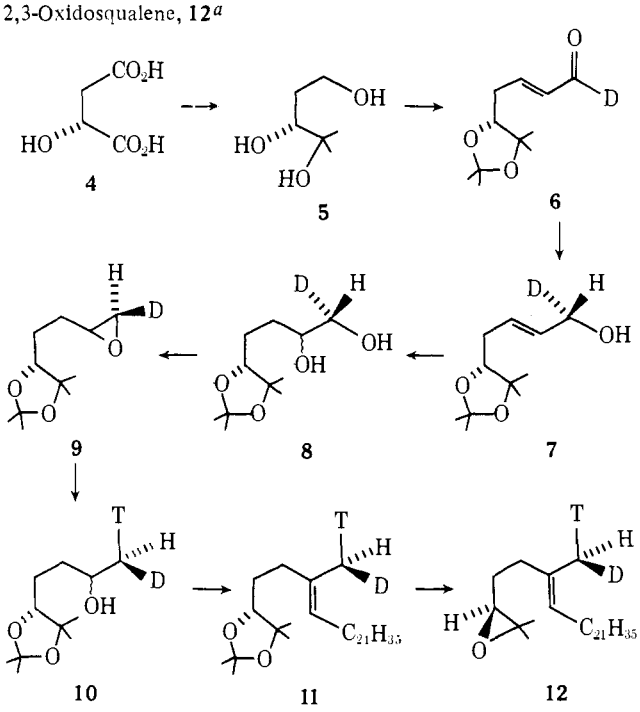
Scheme III. Synthetic Pathway for Chiral, Tritium-labeled 2,3-Oxidosqualene, **12**[a]



[a] Reagents: **4** → **5**, (a)[4] AcCl, (b) EtOH, (c)[5] B_2H_6, (d) CH_3MgBr; **5** → **6**, (a) acetone, H^+, (b) $CrO_3 \cdot pyr_2$, CH_2Cl_2, (c)[6] $Ph_3P{=}CHC(=O)D$; **6** → **7**,[7] HLADH, NADH, pH 6.8; **7** → **8**, (a)[8] *t*-Bu$(CH_3)_2$SiCl, (b)[9] B_2H_6, (c) H_2O_2, ^-OH, (d)[8] $(n\text{-Bu})_4N^+F^-$, THF; **8** → **9**[10,11] (a) TsCl, (b) ^-OH, CH_3OH; **9** → **10**,[12,13] $NaBT_4$, Me_2SO; **10** → **11**, (a)[14] CBr_4, $(n\text{-Bu})_3P$, pyr, THF, (b) Mg, THF, (c)[15] $C_{21}H_{35}CHO$, (d)[16] $(PhO)_3P^+CH_3I^-$, HMPT; **11** → **12**, (a) CH_3OH, H^+, (b) TsCl, (c) ^-OH, CH_3OH.

0.168, 0.438, and 0.456 in a ratio of 4.64:1:1.46. We assign[18] the resonances as follows: the resonance at δ 0.168 is due to an exo cyclopropyl tritium in molecules which also have an endo deuterium; the resonance at δ 0.438 is due to an endo cyclopropyl tritium in molecules which also have an exo deuterium;[19] and the resonance at δ 0.456 is due to an endo cyclopropyl tritium in molecules which also have an exo hydrogen. These assignments are confirmed by the proton-coupled ^3H NMR spectrum (Figure 2b) in which only the resonance at δ 0.456 has been split (J = 4 Hz).

It is thus immediately apparent that this conversion has proceeded with retention of configuration.[20]

Acknowledgments. We gratefully acknowledge financial support of this project from the National Science Foundation (CHE 85-21387) and the New England Nuclear Corporation. ^3H NMR spectra were obtained at the Facility for Biomedical NMR on Radioactive Samples (at Stony Brook) which is supported by the National Institutes of Health, Division of Research Resources, Grant RR 01039. ^1H NMR spectra (270 MHz) were obtained on a Bruker WH 270 spectrometer. The technical assistance of Alan Kook and Howard Corey is also acknowledged.

