

## References and Notes

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- (3) Only traces of the cyclobutadiene complex **4** were observed under our reaction conditions, but this material is formed by thermolysis of **3** at higher temperatures.<sup>1</sup>
- (4) <sup>1</sup>H NMR (CCl<sub>4</sub>): δ 1.41 (d, *J* = 7 Hz, 3 H), 3.90 (q, *J* = 7 Hz, 1 H), 5.07 (br s, 1 H), 5.31 (br s, 1 H), 7.1 (m, 10 H) ppm. Mass spectrum parent peak: *m/e* 208.
- (5) This material is identical (IR, NMR) with that prepared by treating 1,2-diphenyl-2-propanone (cf. Y. Sawaki and Y. Ogata, *J. Am. Chem. Soc.*, **97**, 6983 (1975)) with triphenylphosphonium methylide.
- (6) Identified by comparison of spectral data with those reported by M. A. Umberto and E. H. White, *J. Org. Chem.*, **41**, 479 (1976). (**Z**)-**6** was also prepared by acid-catalyzed isomerization of **5** (see text).
- (7) Metallocycle **3** is an intermediate in the CpCoL<sub>2</sub>-induced cyclotrimerization of diphenylacetylene to hexaphenylbenzene; cf. (a) Y. Wakatsuki, T. Kuramitsu and H. Yamazaki, *Tetrahedron Lett.*, 4549 (1974); see also (b) D. R. McAlister, J. E. Bercauw, and R. G. Bergman, *J. Am. Chem. Soc.*, **99**, 1666 (1977).
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- (10) NMR (C<sub>6</sub>D<sub>6</sub>) of (η<sup>2</sup>-C<sub>5</sub>H<sub>5</sub>)Co(PMe<sub>3</sub>)(CH<sub>3</sub>)<sub>2</sub>: δ 4.34 (s, 5 H), 0.80 (d, *J* = 9 Hz, 9 H), 0.16 ppm (d, *J* = 6 Hz, 6 H).
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- (16) For simplicity, reactions of **5** in Scheme II are illustrated for only one enantiomer of this compound.
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## Photoionization by Green Light in Micellar Solution

Sir:

The last few years have seen a keen interest in many laboratories in the development of chemical systems for the storage

of solar energy. The basis of many suggestions is the production of ions following light absorption, and subsequently to utilize the ions either to degrade water or to produce electric current. In some instances the light induces electron transfer, while in other systems a genuine release of electrons to the solvent is obtained. Increased attention to the effect of phase on photoionization has developed concurrently with increasing interest in solar energy storage. In particular it was shown that aqueous micellar systems strongly promote photoionization of pyrene,<sup>2,3</sup> phenothiazine,<sup>4,5</sup> and tetramethylbenzidine.<sup>6</sup> The energy required for photoionization in these micellar systems is several electronvolts below that required in the gas phase. The energy necessary to reduce the ionization potential is provided by the polarization of the medium by the cation and by the particular energy state that the electron enters into in the system. The solute cation remains associated with the micellar phase and the electron is associated with the aqueous phase as a hydrated electron, e<sub>aq</sub><sup>-</sup>. Subsequent neutralization is inhibited and very effective charge separation is produced with anionic micelles. To date all synthetic systems have operated with light in the near UV part of the sun's spectrum.

In the present letter we wish to report the use of the anionic micellar system sodium lauryl sulfate to produce the photoionization of 3-aminoperylene with green light, λ = 530 nm. This is some 4.6 eV below the gas phase ionization potential and well into the solar spectrum. 3-Aminoperylene in various liquid systems was excited by 20-ns pulses of light, λ = 5500 nm, from a Q switched frequency doubled neodymium laser. The intensity of the laser pulse was systematically varied, over a range from 0.15 to 0.05 J/pulse, to check the intensity dependence of the process. The short-lived ions and excited states produced were monitored by conventional fast spectrophotometry with a response time of 2 ns.<sup>7</sup> In the low-conducting Igepal solutions fast conductivity methods were also used to monitor the ions produced.

