but rather as mechanistic constructs. The chemistry observed here for the episulfonium cation **19** matches perfectly that reported for the 3-nortricyclylcarbinyl cation.[9] The tricyclooctane **11** is the regular skeletal rearrangement product expected in arenesulfenyl chloride addition to norbornenes.[7,10]

Our results display an interesting mechanistic dichotomy about cyclopropylethyl cationic fragments that are embodied in the norbornyl skeleton. Thus, spiroannelated cyclopropanes as in norbornene **4** (eq 2) prefer ring expansion on arenesulfenyl chloride addition, thereby providing a facile and efficient entry into structurally complex molecules such as brendanes. Including the preparation of the norbornene **4**, the parent brendane **12** was prepared in three steps in an overall yield of 15% starting from cheap, commercial compounds. On the other hand, endo-fused cyclopropanes as in norbornene **8** prefer cyclopropane migration on arenesulfenyl chloride addition.

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Registry No. 4, 6572-50-5; **5**, 86146-93-2; **6**, 86146-94-3; **7**, 86146-95-4; **8**, 3635-94-7; **9**, 86146-96-5; **10**, 86146-97-6; **11**, 86162-06-3; **12**, 1521-75-1; **13**, 86146-98-7; **18**, 86146-99-8; *p*-toluenesulfenyl chloride, 933-00-6.

Supplementary Material Available: Experimental, physical, and X-ray data and structures of **13** and **18** (16 pages). Ordering information is given on any current masthead page.

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(10) Of mechanistic interest is to mention that the exo-fused norbornene **8** gave exclusively 6-*endo*-chloro-7-*exo*-thio-*p*-tolueneoxytricyclo[3.2.1.$0^{2,4}$]-octane in 80% yield as the regular trans-addition product with arenesulfenyl chloride.

Proton-Transfer Spectroscopy of 3-Hydroxychromones. Extreme Sensitivity to Hydrogen-Bonding Perturbations[†,‡]

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The discovery of excited-state proton transfer in *o*-hydroxychromones[1] (structure I, R = phenyl in 3-hydroxyflavone and R = methyl in 2-methyl-3-hydroxychromone) has generated considerable interest in laser kinetic[2-4] and piezospectroscopic[5,6] study of the mechanism of the phototautomerization. Our extension of the original work now indicates that the presence of stoichiometric and substoichiometric traces of water, or other H-bonding impurities, in the supposedly dry hydrocarbon solvents controls and competes with the excited-state proton-transfer process.

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[‡]This work was presented at the Gordon Conference on Molecular Electronic Spectroscopy, Wolfeboro, NH, Aug 1982.

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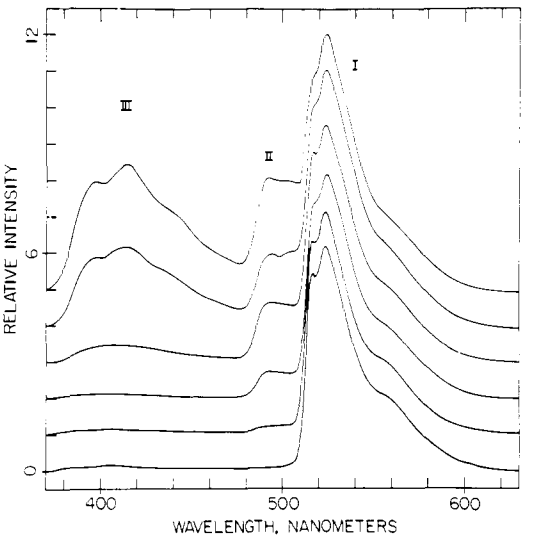
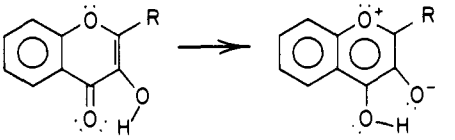
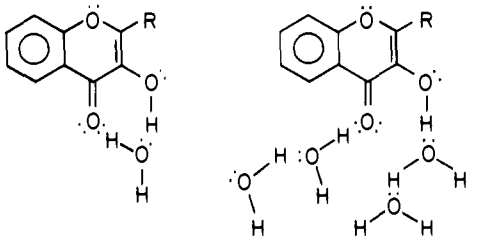


Figure 1. Fluorescence emission spectra of 2.00×10^{-5} M 3-hydroxyflavone in quick-frozen methylcyclohexane glass at 77 K as a function of addition of substoichiometric traces of water. Lowest curve shows unique tautomer fluorescence in the anhydrous solvent; highest curve, for a moderately wet solvent, shows tautomer fluorescence (I), perturbed-tautomer fluorescence (II), and "normal"-molecule fluorescence (III). The curves are normalized at 523 nm for clarity.

