UroP.[27]

Another indication that the axial ligands block π–π aggregation is that dihydroxytin coproporphyrin, which has uroporphyrin's four acetates replaced by methyl groups and, hence, has a lower charge (−4), does not show a change in its absorption spectrum upon extreme dilution (8×10^{-8} M). Other metallocoproporphyrins, e.g., Cu, are normally aggregated down to 10^{-6} M and below this concentration show a characteristic shift in the Soret band upon formation of monomer.[27]

The high activity of anionic Sn(OH)$_2$UroP in photoreduction of MV^{2+} results from (1) prevention of unreactive complexes by the steric constraints provided by the strongly bound axial ligands of tin(IV) and (2) electrostatic interactions of MV^{2+} and charged donor species with the negatively charged porphyrin. At present we cannot distinguish between reductive and oxidative quenching mechanisms for photosensitization, but redox potentials deduced from the dihydroxytin octaethylporphyrin analogue suggest a reductive cycle is operative.[11,12,28-30] Even in the case of a reductive quenching mechanism π–π complexation with MV^{2+} would render the system photochemically inactive. Ag and VO porphyrins also have redox potentials that indicate the possibility of a reductive cycle, but they form strong MV^{2+} complexes and are found to be inactive.[27] Neutral or positively charged electron donors (e.g., TEA) show some advantage over EDTA. The pH dependence of the steady-state concentration probably results from varying the charge at the ring periphery and from successive deprotonations of EDTA. Weak attraction of donors and acceptors coupled with steric blocking of tight, inactive complexes by strongly bound axial ligands may enhance Sn(OH)$_2$UroP activity.

Acknowledgment. Thanks to D. S. Ginley for stimulating and helpful discussions and M. M. Dobry for her technical assistance.

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(24) Gouterman, M.; Shelnutt, J. A.; Dobry, M. M., unpublished results.

(25) Shelnutt, J. A.; Dobry, M. M.; Satterlee, J. D., manuscript in preparation.

(26) Satterlee, J. D.; Shelnutt, J. A., manuscript in preparation.

(27) Shelnutt, J. A.; Dobry, M. M. *J. Phys. Chem.* **1983**, *87*, 3012.

(28) Furhop, J. H.; Kadish, K. M.; Davis, D. G. *J. Am. Chem. Soc.* **1973**, *95*, 5140.

(29) Gouterman, M.; Schwarz, F. P.; Smith, P. D. *J. Chem. Phys.* **1973**, *59*, 676.

(30) Fuhrhop, J.-H.; Krüger, W.; David, H. H. *Liebigs Ann. Chem.* **1983**, 204.

Photocatalytic Conversion of Primary Amines to Secondary Amines and Cyclization of Polymethylene-α,ω-diamines by an Aqueous Suspension of TiO$_2$/Pt

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A number of studies concerning the photocatalytic action of semiconductor materials, particularly n-type TiO$_2$ and related composites, have focused on the utilization of solar energy to produce hydrogen from water.[1] More recently several attempts have been made to extend heterogeneous photocatalysis with dispersed semiconductors to synthetic chemistry.[2-7] We report

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(1) (a) Bard, A. J. *J. Photochem.* **1979**, *10*, 59; (b) *Science (Washington, D.C.)* **1980**, *207*, 139; (c) *J. Phys. Chem.* **1982**, *86*, 172. (d) Nozik, A. J. *Annu. Rev. Phys. Chem.* **1978**, *29*, 189. (e) Wrighton, M. S.; Wolczanski, P. T.; Ellis, A. B. *J. Solid. State Chem.* **1977**, *22*, 17.

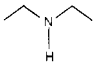
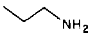
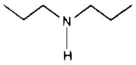
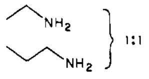
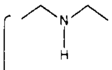
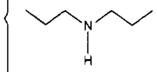
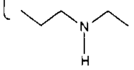
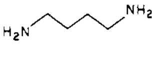
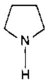
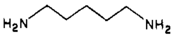
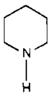
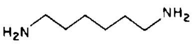
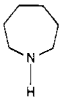
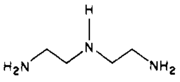
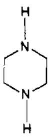
(2) (a) Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 2239; (b) *Ibid.* **1978**, *100*, 5985.

(3) Izumi, I.; Dunn, W. W.; Wilbourn, K. O.; Fan, F. F.; Bard, A. J. *J. Phys. Chem.* **1980**, *84*, 3207.

(4) Kanno, T.; Oguchi, T.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1980**, *21*, 467.

