Scheme I

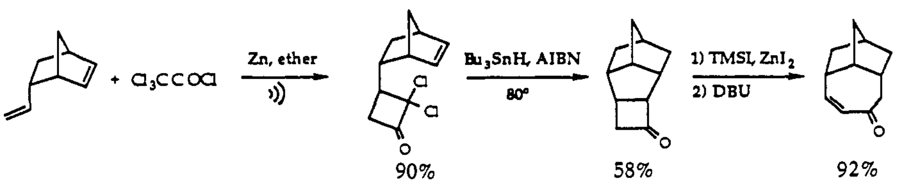
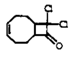
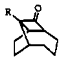
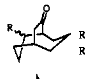
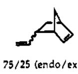
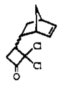
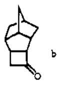
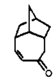
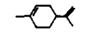
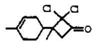
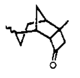
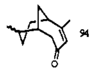
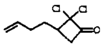
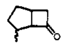
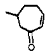
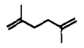
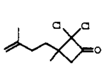
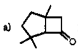
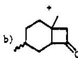
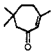
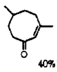
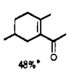
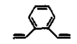
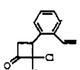
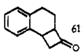
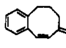
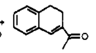


Table I. Bicyclic and Medium Ring Systems from Dichlorocyclobutanone Free Radical Annulation

entry	1,5-diene	ketene adduct[a]	radical-cyclization product	ring-opening product
1			 R=Cl, 91%[b] R=H, 85%[c]	 R=I, 87%[d] (35/65) R=H, 84%[e,f]
2	 75/25 (endo/exo)		 58%[c] based on endo	 92%[e]
3			 51%[c] (87/13)	 94%[e]
4			 85%[c] (84/16)	 90%[e,g]
5			a)  21%[c] → + b)  70%[c] (48/52) →	 87%[e]  +  40%[e] 48%[e]
6			 61%[c]	 +  trace[e] 83%[e]

[a] 1.2–1.5 equiv of Cl_3CCOCl, 2.0 equiv of zinc dust, ether, sonication. Yields: 69–95%. [b] 1.1 equiv of Bu_3SnH (170 mM) with AIBN, benzene, reflux. [c] 2.2–2.5 equiv of Bu_3SnH (70–170 mM) with AIBN, benzene, reflux. [d] 1.5 equiv of TMSI, 0.24 equiv of anhydrous ZnI_2, CH_2Cl_2, 25 °C, then 1.2 equiv of Bu_3SnH with AIBN, benzene, reflux. [e] 1.5 equiv of TMSI, 0.24 equiv of anhydrous ZnI_2, CH_2Cl_2, 25 °C, then 10% DBU, ether, 25 °C. [f] Bingham, R. C.; Schleyer, P. v. R. *J. Org. Chem.* **1971**, *36*, 1198. Coll, J. C.; Crist, D. R.; Barrio, M. d. C. G.; Leonard, N. J. *J. Am. Chem. Soc.* **1972**, *94*, 7092. [g] Heathcock, C. H.; Germroth, T. C.; Graham, S. L. *J. Org. Chem.* **1979**, *44*, 4481.

radicals generated from dichlorocyclobutanones prefer 5-exo ring closure (Table I, entries 1–4), but substitution at the 5-position causes a preference for 6-endo closure (Table I, entry 5). Entry 6 also shows endo ring closure since a stabilized benzyl radical is formed. For 5,4-fused cyclobutanones, TMSI selectively opens the fused bond of cyclobutanones to give the seven-membered ring (Table I, entries 1–5a). However, for 6,4-fused cyclobutanones, ring opening to give the six-membered ring is the major process (Table I, entries 5b and 6).