At temperatures greater than 200 K the roles of water solvates (structure II and III) are disguised, whereas at lower temperatures the properties of the solvated molecules dominate the excitation processes. In rigorously dry dilute hydrocarbon solutions, including both glass-forming and multicrystalline Shpol'skii matrices, we observe only the green tautomer fluorescence at all temperatures between 293 and 77 K.





The luminescence behavior at 77 K of 3-hydroxyflavone (2-phenyl-3-hydroxychromone) is reported in Figure 1. The solute concentration is 2.00×10^{-5} M in methylcyclohexane solvent. Because the effects that are to be described here are found to be strongly temperature and cooling-rate dependent, all spectra are reported for quick-frozen (i.e., sample tube plunged into liquid nitrogen) rigid-glass solutions at 77 K.

The lowest curve gives the luminescence spectrum of an extremely dry 3-hydroxyflavone solution.[7] The yellow-green fluoroescence is completely analogous to the room-temperature tautomer emission previously reported[1] and thus is associated with the unsolvated proton-transferred species (structure I, tautomer). Upon the addition of substoichiometric traces of water to the anhydrous hydrocarbon solution, a fluorescence shoulder, desig-

(7) For drying procedures refer to the full paper, ref 10.

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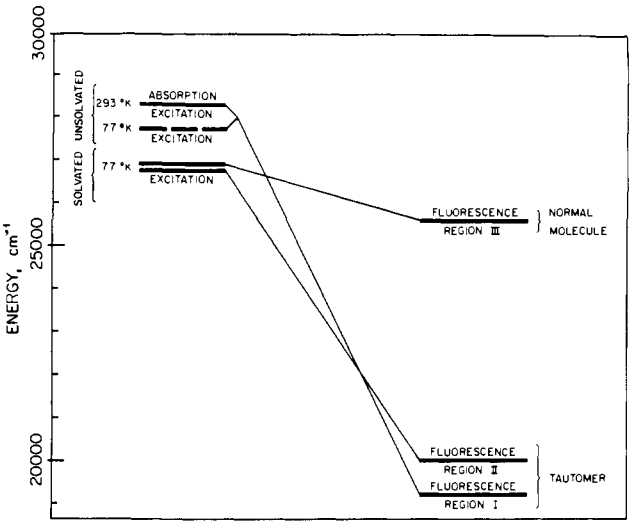

Figure 2. Solvation-fluorescence correlation diagram for 3-hydroxyflavone. First-peak positions of absorption, excitation, and fluorescence spectra are shown.

nated as region II, appears slightly to the blue of the tautomer (region I) fluoroescence band. Because of its location, profile, and initial appearance with the first traces of water, we envision this band as arising from a cyclically hydrogen-bonded monohydrate species (structure II) that is capable of excited-state double-proton transfer, resulting in a perturbed-tautomer fluorescence emission. The complexity of this emission region suggests further solvation species, e.g., dihydrates, all of which we perceive as being capable of proton transfer in the excited state and, subsequently, perturbed tautomer fluorescence.

As larger traces of water are added to the solution, approaching a 1:1 ratio of H_2O to solute (upper curves of Figure 1), the "normal" molecule fluorescence is observed, designated by region III. We interpret this emission as arising from chain-hydrogen-bonded polyhydrate species (structure III) in which tautomerization is inhibited, thus giving rise to the "normal" molecule fluorescence. This interpretation is analogous to that originally proposed to explain the appearance of the "normal" emission in alcoholic solvents at room temperature.[1] When even larger amounts of water are added to the solution, the spectrum is dominated by the "normal" molecule (region III) fluorescence, with only a trace of the tautomer emission evident, as has been reported previously for the 77 K luminescence of 3-hydroxyflavone (Figure 2 of ref 1). It is evident that all previous investigations of the low-temperature spectroscopy of 3-hydroxyflavone have been for solvated species rather than isolated internally H-bonded molecules, as had been assumed.[1-3]