0002-7863/83/1505-7180$01.50/0

Table I. Products of Photocatalytic Reactions of Primary Monoamines and Diamines in Aqueous Solution by TiO_2/Pt Powder[a]

entry	substrate	product	yield,[b] %	selectivity,[c] %	^{13}C NMR[d]
1			33	68	43.33, 13.62
2			24	55	51.20, 22.19, 11.86
3			9	22	
			7	18	
			12	30	50.96, 43.92, 21.96, 13.62, 11.74
4			67	93	46.46, 25.66
5			33	87	46.38, 25.71, 24.31
6			20	67	48.03, 28.77, 27.24
7			8	16	45.68

[a] On irradiation of Ar-purged suspensions of TiO_2/5 wt % Pt (50 mg) in aqueous amine solutions (60–120 μmol, 5 mL) for 20 h at $\lambda_{ex} >$ 300 nm and room temperature. [b] GLC yields based on starting amines. [c] Molar ratio of product secondary amine to NH_3. [d] δ values in 30 vol % D_2O-H_2O, 100 MHz.

here a novel photocatalytic process of synthesizing secondary amines from primary amines in aqueous solution by the use of a powdered mixture of TiO_2 with platinum black. These reactions proceeded efficiently at ambient temperature, in contrast to thermal processes by homogeneous ruthenium[8] and heterogeneous palladium[9] catalysts.

In the general procedure, anatase TiO_2 (Merck) was ground with 5 wt % of Pt black. An Ar-purged suspension of 50 mg of the TiO_2/Pt catalyst in 5 mL of distilled water containing the amine (60–120 μmol) was irradiated with stirring at $\lambda_{ex} > 300$ nm (500-W high-pressure mercury arc), at room temperature, treated with a small amount of NaCl, and then centrifuged to remove the catalyst. The filtrate was analyzed by GLC, ^{13}C NMR, and GC-MS, and the products were confirmed by comparison with authentic samples.

Irradiation of TiO_2/Pt-suspended aqueous solutions of primary amines bearing the α-methylene group ($-CH_2NH_2$) led to several acyclic and cyclic secondary amines (Table I). These products were not produced in the dark, nor with irradiation without the TiO_2/Pt. The rate of the overall conversion of the starting amine was negligibly small[10] when TiO_2 powder without Pt was used, while TiO_2/Pt showed much higher activity. Although the reaction rate increased linearly upon increasing the Pt content up to 20 wt %, the best selectivity[11] of secondary amine formation was achieved with ~5 wt % of Pt.

Typically, propylamine (entry 2) was converted to symmetrical dipropylamine (24% GLC yield at a 34% conversion of propylamine), with liberation of NH_3 (22%, by indophenol blue method) in aqueous solution (pH 11.4). Minor products, 1-propanol (7%), propionaldehyde (2%), and H_2 (3%, by GC), were also formed. The formation of such oxygenated compounds under Ar suggests the participation of water in this reaction system. Furthermore, the molar ratio of the total carbon-containing product to the liberated NH_3 was nearly unity (~0.95).[11] The yield of dipropylamine rapidly decreased, whereas that of propionaldehyde increased upon raising the pH with NaOH (dipropylamine was not produced at pH 14.0).

In a comparative experiment, similar photocatalytic reaction (10 h) of propylamine (600 μmol) in acetonitrile (5 mL, not dehydrated) produced *N*-propylidenepropylamine (*m/e* 99 (M^+, relative intensity 7.1%), 84 ($(M - CH_3)^+$, 3.9%), 70 ($(M - CH_3CH_2)^+$, 100%)) along with dipropylamine (2%), propionaldehyde (3%), and H_2 (7%). Post-addition of 5 mL of water to the acetonitrile solution decreased the imine to a negligible amount and increased the overall yield of the aldehyde to 8%.

An Ar-purged solution of propylamine (608 μmol) in 2 mL of D_2O (99.85%) with a suspension of TiO_2/Pt was also irradiated. In contrast to the mass spectrum of dipropylamine produced in H_2O (*m/e* 101 (M^+, relative intensity 5.6%), 72 ($(M - CH_3CH_2)^+$, 44%), 30 ($(M - CH_3CH_2 - CH_3CH{=}CH_2)^+$, 100%)), the distribution of deuterium-labeled M^+ signals was observed for dipropylamine from the D_2O solution: i.e., d_0 (*m/e* 101, unla-

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(5) (a) Fox, M. A.; Chen, C. C. *J. Am. Chem. Soc.* **1981**, *103*, 6757. (b) Fox, M. A.; Chen, M.-J. *J. Am. Chem. Soc.* **1983**, *105*, 4497.

(6) Pavlik, J. W.; Tantayanon, S. *J. Am. Chem. Soc.* **1981**, *103*, 6755.

(7) Fujihira, M.; Satoh, Y.; Osa, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 666.