In summary, we have discovered a new free radical annulation reaction that promises to become a powerful method for assembling fused and bridged ring systems of some complexity. The synthetic sequence employs 1,5-dienes; many are at hand, having been developed in the context of the Cope rearrangement.[12] The new method also takes advantage of the ready synthesis of dichlorocyclobutanones from alkenes.[2]

Acknowledgment. This research was generously supported by the Institute of General Medical Sciences of the National Institutes of Health under Grant 39825.

Supplementary Material Available: Listings of experimental procedures and spectral data for the cyclization and ring-opened products (7 pages). Ordering information is given on any current masthead page.

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Measurement of Electric Fields at Rough Metal Surfaces by Electrochromism of Fluorescent Probe Molecules Embedded in Self-Assembled Monolayers

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We describe here a new experimental strategy for measurement of electric field strengths at charged surfaces which employs a surface-immobilized, oriented fluorescent dye as probe. The method takes advantage of interactions of dipolar ground and excited states of the dye with the interfacial electric field which lead to shifts in the absorption and emission spectra, referred to as the electronic Stark effect or the electrochromic effect. This strategy has been used previously to measure electric fields in both model and biological membranes,[1,2] but has not to our knowledge been applied to the measurement of electric fields at charged solid surfaces. The electric field at a charged interface has enormous impact on interfacial chemistry and physics. While interest in interfacial electric fields has a long history[3] and several mathematical models of interfacial electric fields have been developed and applied in attempts to explain interfacial phenomena,[3-5] there have been only a very few actual measurements of interfacial field strengths or potential differences.[6-10]

We have chosen an (aminostyryl)pyridinium derivative (also referred to as a hemicyanine or stilbazolium derivative) as the probe molecule because the extent of charge displacement during its optical transition is both large and well studied[2a] and because its structure allows relatively simple synthetic elaboration[2b] to

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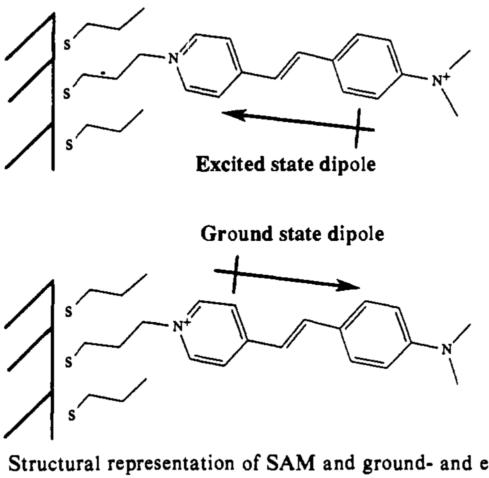

Figure 1. Structural representation of SAM and ground- and excited-state dipoles of immobilized dye.

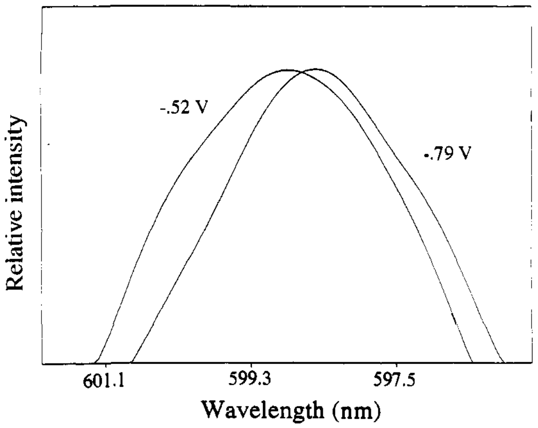

Figure 2. Fluorescence emission peaks at −0.52 and −0.79 V vs Ag/AgCl in 0.1 M $NaNO_3$, recorded with an ISA single monochromator and Photometrics CCD detection system. Only the tops of the peaks are plotted to show clearly the peak shift.

achieve coimmobilization within a self-assembled monolayer of an alkyl thiol. Maintaining a fixed orientation of the dye is achieved by immobilizing the probe molecule within a self-assembled monolayer at the metal surface.[11]

