the flash technique described in this article are in progress. *In general, however, the application of this flash-scavenging technique should provide valuable information concerning the nature of short-lived intermediates in the photolysis of complex organic systems.*

(25) On leave from the Department of Organic Chemistry, Poznan University, Grunwaldzka 6, Poland.

Richard S. Givens,* **Lucjan Strękowski**[25]
Department of Chemistry, University of Kansas
Lawrence, Kansas 66044

Robin Devonshire
Department of Chemistry, Sheffield University
Sheffield, England S10

Photochemistry of Carbonyl Compounds through the Enol Form. Studies on the Photorearrangement of 3-Carbomethoxyisochromanone[1]

Sir:

The concept of internal photoactivated hydrogen transfer (photoenolization) was originally postulated to explain the apparent lack of bimolecular photoreduction of 2-alkyl-, 2-amino-, and 2-hydroxybenzophenones.[2,3] Recently, a number of widely scattered and isolated reports[4-9] have appeared which indicate that 1,3-tautomerization of certain ketones can also occur upon electronic excitation.[10] Usually, the enol and enolate anions formed from the excited-state either emit phosphorescence or undergo reketonization.[4-9,11] Of special significance and interest is the possibility of observing further photochemistry from the excited enol (or enolate) when the keto tautomer is the absorbing species. Outside of several examples of intermolecular photocycloaddition of conjugated enols,[12-15]

(1) Photochemical Transformations of Small Ring Carbonyl Compounds. LIV. For LIII see A. Padwa and J. Smolanoff, *Tetrahedron Lett.*, 33 (1974).

(2) N. C. Yang and C. Rivas, *J. Amer. Chem. Soc.*, **83**, 2213 (1961).

(3) J. N. Pitts, Jr., H. W. Johnson, Jr., and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962).

(4) J. Lemaire, *J. Phys. Chem.*, **71**, 2653 (1967).

(5) R. Bishop and N. K. Hamer, *J. Chem. Soc. C*, 1197 (1970).

(6) Y. Kanda, J. Stanislaus, and E. C. Lim, *J. Amer. Chem. Soc.*, **91**, 5085 (1969).

(7) R. G. Zepp and P. J. Wagner, *J. Amer. Chem. Soc.*, **92**, 7466 (1970).

(8) N. J. Turro and T. J. Lee, *J. Amer. Chem. Soc.*, **92**, 7467 (1970).

(9) F. Bergmann and Y. Hirshberg, *J. Amer. Chem. Soc.*, **65**, 1429 (1943).

(10) Whether the photoenolization can be viewed simply as an allowed [1,3] sigmatropic shift is a question which is currently being pursued in our laboratories.

(11) For two notable exceptions see A. Padwa and G. A. Lee, *J. Amer. Chem. Soc.*, **95**, 6147 (1973); and E. E. van Tamelen, J. Schwartz, and J. I. Brauman, *ibid.*, **92**, 5798 (1970).

(12) P. de Mayo and H. Takeshita, *Can. J. Chem.*, **41**, 440 (1963).

(13) H. Nozaki, M. Kurita, T. Mori, and R. Noyori, *Tetrahedron*, **24**, 1821 (1968).

the behavior of excited state enols has not been studied in any detail. As part of a program directed toward determining the scope and limitations of the photoenolization process, we have discovered a novel intramolecular photorearrangement of a cyclic β-keto ester which involves the enol form. In this communication we describe some of the salient features associated with this reaction.

Using procedures similar to those described for the preparation of other isochromanones, 3-carbomethoxyisochromanone (1), mp 47–48°, was prepared in high yield from the corresponding carboxylic acid.[16] The nmr spectrum of 1 in a carbon tetrachloride solution indicates the existence of an equilibrium between the keto (47%) and enol (53%) forms.[17] As the polarity of the solvent increased, the concentration of the enol form increases (*i.e.*, acetone-d_6, enol/keto = 1.86). The uv spectrum of 1 in methanol showed absorption maxima at 342 (ϵ 4500) and 247 nm (ϵ 9250) suggesting that, even in a dilute solution, the concentration of the enol form is substantial.[18]