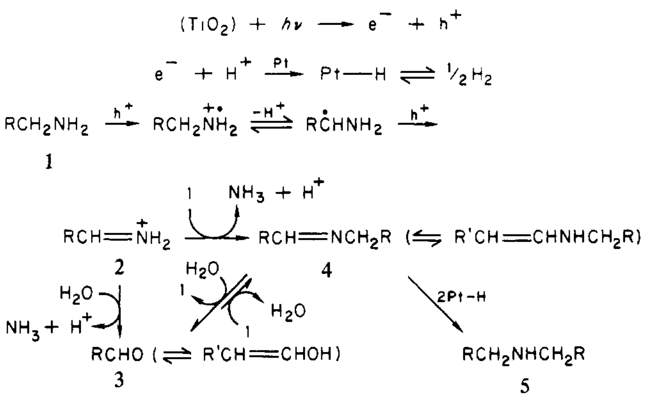
(8) (a) Khai, B.-T.; Concilio, C.; Porzi, G. *J. Organomet. Chem.* **1981**, *208*, 269. (b) Khai, B.-T.; Concilio, C.; Porzi, G. *J. Org. Chem.* **1981**, *46*, 1756.

(9) Yoshimura, N.; Moritani, I.; Shimamura, T.; Murahashi, S.-T. *J. Am. Chem. Soc.* **1973**, *95*, 3038.

(10) Only minor amount of H_2 could be detected after 20-h irradiation.

(11) The net reactions involved are as follows: $2RCH_2NH_2 \rightarrow (RCH_2)_2NH + NH_3$; $RCH_2NH_2 + H_2O \rightarrow RCH_2OH + NH_3$; $RCH_2NH_2 + H_2O \rightarrow RCHO + NH_3 + H_2$. Thus, each of the reactions produces NH_3 in amounts equimolar with secondary amine, alcohol, or aldehyde. In this light, the molar ratio of secondary amine to NH_3 was used for convenience to estimate the selectivity of secondary amine formation listed in Table I.

Scheme I



beled):d_1 (102):d_2 (103):d_3 (104):d_4 (105):d_5 (106) = 3:17:23:37:17:3.

A possible mechanism based on photoelectrochemical principles[1] is outlined in Scheme I. The initial step involves the creation, on the illuminated TiO_2, of an electron-hole pair, which is effectively separated by the partial Pt coverage. The electron (e^-) reduces a proton on the Pt site, producing an adsorbed hydrogen atom (Pt-H) and H_2. The hole (h^+) oxidizes the primary amine **1** at the TiO_2-water interface to form immonium ion **2**, which is expected to undergo hydrolysis to aldehyde **3** and NH_3.[12] The key step leading to secondary amine **5** would be the formation of a Schiff base intermediate **4** by reactions of **1** with **2** and more probably with **3**.[13] Although the aqueous solution system does not favor the formation of **4**, which is in equilibrium with **1** and **3**, hydrogenation across the C=N and/or C=CN bond of **4** by the Pt-H may occur to produce **5**. Indeed, dipropylamine (42%) was obtained from a H_2-purged aqueous solution (5 mL) of equimolar (122 μmol) mixture of propylamine and propionaldehyde when treated with Pt (2.5 mg) for 20 h in the dark.[14]

According to Scheme I, the Pt-catalyzed deuteration of **4** can lead to the d_2 product in D_2O and additional ($\geq$3) deuterium incorporation can be accounted for by the keto-enol and imine-enamine tautomerisms of **3** and **4**. Upon raising the pH, the concentration of **4** would decrease, which would be responsible for the decreased yield of **5**. It is also obvious that the conversion of **1** to **5** depends on a dual function of the TiO_2/Pt, which has oxidizing and reducing sites acting as short-circuited electrode systems. Bard et al. have previously demonstrated the analogous property of partially metalized semiconductor photocatalysts in the Kolbe reaction,[2] but these results provide a potentially new mode of photocatalytic synthetic application.

Table I also shows a few extensions of this photocatalytic reaction. A 1:1 mixture of ethylamine and propylamine (entry 3) led to unsymmetrical *N*-ethylpropylamine (12%) accompanied by symmetrical diethylamine (9%) and dipropylamine (7%). Several cyclic secondary amines could be derived from polymethylene-α,ω-diamines (entries 4-6). Clearly, the present method is more favorable for intramolecular conversion of primary diamines to cyclic secondary amines (ca. 70-90% selectivity).[15]

Further extensions of this photocatalytic synthesis are now being explored.

Registry No. Anatase, 1317-70-0; platinum black, 7440-06-4; ethylamine, 75-04-7; propylamine, 107-10-8; 1,4-butanediamine, 110-60-1; 1,5-pentanediamine, 462-94-2; 1,6-hexanediamine, 124-09-4; *N*-(2-aminoethyl)-1,2-ethanediamine, 111-40-0.