As already noted, *all of the fluorescence curves of Figure 1 are for the rigid*-glass *solutions at 77 K.* The behavior of each of these solutions at 293 K is to exhibit only tautomer (region I) fluorescence. The present observation that at both 293 and 77 K only tautomer (region I) fluorescence is observed for isolated molecules in dry solvents indicates that there exists *little* or *no intrinsic* Boltzmann barrier to the excited-state proton-transfer process for structure I. Thus, it is clear that the kinetic analyses and conclusions of previous workers must be reinterpreted in light of the present results, since an *intrinsic* potential barrier was assumed to be present. Specifically, the rate of tautomerization measured by them (via the rise time to tautomer fluorescence) must now be associated with a *temperature- and viscosity*-dependent rate of solvent reorganization[8] about the solvated 3-hydroxyflavone molecule prior to, and allowing for, the formation of an intramolecular hydrogen bond. Rapid proton transfer then occurs subsequent to this hydrogen-bond formation, the rate of which appears to be *temperature independent* and may be measured in rigorously dry hydrocarbon solvents.

(8) The relaxation referred to is that of the water molecules H-bonded to the 3-hydroxyflavone molecules.

The solvation fluorescence correlation diagram, Figure 2, summarizes the behavior of the 3-hydroxyflavone/water interaction in the proton-transfer process. At 293 K the normal molecule UV absorption (first peak 253 nm) is very closely mimicked by the excitation spectrum of the tautomer (region I) luminescence; at 77 K there is a sharpening and a shift of this excitation spectrum to longer wavelengths. When the region II luminescence is monitored in wet solutions at 77 K, a strongly red-shifted excitation spectrum results (first peak, 372 nm), clearly indicating the presence of a *ground-state solvated species.* When region III is monitored, the excitation spectrum is similarly shifted and somewhat broadened. The sharply contrasting nature of these two luminescences (region II and III) clearly indicates that at least two different solvation modes occur. Although both solvation modes have analogous effects on excitation spectra, the consequent behavior in the excited state differs vastly, one solvation mode (viz., structure II) permitting rapid proton-transfer tautomerization with the polysolvation mode (structure III) interfering with and preventing this process. Parallel research on 2-methyl-3-hydroxychromone indicates similar behavior.

Freed and Sancier[9] made general observations of such low-temperature solvation effects, and the present study shows the sensitivity of hydrogen-bonding sites to traces of H-bonding solvents. Low-temperature spectra of heteroaromatic molecules such as ketones and azines may be expected to be especially sensitive to H-bonding solvation effects such as described here.

A full report on this research will be published elsewhere.[10]

Acknowledgment. We thank Professor Thijs Aartsma for many stimulating discussions.

Registry No. I (R = phenyl), 577-85-5; I (R = methyl), 22105-10-8.

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2-Oxabicyclo[2.2.0]hexene/3-Oxatricyclo[3.1.0.0^{2,6}]hexane Isomerization

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The irradiation of a mixture of the stable cyclobutadiene **1**[1] and benzophenone (pentane, >280 nm) affords an oxabicyclo[2.2.0]hexene (**2** or **3**, respectively) (Scheme I) in a Paterno–Büchi reaction;[2] this represents the first example of a photochemical cycloaddition reaction of a [4]annulene. The question, whether the cycloadduct has structure **2** or **3**[2] is decided unequivocally in favor of **2** by the results reported in this communication: Only isomer **2** can undergo a rearrangement to **7**, the structure of which has been determined by X-ray analysis.

When the oxabicyclo[2.2.0]hexene **2** is dissolved in a mixture of chloroform/acetonitrile (1:1) containing catalytic amounts of hydrogen chloride at room temperature, the oxatricyclo[3.1.0.0^{2,6}]hexane **7** crystallizes after some minutes [70%; mp 193–195 °C; IR (KBr) 1712 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 18 H, *t*-Bu 1 and 6), 1.37 (s, 9 H, *t*-Bu 2), 1.48 (s, 9 H, *t*-Bu ester), 7.13–7.70 (m, 10 H, H phenyl); ^{13}C NMR ($CDCl_3$) δ 48.4 (C1 and -6), 59.6 (C5), 82.0, 82.8, 87.2 (C2, -4, and Me_3C ester), 126.9, 127.2, 129.9, 145.1 (C phenyl); MS (18 eV), *m/e* 502 (2%,

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