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(11) Subsequent careful investigation of **9** by 270-MHz ^1H NMR reveals the presence of (3*R*,6*S*,7*S*)-**9** in addition to the expected (3*R*,6*R*,7*R*)-**9** in a ratio of 2:8. Thus, some secondary tosylate must have been formed. Indeed, reinvestigation of the tosylation reaction (**8** → **8**-OTs) revealed the presence of two separable tosylates in a ratio of ~4:1. Reduction of each separately with $LiAlH_4$ allows for the assignment of the major tosylate as the primary tosylate and the minor tosylate as the secondary tosylate.
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(18) The assignment of the low-field (δ 0.45) resonance to the endo cyclopropyl proton (or tritium) is based upon the long-range coupling between $H_{1\alpha}$ and the endo cyclopropyl proton (in unlabeled cycloartenol) which causes a selective broadening of the δ 0.45 resonances. Deuteration of the 1α position removes this broadening. In addition, irradiation at δ 1.39 (in unlabeled cycloartenol) also removes the broadening. The low-field cyclopropyl resonance of 2β-cycloartanol was also selectively broadened. Lanthanide shift experiments utilizing $Pr(fod)_3$ demonstrated that the low-field cyclopropyl resonance in 2β-cycloartanol was due to the endo proton. These assignments (the low-field, broadened cyclopropyl resonances being due to the endo cyclopropyl proton) are further corroborated by T_1 measurements—80-MHz ^1H NMR spectra of unlabeled **2** show T_1 (endo H) = 0.48 s; T_1 (exo H) = 0.68 s. ^3H NMR spectra (106.7 MHz) of tritium-labeled cycloartenol show tritium T_1 (exo T, endo D) = 1.41 s; T_1 (endo T, exo D) = 0.98 s. The additional relaxation of the endo proton (or tritium) we presume to be coming from the 6β proton. The resonance of the 6β proton in 3β-cycloartenol was observed at 270 MHz at δ 0.66 as a quartet of doublets ($J_{6\beta,5\alpha} = J_{6\beta,6\alpha} = J_{6\beta,7\alpha}$ = 12.5 Hz, $J_{6\beta,7\beta}$ = 4.5 Hz) indicating that the 6β proton is in an axial conformation. Models of this conformation place the 6β proton ~0.18 nm from the endo cyclopropyl resonance thus allowing for the 6β proton's candidacy as being capable of selectively relaxing the endo cyclopropyl resonance. The unusual, downfield shift of the resonance of an endo cyclopropyl proton has been observed before by W. G. Dauben and W. T. Wipke, *J. Org. Chem.*, **32**, 2976 (1971).
(19) This resonance is derived from the 20% (*S*)-methyl impurity.
(20) Professor D. Arigoni has independently observed retention of configuration for this transformation using Zea Mays. We thank Professor Arigoni for discussions concerning these results prior to publication.

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Stereospecific Double Alkylation of Diphenylacetylene by η^5-Cyclopentadienyl-(triphenylphosphine)dimethylcobalt(III). Evidence for Noninterconvertible Diastereomeric Complexes in the Cobalt-Catalyzed Isomerization of Alkenes, and Some Comments on Factors Influencing the Rates of Reductive Elimination Reactions

Sir:

Yamazaki and Hagihara reported in 1971 that treatment of η^5-cyclopentadienyl(triphenylphosphine)dimethylcobalt(III) (**1**) with 2.8 equiv of diphenylacetylene (**2**) in refluxing benzene led to metallocycle **3** (Scheme I) and η^4-tetraphenylcyclobutadiene(η^5-cyclopentadienyl)cobalt(I) (**4**) in 49 and 13% yield, respectively.[1] Because this report left the methyl groups in **1** unaccounted for, and **1** "doubly alkylates" CO to give acetone quantitatively,[2] we have reinvestigated this reaction. We find that, when **1** is dissolved in oxygen-free benzene-d_6 and heated at 56 °C with 3.4 equiv of diphenylacetylene, **3** is observed, as reported earlier.[3] However,