Figure 1 shows the transient absorption spectra of 6 × 10<sup>-5</sup> M 3-aminoperylene (Amper) in sodium lauryl sulfate (NaLS) and cetyltrimethylammonium bromide (CTAB) in the range 500–800 nm. In NaLS solutions a strong absorption is observed above 650 nm which is removed by typical electron scavengers such as O<sub>2</sub> and N<sub>2</sub>O. The difference between the spectra in N<sub>2</sub> and N<sub>2</sub>O is also shown, and this compares favorably with the literature spectrum for the hydrated electron e<sub>aq</sub><sup>-</sup>. In the presence of O<sub>2</sub> the absorption decays rapidly with *k* = 1.8 × 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup> which is in excellent agreement with the rate constant for e<sub>aq</sub><sup>-</sup> + O<sub>2</sub> given in the literature.<sup>9</sup> Hence the absorption is attributed to the hydrated electron, e<sub>aq</sub><sup>-</sup>, which has a reported absorption maximum at 720 nm. The yield of e<sub>aq</sub><sup>-</sup> is lower in the cationic micelle, CTAB, and parallels previous data with pyrene<sup>2</sup> and phenothiazine.<sup>4</sup> The absorption at 630–640 nm is unaffected by O<sub>2</sub> and is due to the radical cation, (Amper)<sup>+</sup>. The strong maxima 560 and 600 nm in the CTAB spectrum decay in the presence of O<sub>2</sub> and are due to excited triplet aminoperylene. The yield of excited states is larger in CTAB than in NaLS which is consistent with the decreased yield of photoionization in the CTAB system compared with that in NaLS.

The insert in Figure 1 illustrates the dependence of the photoionization yield of AP on the intensity of the laser beam, as the ODX1000 of the hydrated electron at 720 nm vs. the laser beam intensity in arbitrary units. The photoionization of AP is linearly dependent on beam intensity in the anionic, NaLS micelles, and only one photon of 2.34 eV is required to promote ionization. This corresponds to a lowering of the ionization threshold by greater than 4.6 eV. The gas phase ionization potential is ~7.0 eV as estimated by appearance potential measurements. However, in both cationic, CTAB, and nonionic, Igepal CO-630, micelles the photoionization process varies as the square of the laser intensity indicating a

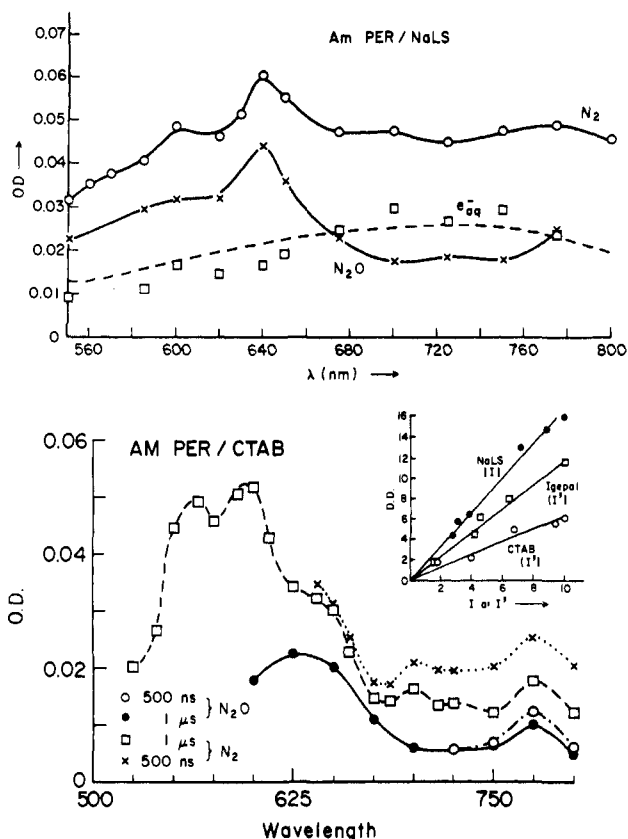


Figure 1. Photoionization of aminoperylene in micellar solution and spectra of short-lived transients with pulses of 530-nm light. Insert: effect of laser intensity or square of laser intensity on the yield of photoionization in NaLS, CTAB, and Igepal micelles.

biphotonic mechanism. The measurement of photocurrent produced in the Igepal sample also supports a biphotonic mechanism for photoionization.

