GLC assay of the crude product revealed no contamination of the cis isomer.

Reduction of bromobenzene with dibutylcopperlithium in THF and subsequent treatment with excess allyl bromide afforded allylbenzene (64% isolated yield). This and previous findings by Whitesides et al.[4] suggest the present method is applicable not only to bromocyclopropanes but to bromoarenes. A study to find the scope and limitations of this method is now in progress.

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Hydrogen Transfer Photocatalyzed by Metalloporphyrins in Visible Light. Photoinduced Redox Cycling of the Catalyst

Sir:

Porphyrins have been shown to be active as chemical catalysts and electrocatalysts for hydrogen-transfer reactions.[1] Here we report the photochemical hydrogen transfer from a donor (tertiary amine) to an acceptor (nitrobenzene) at room temperature, photocatalyzed by metalloporphyrins excited with visible light. The photocatalyst cycles in these reactions between its oxidized and reduced forms, porphyrin, chlorin, and isobacteriochlorin. Similar photochemical cycles have been attempted in the past. Phlorin formed on photoreduction of water-soluble free-base porphyrins by EDTA was oxidized back to parent porphyrin in the dark by oxygen.[2] Zinc tetraphenylporphyrin (ZnTPP) was photoreduced by benzoin, using UV light absorbed by benzoin, to dihydro- and tetrahydroporphyrins which were reoxidized by oxygen in the dark.[3] Zinc tetraphenylchlorin (ZnTPC) was photooxidized to ZnTPP by quinones with visible light.[4] Pyrochlorophyll was found to sensitize the photoreduction of nitro compounds using hydrazobenzene in ethanol-pyridine solutions.[5] Tin(IV) octaethylporphyrin dihydroxide and germanium(IV) octaethylporphyrin dihydroxide were photoreduced to a mixture of the corresponding chlorins and isobacteriochlorins with EDTA in acetic acid.[6] Both octaethylporphyrin and tetraphenylporphyrin tin(IV) dichloride complexes were photoreduced to isobacteriochlorins through the chlorins by $\mathrm{SnCl_2 \cdot 2H_2O}$ in pyridine.[7]

Table I. Conversion[a] to Products as Function of Irradiation[b] Time for a Solution of 5×10^{-4} M $\mathrm{Sn^{IV}TPPCl_2}$, 1 M NMP, and 1 M $\mathrm{PhNO_2}$ in Benzene at Room Temperature

Irradiation time, h	Aniline	Azoxybenzene	Azobenzene	*N*-Methylpyrrole
10	0.20	0.28	0.10	0.60
20	0.33	0.65	0.12	1.10
30	0.46	0.77	0.14	1.56
50	0.63	1.10	0.15	2.32
80	0.96	1.60	0.19	2.80

[a] Percent of initial nitrobenzene. [b] $\lambda_{\mathrm{excit}} > 500$ nm.

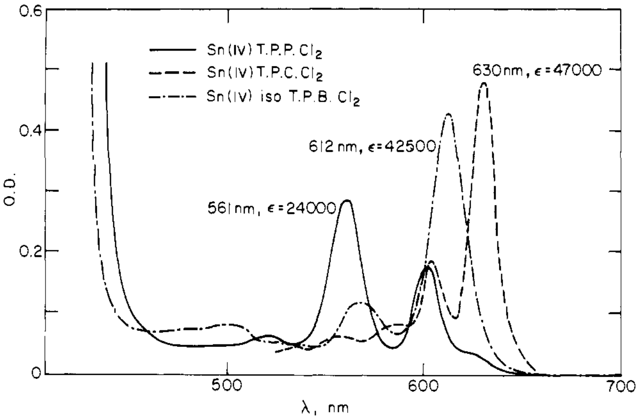

Figure 1. Absorption spectra of $\mathrm{Sn^{IV}TPPCl_2}$, $\mathrm{Sn^{IV}TPCCl_2}$, and $\mathrm{Sn^{IV}TPisoBCl_2}$ in benzene solution.