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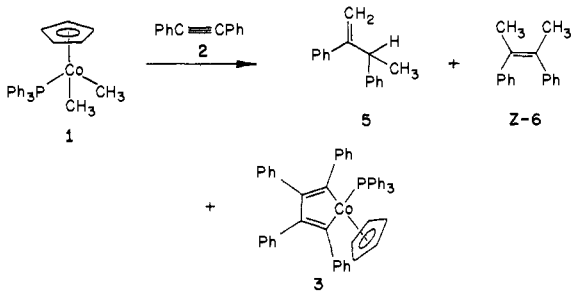
Scheme I



an organic product is also formed (93% yield based on cobalt), which on the basis of spectral data[4] and independent synthesis[5] we have shown to be 2,3-diphenyl-1-butene (**5**). In addition, smaller amounts of (*Z*)-2,3-diphenyl-2-butene[6] ((*Z*)-**6**, 7%) and hexaphenylbenzene[7] (trace) are formed. No (*E*)-2,3-diphenyl-2-butene ((*E*)-**6**, <1%) is observed. This reaction therefore involves overall transfer of both methyl carbons in **1** to diphenylacetylene,[8] the cobalt fragment being scavenged by excess acetylene to give **3**. In experiments designed to further investigate this reaction, we have obtained information relevant to the general mechanisms of acetylene insertion, reductive elimination and olefin isomerization.

Our results are the following.

(1) In the absence of diphenylacetylene, starting complex **1** is quite stable. Decomposition (solid state) occurs only at temperatures ≥140 °C, at which point *methane* is formed in 30% yield.[9]

(2) Although metal-carbon bond cleavage is slow at our reaction temperatures, complex **1** (0.08 M in benzene) is converted (>95%) to η^5-cyclopentadienyl(trimethylphosphine)dimethylcobalt(III)[10] in the presence of 0.17 M $P(CH_3)_3$ in <5 min at 56 °C.

(3) To investigate the intramolecularity of the diphenylacetylene alkylation, we treated a mixture of **1**-d_0 and **1**-d_6 (completely deuterated methyl groups) with **2**. The product **5** was isolated and purified by VPC; mass spectrometric analysis showed that it contained only **5**-d_0 and **5**-d_6. This result demonstrates that each cobalt atom transfers both its methyl groups to the same acetylene molecule, and hydrogen transfer is intramolecular as well.

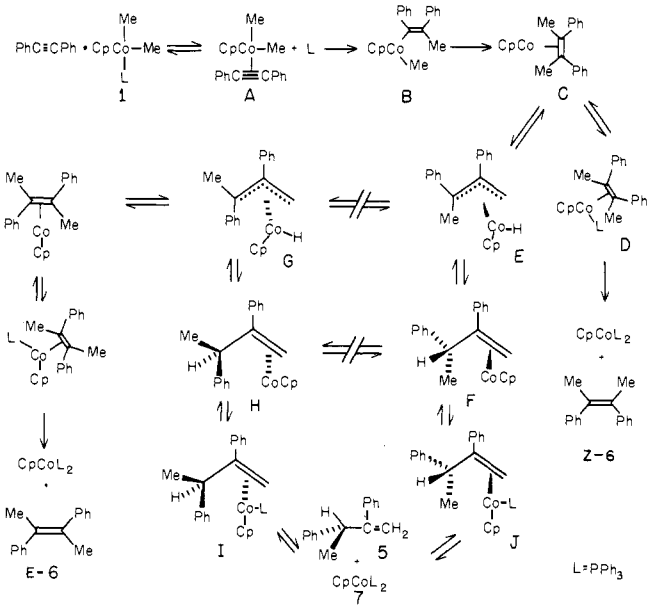
(4) At early reaction times, the disappearance of **1** obeys a first-order rate law ($k_{56\,°C} = 8.8 \times 10^{-5}$ s^{-1}). In a 50:50 mixture of **1**-d_0 and **1**-d_6, monitoring the rate of disappearance of **1**-d_0 and **1**-d_6 by NMR showed that the reaction exhibits a negligible isotope effect ($k_{h_6}/k_{d_6} = 1.01 \pm 0.05$).

(5) Acid-catalyzed isomerization of **5** proceeds uneventfully toward the equilibrium mixture of olefins; starting with pure **5** (or pure (*E*)-**6** or (*Z*)-**6**), the final mixture contains 2% **5**, 63% (*E*)-**6** and 35% (*Z*)-**6**. However, when **5** is treated with η^5-cyclopentadienylbis(triphenylphosphine)cobalt(I)[11,12] (**7**) in benzene-d_6 at 56 °C, the tetrasubstituted olefins are once again formed, but the (*E*)-**6**/(*Z*)-**6** ratio is 92:8. Consistent with our ability to observe this kinetic product ratio, (*E*)-**6** and (*Z*)-**6** are isomerized only very slowly by **7** at this temperature.