Irradiation of 1 in methanol at 25° for 8 hr under an argon atmosphere with Pyrex-filtered light gave a 95% yield of a mixture of two compounds, 2 and 3, in nearly equal amounts. The two components were separated by thick-layer chromatography. Elemental analysis, the ultraviolet spectrum (methanol, 227, 233, and 296 nm (ϵ 8900, 8000, and 16,300)), and the nmr spectrum (100 MHz, τ 6.15 (s, 3 H), 5.20 (broad s, 1 H), 3.43 (s, 1 H), 2.90 (s, 1 H), and 2.65 (m, 4 H)) suggested 1-hydroxy-3-carbomethoxyisochromene (3), mp 110–111°,
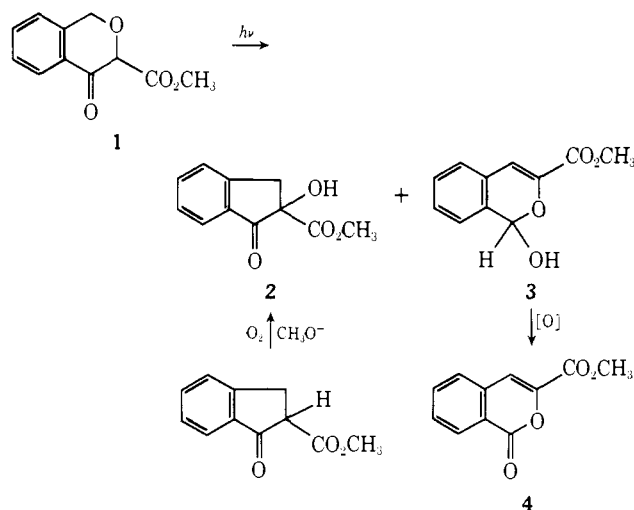
as the structure of the slower moving component. Chemical confirmation was obtained by oxidation of 3 to 1-oxo-3-carbomethoxyisochromene (4) which was, in turn, independently synthesized.[19] Spectral and ana-

(14) G. Büchi, J. A. Carlson, J. F. Powell, Jr., and L. F. Tietze, *J. Amer. Chem. Soc.*, **92**, 2165 (1970); **95**, 540 (1973).

(15) H. Takeshita and S. Tanno, *Bull. Chem. Soc. Jap.*, **46**, 880 (1973).

(16) C. N. Chefnay, *Bull. Soc. Chim. Fr.*, 1351 (1971).

(17) The nmr spectrum (100 MHz) of the keto tautomer showed signals at τ 6.25 (s, 3 H), 5.2 (s, 1 H), 4.7–5.25 (q, 2 H, J = 14.0 Hz), 2.0–3.2 (m, 4 H) while that of the enol form contained signals at τ 6.18 (s, 3 H), 6.1 (s, 2 H), 2.0–3.2 (m, 4 H), and −0.2 (s, 1 H, exchanged with D₂O).

(18) The n–π* absorption associated with the keto tautomer of 1 should resemble acetophenone and consequently would be expected to have a very low extinction coefficient at 342 nm.

lytical data for **2**, mp 131–132°, showed that (a) it was isomeric with **3**, (b) it also possessed a hydroxyl function, and (c) its nmr spectrum consisted of a pair of doublets at τ 6.75 and 6.28 (J = 18.0 Hz), a methyl ester singlet at 6.26, an exchangeable proton at 6.02, and four aromatic protons at τ 2.1–2.7. That the actual structure of **2** was 2-hydroxy-2-carbomethoxyindanone was established by an independent synthesis.

A study of product distribution *vs.* extent of irradiation established that the ratio of **2**:**3** varied as a function of time. With short exposures, 2-hydroxy-2-carbomethoxyindanone (**2**) accounts for nearly all of the product produced. At longer exposures, owing to a secondary photoreaction of **2**, the amount of **3** increased. This was independently demonstrated by the quantitative conversion of **2** to **3** in methanol under comparable photolytic conditions. The quantum yield of formation of **2** on direct irradiation of **1** was found to be Φ = 0.32 and that for **3** from **2** was 0.08. This result demonstrates that the rates of formation of **2** and **3** are sufficiently similar to account for the genesis of **3** in the photorearrangement of **1**.
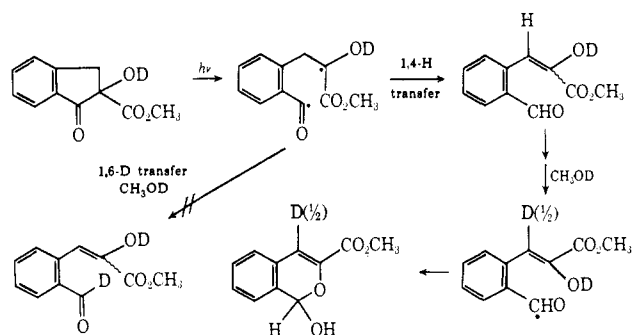