When degassed solutions of 10^{-4}–10^{-3} M of tin(IV) tetraphenylporphyrin dichloride ($\mathrm{Sn^{IV}TPPCl_2}$) or germanium(IV) tetraphenylporphyrin dichloride ($\mathrm{Ge^{IV}TPPCl_2}$) in benzene containing 1 M *N*-methylpyrrolidine (NMP) and 1 M nitrobenzene ($\mathrm{PhNO_2}$) are irradiated with visible light ($\lambda > 500$ nm), aniline, azoxybenzene, and azobenzene are formed as the reduction products of $\mathrm{PhNO_2}$, and *N*-methylpyrrole as the dehydrogenation product of NMP.[8] No reaction occurs in the dark or when solutions are irradiated in the absence of the porphyrin complex. Results for a typical photocatalytic run are presented in Table I.

The photoreduction and photooxidation steps can be studied separately. Irradiation of benzene solutions of $\mathrm{Sn^{IV}TPPCl_2}$ or $\mathrm{Ge^{IV}TPPCl_2}$ in the presence of an aliphatic tertiary amine results in the complete photoreduction of the porphyrin complexes to the corresponding metallo isobacteriochlorins via the chlorin complexes. The optical absorption spectra for $\mathrm{Sn^{IV}TPPCl_2}$ and its reduced complexes are given in Figure 1 and are identical with those reported in the literature.[9] The rate of the photoreduction depends on the electron donor properties of the amines as was found before in the photoreduction of free base porphyrins.[10]

Irradiation of benzene solutions of tin(IV) tetraphenylisobacteriochlorin ($\mathrm{Sn^{IV}TPiso\text{-}BCl_2}$) or $\mathrm{Ge^{IV}TPisoBCl_2}$ in the presence of $\mathrm{PhNO_2}$ results in their photooxidation to the corresponding porphyrins, via the chlorin complexes. The photooxidation reaction appears to be rate determining and is responsible for the low rate of the photocatalysis reaction as given in Table I. Acetic anhydride ($\mathrm{Ac_2O}$) was found to accelerate the photooxidation reaction and therefore was added

Table II. Conversion[a] to Products as a Function of Photocatalyst in the Presence of 0.5 M Ac_2O for 1 M $PhNO_2$ and 1 M NMP in Benzene after 15 h of Irradiation[b]

Porphyrin[c]	PhNHCOMe	PhNHOCOMe	*N*-Methylpyrrole
ZnTPP	3.84	0.50	5.50
$Sn^{IV}TPPCl_2$	14.80	2.50	17.70

[a] Percent of initial nitrobenzene. [b] λ_{excit} >500 nm. [c] 5×10^{-4} M porphyrin.

Table III. Concentration of Photocatalyst[a] in Its Steady-State[b] as a Function of Donor and Acceptor Substrates

Donor	Acceptor	TPC, %	IsoB, %
Triethylamine, 1 M	Nitrobenzene[c], 1 M	60	40
N-Methylpyrrolidine, 1 M	Nitrobenzene,[c] 1 M	0	100
N-Methylpyrrolidine, 1 M	*p*-Dinitrobenzene,[d] 0.1 M	50	50

[a] 5×10^{-4} M $Sn^{IV}TPPCl_2$ in benzene. [b] 1 h of irradiation. [c] λ_{excit} >500 nm. [d] λ_{excit} >550 nm.