The data clearly show the marked effect of micellar environment on the yield of photoionization of 3-aminoperylene. By comparison with other systems<sup>10</sup> this molecule is most probably situated in the surface region of the micelle between the polar head groups and the decrease in the ionization potential is due to the energy gained by the excited molecule at the micelle surface. The ionization potential in solution,  $I_s$ , is related to that in the gas phase  $I_g$  by the expression

$$I_s = I_g + P_+ + V_0$$

where  $V_0$  is the energy state of the electron in water which is reported  $-1.5$  eV,<sup>11</sup> and the cation polarization  $P_+$  which is reported as  $-1.6$  eV for 3-aminoperylene in alkanes.<sup>12</sup> The polarization energy may be approximated by the Born equation

$$P_+ = -\frac{e^2}{2r} \left(1 - \frac{1}{\epsilon}\right)$$

where  $r$  is the separation of the solvent and ion,  $e$  the electron charge, and  $\epsilon$  the effective high frequency dielectric constant of the medium. In isoctane with  $\epsilon \approx 2$  and  $r \approx 2.1$  Å a  $P_+$  of  $-1.5$  eV is calculated in agreement with experimental data. Aminoperylene is situated between the negatively charged sulfate groups of the NaLS micelle. The polarization energy of the cation could be much larger under these conditions owing to the availability of the delocalized electron of the head group which can participate in and enhance the polarization effect. A cationic or neutral micelle cannot participate to the same enhanced degree in the polarization effect. The Born equation value for  $P_+$  in NaLS may be as large as  $-3.2$  eV or double that in an alkane if the effective  $\epsilon$  on the micelle surface is large. The total lowering of the IP is then  $-4.7$  eV.

The experimental data give the first example of the one photon photoionization of a simple molecule with long wavelength light, and illustrate possible designs for systems where light energy is converted to ion chemistry which may be later utilized to recover the stored energy. This latter aspect of the energy storage cycle is now under further study.

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## References and Notes

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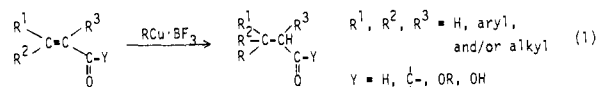
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## RCu·BF<sub>3</sub>. 3.1 Conjugate Addition to Previously Unreactive Substituted Enoate Esters and Enoic Acids<sup>2</sup>

Sir:

Conjugate addition reaction of an organometallic reagent to an  $\alpha,\beta$ -unsaturated carbonyl compound is highly useful synthetic operation.<sup>3</sup> Today's method of choice is definitely the use of organocuprates (Gilman reagents). Unfortunately, however,  $\beta,\beta$  disubstitution prevents conjugate addition to enoate esters,<sup>3,4</sup> and  $\alpha,\beta$  disubstitution also leads to poor results.<sup>3</sup> Furthermore, conjugate addition to  $\alpha,\beta$ -ethylenic carboxylic acids has never been achieved by using any organometallic reagent. We wish to report that these difficulties, for the first time, can be overcome by using a new alkylating reagent, RCu·BF<sub>3</sub> (eq 1).



We recently reported that the substitution of allyl halides with complete allylic rearrangement is achieved by the use of RCu·BF<sub>3</sub>.<sup>5</sup> As part of an attempt to broaden the scope of this new alkylating reagent it became of interest to explore the behavior toward  $\alpha,\beta$ -unsaturated carbonyl compounds. The results are summarized in Table I.

As is apparent from Table I, conjugate addition of this new reagent to the ordinary  $\alpha,\beta$ -unsaturated ketones and esters may be as effective as 1,4 addition of other organocuprate reagents (entries 1-5). Although the new reagent also undergoes conjugate addition to  $\alpha,\beta$ -unsaturated aldehydes, the reaction proceeds much better with R<sub>2</sub>CuLi than with RCu·BF<sub>3</sub>. The most remarkable feature is that this new reagent undergoes effective conjugate addition to the  $\alpha,\beta$ - (entry 6) and  $\beta,\beta$ -disubstituted (entries 7-10) enoate esters, and even to the