Evidence concerning the mechanism of formation of **3** was obtained by carrying out the photolysis of **2** in deuteriomethanol. In this case, the final product was found to have incorporated 50% deuterium in the vinylic position. This observation is consistent with a mechanism involving an initial Norrish type I scission followed by a 1,4-hydrogen transfer from the benzylic carbon. In order to account for the distribution of deuterium in the final product, it is necessary to assume that the initially produced enol undergoes ketonization at a faster rate than it cyclizes. The lack of deuterium incorporation in the 1-position of the isochromene (**3**) eliminates the alternative 1,6-hydrogen atom transfer process.[20]

Prior to concerning ourselves with the molecular details of the reaction mechanism for the formation of **2**, two points are of interest. First, the reaction clearly proceeds *via* the singlet state of **1**, since the reaction could not be sensitized (acetophenone) or quenched (piperylene). Second, irradiation of **1** in an aerated methanol solution resulted in the formation of 3-hydroxy-3-carbomethoxyisochromanone (**5**) as the major photoproduct. The formation of **5** can be attributed to the reaction of ground-state oxygen with the excited enol tautomer.[21]

With regard to the mechanism of the photoisomerization of **1** → **2**, direct excitation of the enol tautomer of **1** followed by ring opening and a subsequent internal aldol reaction nicely accommodates the formation of the observed product. The photochemical ring opening step is somewhat analogous to the photochemistry observed with other structurally related benzo heterocyclic olefins.[22] It is interesting to note that the chemical fate of the excited enol depends on the reaction conditions. In the presence of oxygen it is trapped to give a transient hydroperoxide which is subsequently converted to **5**. In the absence of oxygen it rearranges to an *o*-quinone methide which proceeds on to the final product.
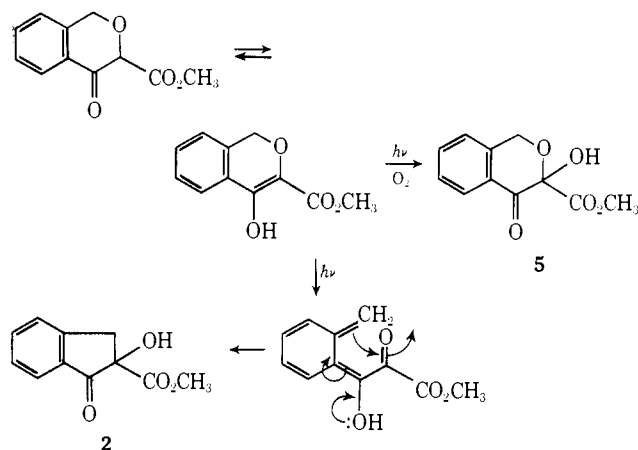
(21) An alternate possibility is generation of singlet oxygen which then reacts with the enol. Although isochromanone **1** will be converted to **5** in an aerated methanol solution in the dark, the dark reaction requires a much longer period of time.

(22) See B. Singh, *J. Amer. Chem. Soc.*, **90**, 3893 (1968), for some leading references.

(23) Alfred P. Sloan Foundation Fellow, 1968–1972; NATO Senior Postdoctoral Fellow, 1973.

Albert Padwa,* [23] **Andrew Au**

Department of Chemistry, State University of New York at Buffalo
Buffalo, New York 14214

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Involvement of an Enol Tautomer in the Photoisomerization of 4-Phenyl-3-chromanone to 4-Phenyldihydrocoumarin[1]

Sir:

Photoenolization of carbonyl compounds is a reaction of considerable importance and current interest.[1] Particular attention has been focused on relatively acidic ketones[2–5] and esters[6] and the question as to

(19) H. W. Johnston, C. E. Kaslow, A. Langsjoen, and R. L. Shriner, *J. Org. Chem.*, **13**, 477 (1948).

(20) It should be pointed out that isochromene **3** does not undergo deuterium exchange under the reaction conditions.

(1) Photochemical Transformations of Small Ring Carbonyl Compounds. LV. For LIV see A. Padwa and A. Au, *J. Amer. Chem. Soc.*, **96**, 1633 (1974).

(2) P. de Mayo and H. Takeshita, *Can. J. Chem.*, **41**, 440 (1963).

(3) H. Nazaki, M. Kurita, T. Mori, and R. Noyori, *Tetrahedron*, **24**, 1821 (1968).