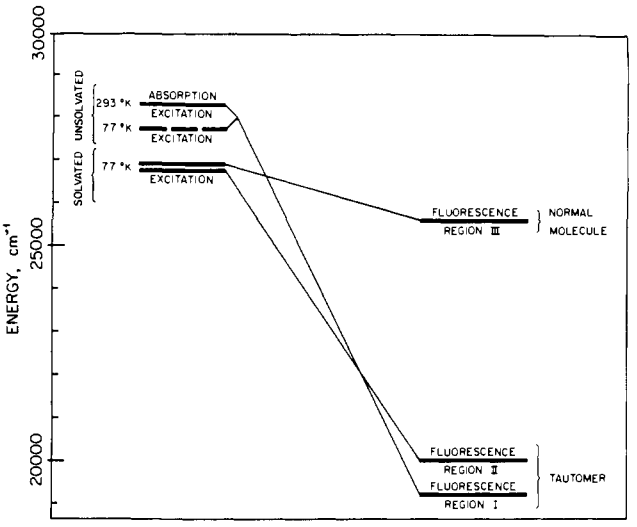

Figure 2. Solvation-fluorescence correlation diagram for 3-hydroxyflavone. First-peak positions of absorption, excitation, and fluorescence spectra are shown.

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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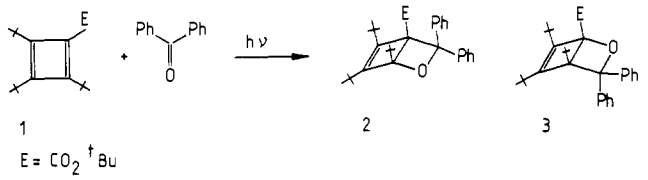
Scheme I



Scheme II

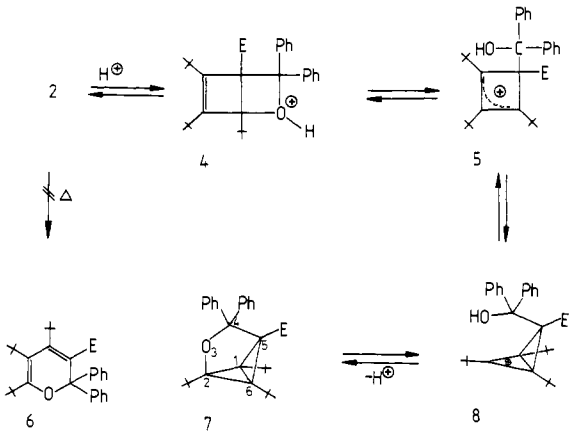


Table I. Selected Bond Lengths (Å) and Angles (deg) in 7 (Standard Deviations Are in Parentheses)

O1–C1	1.435 (2)	O1–C1–C2	99.3 (1)
O1–C4	1.447 (3)	C1–C2–C3	107.8 (2)
C1–C2	1.561 (3)	C1–C2–C5	111.7 (2)
C1–C6	1.528 (3)	C3–C2–C5	59.3 (1)
C1–C12	1.532 (3)	C2–C3–C5	60.7 (1)
C2–C3	1.526 (3)	C3–C5–C2	60.1 (1)
C2–C5	1.535 (3)	C2–C3–C4	88.0 (2)
C2–C18	1.487 (3)	C2–C5–C4	87.7 (2)
C3–C4	1.517 (3)	C4–C3–C5	60.0 (1)
C3–C5	1.513 (3)	C4–C5–C3	60.2 (1)
C3–C23	1.546 (3)	C3–C4–C5	59.9 (1)
C4–C5	1.514 (3)	C3–C4–O1	111.7 (2)
C4–C27	1.530 (3)	C5–C4–O1	110.5 (2)
C5–C31	1.551 (3)	C4–O1–C1	106.5 (1)

M^+), 389 (100%, M − C_4H_9 − C_4H_8), 208 (40%, M − Ph_2CO − $2C_4H_8$), 182 (51%, Ph_2CO)].[3] If the solvent of this reaction mixture is evaporated instead of filtering off **7**, the residue consists of **2** and **7** (ratio 20:80, ^1H NMR in $CDCl_3$). The same results are obtained when crystalline **7** is dissolved in acid containing chloroform/acetonitrile; this means that both isomers **2** and **7** are obviously connected by a proton-catalyzed equilibrium.