(6) The rate of the **1** + **2** reaction is inhibited, and the product distribution is strongly modified, by excess phosphine. The initial reaction, run with 0.20 M **1**, 0.68 M alkyne, and no excess PPh_3, required 22.5 h to reach 88% completion; in the presence of 0.10 M **1**, 0.90 M alkyne, and 0.90 M PPh_3, the reaction required 106 h to reach 66% completion. The **5**/(*Z*)-**6** ratio changes to 0.9 in the excess-phosphine run.

A mechanism which accounts for the above observations is outlined in Scheme II. The rate inhibition by phosphine (and the facile substitution of PPh_3 in **1**) suggests that the process begins by formation of intermediate A in a reversible ligand-exchange reaction. Acetylene insertion into a metal-methyl

Scheme II



bond[13] in A gives B. Consistent with recent mechanistic studies of reductive elimination at other metals (e.g., platinum(IV), gold(III)),[14] we propose that stereospecific reductive elimination occurs in this unsaturated intermediate, leading to η^2-alkene complex C. C is also coordinatively unsaturated, and we believe it is the partitioning point which accounts for the effect of phosphine on the product distribution. Excess phosphine traps C, leading to saturated intermediate D, which easily releases cis olefin (*Z*)-**6**. When less phosphine is available, insertion into an adjacent C–H bond occurs competitively, forming η^3-allyl complex E. This initiates the isomerization process and results in the eventual production of **5**.

In our view, the significant parts of this mechanism concern the reductive elimination step (B → C) and the reaction stereochemistry. With regard to the former, it is interesting that **1** does not give ethane even at 140 °C, but B is converted to C rapidly at 56 °C. The difference between B and the corresponding dimethyl complex is, of course, that B contains one σ-ligand with π electrons. It seems likely that coordination of these electrons to the metal *in the reductive elimination transition state* provides a low-energy route for this process not available in reductive elimination of dialkyls. The related cobalt complex containing a methyl and an acyl ligand, which is presumably responsible for the rapid formation of acetone[2] on carbonylation of **1**, may also reductively eliminate rapidly because the eliminating ligand can simultaneously donate π- or lone-pair electrons to the metal.[15] With regard to the stereochemistry of the reaction, our mechanism must explain why both **5** and (*Z*)-**6**, but not (*E*)-**6**, are formed in the **1** + **2** reaction, but re-entry into the system by mixing **5** and **7** gives mostly (*E*)-**6**.[16] We believe this is most easily understood by assuming that *diastereomeric* η^2-alkene and η^3-allyl complexes are involved in these reactions.[17] Only diastereomers E, F, and J are formed in the double-alkylation route, but both this set of isomers and the I, H, and G set are reached by treating **5** with **7**. No interconversion of the η^3-allyl diastereomers (e.g., by reversible conversion to η^1- allyl complexes and rotation)[18] or η^2-alkene complexes (e.g., by reversible dissociation of olefin ligand)[19] occurs under the **1** + **2** reaction conditions.

Acknowledgments. Support of this work by the National Institutes of Health (Grant No. GM-16231) is gratefully acknowledged. We also thank Mr. Donald McAlister for supplying samples of cyclopentadienylbis(triphenylphosphine)cobalt.