Figure 1 shows a schematic diagram of the monolayer structure along with the directions of the ground- and excited-state dipole moments. Monolayer formation is simply achieved by exposing an electrochemically roughened Ag electrode[12-15] to a solution of the thiol derivative of the dye (0.5 mM) and 1-mercaptopropane (0.5 mM) in methanol for ca. 25 min, followed by thorough rinsing in pure methanol.[16] The Stark shift of the fluorescence maximum was measured in situ using the 5145-Å line of an Ar laser as the excitation source and a locally designed spectroelectrochemical cell. Figure 2 shows the region of the fluorescence spectrum around the fluorescence maxima at two applied potentials, with the Stark shift clearly observable from the shift in peak maximum. That fluorescence can be observed at rough metal electrodes is well established and results from essentially the same phenomena which provide the large enhancements in the surface-enhanced Raman effect.[17-19] We take advantage of this to allow the experimentally simpler measurement of the Stark shift in fluorescence rather than absorption.

The data in Figure 2 demonstrate that the fluorescence maximum shifts to the red as the potential is made more positive, as expected. The quantitative relationship between this shift and the electric field experienced by the molecule is given by the following equation:[20-22]

$$h\Delta\nu = -qrE\cos\theta \qquad (1)$$

where $h\Delta\nu$ is the experimentally obtained shift, q is the charge displaced during the optical transition, r is the distance of charge displacement, E is the magnitude of the electric field, and $\cos\theta$ is the cosine of the angle between the direction of charge displacement and the electric field vector (i.e., the surface normal). For this case, q is the charge on the electron, and r values of 3.4 and 3.0 Å have been determined from both experimental measurements[22] and PPP-SCF calculations,[2a] respectively. We have used the experimental value here. Note that this treatment of the Stark shift is for isolated dye molecules.

At the present time, the exact value of θ is not known very precisely, but it is probably in the range of 0–50°.[11,13-15] We believe this is a reasonable range because molecular models of these monolayers show that the ortho hydrogens on the pyridinium rings experience severe steric interaction with the methyl hydrogens of the 1-mercaptopropane coadsorbates, which should serve to impose a roughly perpendicular orientation for the long axis of the dye. Also, the cos function is close to 1 for a fairly large range of angles around 0°, so that $\cos\theta$ is only a weak function of θ within a reasonable range of values. For example, even if θ is as large as 60°, the calculation of the electric field is only in error by a factor of ca. 2.

These data allow calculation of the field strength experienced by the probe using the experimentally determined value of $h\Delta\nu = 9\ \text{cm}^{-1}$, where this shift occurs on changing the applied potential from −0.79 (near the potential of zero charge on Ag[23,24]) to −0.52 V. Due to the uncertainty in θ, we simply choose $\theta = 0$, keeping in mind the uncertainty which this assumption may introduce into the calculation of E. This gives an electric field strength of $4 \times 10^4\ \text{V cm}^{-1}$. Note that this is the field strength outside the propyl region of the SAM. Thus, this particular experiment actually provides a measure of the field in the diffuse region of the interfacial electrical double layer. Fields within the alkyl chain region are likely to be 1–2 orders of magnitude larger.[4] Additional experiments are in progress which will provide a distance map of the field near the surface, both inside and outside the SAM, as well as the Stark shifts and fields both positive and negative of the potential of zero charge.

These results are in qualitative agreement with recent predictions of interfacial potential profiles within monolayers[4] which suggest that the potential should drop linearly and steeply within the alkyl region, leaving only a small potential drop in the diffuse double layer. Quantitative comparisons of our experimental data and this model are in progress. Finally, while these measurements have been made on rough surfaces, it should be possible to apply these methods to smooth surfaces using modern, sensitive detection systems.

Acknowledgment. We are grateful to the Office of Naval Research for the full support of this work. We also thank Professor Keith Carron for the use of his CCD detection system.

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