The isomerization reaction most probably starts with the protonation step **2** → **4**, followed by ring opening to the cyclobutenyl cation **5**. Subsequent thermal disrotatory ring closure is regarded to be responsible for the formation of the cyclopropyl cation **8**, which is the immediate precursor of the tricycle **7** (Scheme II). It may be that the reaction step **5** → **8**,[4] which is unfavorable because of increasing ring strain, profits by the decrease of steric hindrance between the *tert*-butyl groups in the planar cyclobutenyl cation **5**. Nevertheless we cannot rule out a direct product formation according to **5** → **7** by a synchronous mechanism including both ring-closure modes. As far as we know only one comparable rearrangement reaction of this type is described in the literature: 2-Oxabicyclo[2.2.0]hex-5-en-3-one ("Corey-lactone") rearranges at 25 °C to an extremely unstable heterotricyclic product.[5] The structure of **7** has been confirmed

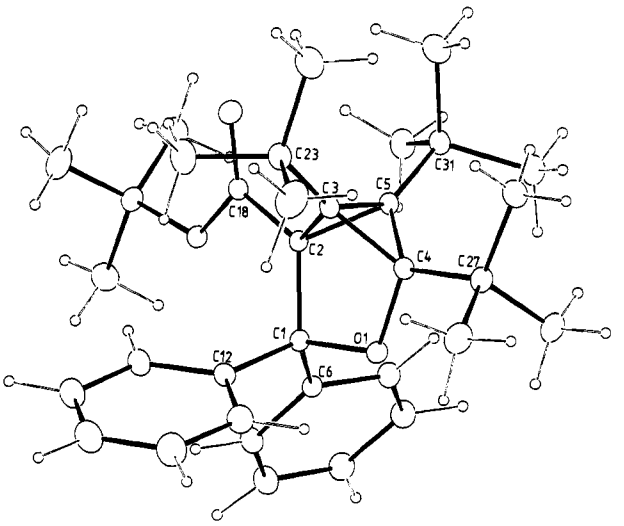


Figure 1. ORTEP plot of **7**.

by an X-ray analysis.[6] Figure 1 shows an ORTEP plot of the molecule; some bond lengths and angles are given in Table I.

Whereas NMR data of **7** are indicative of a C_m symmetry for this molecule in solution, no mirror plane is present in the crystalline state, although a symmetrical distribution of the corresponding bond lengths is observed in the bicyclic framework. It should be noted that the distances between the bicyclobutane unit and its bridging group are markedly longer than for simple cyclopropane substitution: C1–C2 exceeds the average C(cyclopropane)–C(*tert*-butyl) bond length in this structure by 0.019 Å, and C4–O1 is by 0.04–0.07 Å longer than the usual C(cyclopropane)–oxygen distance.[7] The dihedral angle between the two cyclopropane ring planes is 106.2°. For a number of bridged and "normal" bicyclobutanes a linear correlation between this angle and the central bond in the bicyclobutane has been established experimentally[8,9] and supported by theoretical arguments.[10] However, **7** does not fit into this scheme, as C3–C5 is much longer than predicted by this relationship. Certainly, the presence of the *tert*-butyl groups on C3 and C5, held firmly in an eclipsed configuration, causes a lengthening of the C3–C5 bond.

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Registry No. 1, 83747-03-9; **2**, 86260-40-4; **7**, 86260-41-5; benzophenone, 119-61-9.

Supplementary Material Available: Tables of positional and anisotropic thermal parameters of non-hydrogen atoms, coordinates of hydrogen atoms, and a list of observed and calculated structure factors (47 pages). Ordering information is given on any current masthead page.

(3) The rearrangement **2** → **7** was also observed when **2** was heated in toluene or 1,1,2,2-tetrachloroethane; after 1 h, 10% of **7** was formed. Cyclobutene → butadiene isomerization (i.e., **2** → **6**) was not detected.

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(6) Crystal data: $C_{34}H_{46}O_3$; triclinic, space group $P\bar{1}$, a = 17.306 (10) Å, b = 10.453 (6) Å, c = 8.864 (4) Å, α = 109.32 (4)°, β = 89.87 (4)°, γ = 104.15 (4)°, Z = 2, d_{calcd} = 1.142 g cm^{-3}. Data collection: Philips PW 1100 ($\theta/2\theta$ mode, Mo Kα; Nb filter). Out of 3824 reflections measured (1.90° < θ < 22.50°), 3109 had $F_o > 3\sigma(F_o)$ and were used in the refinement procedure. Final R values: R = 0.0472, R_w = 0.0501 (weighting scheme: $w = (\sigma^2 + (0.015F_o)^2)^{-1}$).

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