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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.[1]
(4) ^{1}H NMR (CCl_4): 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. Umbert 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 $CpCoL_2$-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. Bercaw, and R. G. Bergman, *J. Am. Chem. Soc.*, **99**, 1666 (1977).
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(10) NMR (C_6D_6) of (η^5-C_5H_5)Co(PMe_3)(CH_3)$_2$: 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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(12) A. Misano, *Inorg. Syn.*, **12**, 12 (1970).
(13) For other examples of apparent acetylene insertion into M–R bonds, see (a) H. C. Clark and K. von Werner, *J. Organomet. Chem.*, **101**, 347 (1975); (b) M. H. Chisholm and H. C. Clark, *J. Am. Chem. Soc.*, **94**, 1532 (1972); (c) T. G. Appleton, M. H. Chisholm, and H. C. Clark, *ibid.*, **94**, 8912 (1972); (d) N. Chandburg, M. G. Kekre, and R. J. Puddephatt, *J. Organomet. Chem.*, **73**, C17 (1974); (e) S. J. Tremont and R. G. Bergman, *ibid.*, **140**, C12 (1977). For an insertion reaction involving dimethyltitanocene and diphenylacetylene which apparently does not proceed on to doubly alkylated product, see (f) W. H. Boon and M. D. Rausch, *J. Chem. Soc., Chem. Commun.*, 397 (1977); (g) M. D. Rausch, W. H. Boon, and H. G. Alt, *J. Organomet. Chem.*, **141**, 299 (1977).
(14) (a) S. Komiya, T. A. Albright, R. Hoffman, and J. K. Kochi, *J. Am. Chem. Soc.*, **98**, 7255 (1976); (b) M. P. Brown, R. J. Puddephatt, and C. E. E. Upton, *J. Chem. Soc., Dalton Trans.*, 2457 (1974).
(15) For a complex in which η^2-acyl bonding has been identified crystallographically, see G. Fachinetti, C. Floriani, F. Marchetti, and S. Merlino, *J. Chem. Soc., Chem. Commun.*, 522 (1976).
(16) For simplicity, reactions of **5** in Scheme II are illustrated for only one enantiomer of this compound.
(17) For a case in which prochiral olefin π-complex diastereomers have been isolated in the Cp-molybdenum series, see J. W. Faller, B. V. Johnson, and C. D. Schaeffer, Jr., *J. Am. Chem. Soc.*, **98**, 1395 (1976).
(18) Normally $\eta^3 \rightleftharpoons \eta^1$ rearrangement is quite a facile process. See, for example, (a) B. I. Cruikshank and N. R. Davies, *Aust. J. Chem.*, **26**, 1935 (1973); (b) G. W. A. Fowles, L. S. Pu, and D. A. Rice, *J. Organomet. Chem.*, **54**, C17 (1973); (c) M. C. Rakowski, F. J. Hirsekorn, L. S. Stuhl, and E. L. Muetterties, *Inorg. Chem.*, **15**, 2379 (1976); (d) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 6785 (1970); (e) J. W. Faller and A. M. Rosan, *ibid.*, **98**, 3388 (1976); (f) M. Green and R. P. Hughes, *J. Chem. Soc., Chem. Commun.*, 619 (1975); (g) J. W. Faller, C. C. Chen, M. J. Mattina, and A. Jakubowski, *J. Organomet. Chem.*, **52**, 361 (1973); (h) C. R. Graham and L. M. Stephenson, *J. Am. Chem. Soc.*, **99**, 7098 (1977). For a system in which $\eta^3 \rightleftharpoons \eta^1$ rearrangement seems to be slow, see (i) T. H. Whitesides, R. W. Arhart, and R. W. Slaven, *ibid.*, **95**, 5792 (1973).
(19) A similar conclusion has been reached in an iron-catalyzed olefin isomerization; cf. C. P. Casey and C. R. Cyr, *J. Am. Chem. Soc.*, **95**, 2248 (1973).
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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,[2,3] phenothiazine,[4,5] and tetramethylbenzidine.[6] 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^-_{aq}. 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 = 5300 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.[7] 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^{-5} 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_2 and N_2O. The difference between the spectra in N_2 and N_2O is also shown, and this compares favorably with the literature spectrum for the hydrated electron e^-_{aq}. In the presence of O_2 the absorption decays rapidly with $k = 1.8 \times 10^{10}$ M^{-1} s^{-1} which is in excellent agreement with the rate constant for $e^-_{aq} + O_2$ given in the literature.[9] Hence the absorption is attributed to the hydrated electron, e^-_{aq}, which has a reported absorption maximum at 720 nm. The yield of e^-_{aq} is lower in the cationic micelle, CTAB, and parallels previous data with pyrene[2] and phenothiazine.[4] The absorption at 630–640 nm is unaffected by O_2 and is due to the radical cation, $(Amper)^+$. The strong maxima 560 and 600 nm in the CTAB spectrum decay in the presence of O_2 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

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