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[12] Barnes, K. K.; Mann, C. K. *J. Org. Chem.* **1967**, *32*, 1474.

[13] Recently, Fox et al. have suggested a similar mechanism of the Schiff base formation (see ref 5b).

[14] Similar treatment of propionaldehyde (125 μmol) gave 1-propanol (3%, 24 h) under H_2.

[15] Reaction of 1,3-butanediamine (100 μmol) in the presence of $RuCl_2(Ph_3P)_3$ (2 μmol) in 5 mL of THF (26 h at 30 °C under Ar) resulted in a negligible amount of pyrrolidine (<1 μmol). At much higher temperature a good yield has been achieved (see ref 8b).

Homoenolate Dianions. Intramolecular Rearrangements of 1,4-Dilithio-*N*-phenyl Amides

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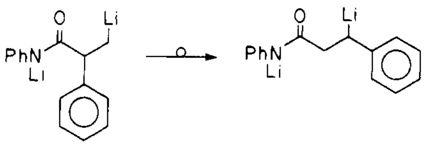
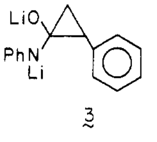
We report here the rearrangement of α-phenyl-1,4-dilithio-*N*-phenyl amide **1** to the more stable β-phenyl-1,4-dilithio derivative **2** (at -40 °C in THF). This rearrangement most likely proceeds through a transient dilithiocyclopropane intermediate such as **3**.



1 **2**



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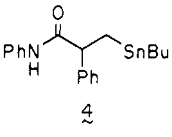

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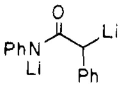

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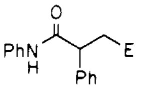

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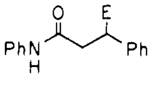

7

In contrast to the transient homoenolates generated by the well-known base-catalyzed opening of cyclopropanol derivatives,[1] the homoenolate dianion **2**, derived from **3**, can be used to functionalize the β-carbon atom with various electrophiles.[2] Although the highly deactivated carbonyl groups of *N*-lithio-*N*-phenyl amides are quite inert toward intermolecular nucleophilic attacks by organolithium reagents,[3] they appear susceptible to intramolecular reactions to form dilithiocyclopropane derivatives.[4]

The precursor *N*-phenyl-2-phenyl-3-(tri-*n*-butylstannyl)propionamide (**4**) was prepared in 80% yield by treatment of the 1,3-dilithio derivative **5** with (iodomethyl)tri-*n*-butyltin in THF.[5] Addition of 2 equiv of *n*-butyllithium to a cold (-70 °C) THF solution of **4** containing 1,4-diazabicyclo[2.2.2]octane (DABCO, 2 equiv) produced a light yellow solution containing **1**.[6,7] This dilithio species is stable at -70 °C for >90 min. Reaction of electrophiles (D_2O and Me_3SiCl) with this light yellow solution at -70 °C gave only **6** (E = D and E = Me_3Si) (Table I). When the light yellow solution was warmed to 0 °C, it turned dark orange. Addition of various electrophiles (D_2O, Me_3SiCl, Bu_3SnCl, and 5-nonanone) to this orange solution gave only **7** (Table I).

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[1] For a review, see: Werstiuk, N. H. *Tetrahedron* **1983**, *39*, 206-268.

[2] Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1983**, *105*, 651-652.

[3] Gay, R. L.; Hauser, C. R. *J. Am. Chem. Soc.* **1967**, *89*, 1647-1651. Goswami, R. Ph.D. Dissertation, Washington State University, Pullman, WA, 1977, p 78; *Diss. Abstr. Int. B* **1977**, *38* (3), 1206-1207. Fuhrer, W.; Gschwend, H. W. *J. Org. Chem.* **1979**, *44*, 1133-1136. Baldwin, J.; Dupont, W. *Tetrahedron Lett.* **1980**, *21*, 1881-1882. Mpango, G. B.; Mahalanabis, K. K.; Mahdavi-Damghani, Z.; Snieckus, V. *Ibid.* **1980**, *21*, 4823-4826.

[4] Houlihan, W. J.; Parrino, V. A.; Uike, Y. *J. Org. Chem.* **1981**, *46*, 4511-4515 and references cited therein.

[5] (a) Seyferth, D.; Andrews, S. B. *J. Organomet. Chem.* **1971**, *30*, 151-166. (b) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481-1487.

[6] For previous reports, see: Goswami, R. *J. Am. Chem. Soc.* **1980**, *102*, 5973-5974. Goswami, R.; Corcoran, D. E. *Tetrahedron Lett.* **1982**, *23*, 1463-1466.

[7] Meyer, N.; Seebach, D. *Chem. Ber.* **1980**, *113*, 1290-1303.

0002-7863/83/1505-7182$01.50/0