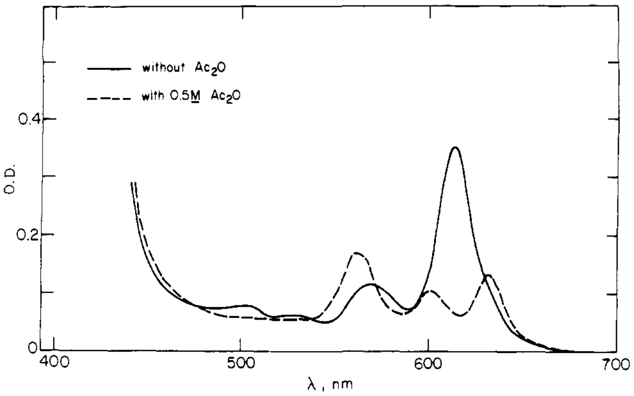

Figure 2. Optical spectra of photocatalyst ($Sn^{IV}TPPCl_2$) steady state with and without Ac_2O.

as a cocatalyst in the photocatalytic reaction. Table II gives the results. The reduction step is relatively unaffected by the addition of acetic anhydride. The reduction products are mostly acetanilide (PhNHCOMe) and some ester (PhNHOCOMe).

In Table III is shown how a steady-state concentration of chlorin and isobacteriochlorin establishes itself soon after the start of the photocatalytic run. This steady state depends on the donor and acceptor properties of the substrates. Replacement of triethylamine by the better donor NMP moves the steady state entirely to isobacteriochlorin, while replacement of $PhNO_2$ by the better acceptor, *p*-dinitrobenzene, moves it back toward a chlorin-isobacteriochlorin mixture. In Figure 2 is shown how the addition of Ac_2O, which accelerates the phooxidation reaction, moves the steady state from isobacteriochlorin toward a chlorin-porphyrin mixture.

ZnTPP in the absence of Ac_2O is inactive as a photocatalyst, but from Table II it can be seen that in the presence of Ac_2O it is active. Because ZnTPP is not photoreduced by tertiary amines the cocatalytic effect of Ac_2O cannot be attributed to an acceleration of the photooxidation step in this case and the mechanism must be different.

The mechanism of porphyrin photocatalysis in photosynthesis is of great importance. Our observations prove that metalloporphyrins can act as photocatalysts in vitro and produce chemical conversions under specific conditions. Work is in progress to study the mechanism of these reactions in more detail and to search for other metalloporphyrins with photocatalytic properties.

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Intrinsic Acidities of Ketones and Aldehydes. Bond Dissociation Energies and Electron Affinities

Sir:

Recently[1] we reported the gas phase acidities of a number of carbon acids RH. These were obtained from measurement of the gas phase equilibria 1.

$$R_1H + R_2^- = R_1^- + R_2H \qquad (1)$$

The data included the acidities of several ketones and diketones. The present communication reports new measurements for several ketones and aldehydes. The new data, when combined with Brauman's[2] recent results on the electron affinities of the corresponding enolate radicals R, reveal some interesting regularities in the changes of the gas phase acidities of RH, the electron affinities of R, and the bond dissociation energies of R-H.

The results from the measured equilibria 1 are displayed in Figure 1. The measurements were made in a high pressure mass spectrometer,[3] using procedures similar to those described earlier.[1]

The free energy changes determined at 500 K, $\Delta G_1°(500) = RT \ln K_1$ shown in Figure 1, include multiple thermodynamic cycles which are consistent to better than ±0.3 kcal/mol. The $\Delta G_2°(500)$ values relating the acidities to that of the primary standard HCl (eq 2) were obtained via pyrrole whose $\Delta G_2°(500)$ was determined in separate measurements.[1,4] The $\Delta G_2°(600)$ values for pyrrole, acetophenone, and acetone determined in the earlier publication[1] (at 600 K) are also shown in Figure 1. As can be seen the present values for pyrrole and acetophenone are very close to those obtained earlier. However the new $\Delta G_2°(500)$ value for acetone is some 2 kcal/mol higher.[5] From $\Delta G_2°$, $\Delta H_2°$ can be evaluated by calculating[7] $\Delta S_2°$. In turn the $\Delta H_2°$ combined with the known $D(\text{H-Cl}) - \text{EA(Cl)} = 20$ kcal/mol[8,9] leads to $D(\text{R-H}) - \text{EA(R)}$.

$$RH + Cl^- = R^- + HCl \qquad (2)$$