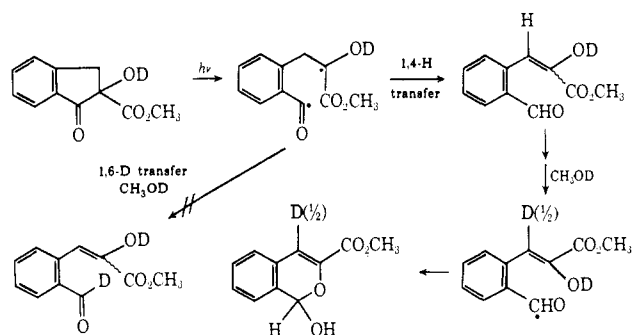


lytical data for **2**, mp 131–132°, showed that (a) it was isomeric with **3**, (b) it also possessed a hydroxyl function, and (c) its nmr spectrum consisted of a pair of doublets at τ 6.75 and 6.28 ($J = 18.0$ Hz), a methyl ester singlet at 6.26, an exchangeable proton at 6.02, and four aromatic protons 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 $\Phi = 0.32$ 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**.



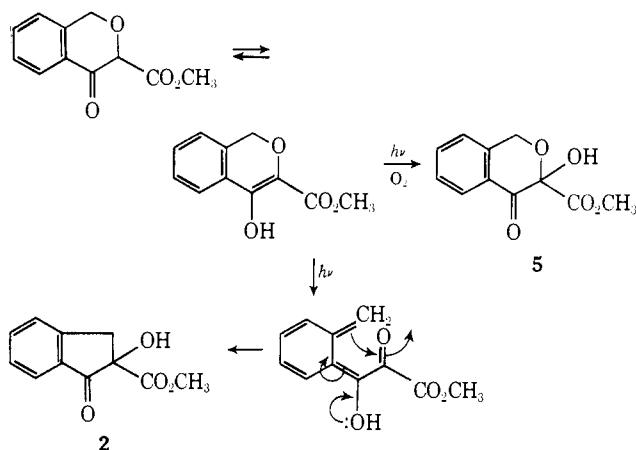
Evidence concerning the mechanism of formation of **3** was obtained by carrying out the photolysis of **2** in deuteriomethanol. In this case, the final product was found to have incorporated 50% deuterium in the vinylic position. This observation is consistent with a mechanism involving an initial 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

(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.

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.



Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. The National Science Foundation provided financial assistance in the purchase of the nmr spectrometer used in this research.

(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.

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Involvement of an Enol Tautomer in the Photoisomerization of 4-Phenyl-3-chromanone to 4-Phenyldihydrocoumarin¹

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 esters⁶ and the question as to

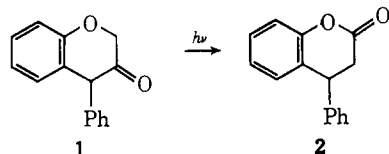
(1) Photochemical Transformations of Small Ring Carbonyl Compounds. LV. For LIV see A. Padwa and A. Au, *J. Amer. Chem. Soc.*, **96**, 1633 (1974).

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

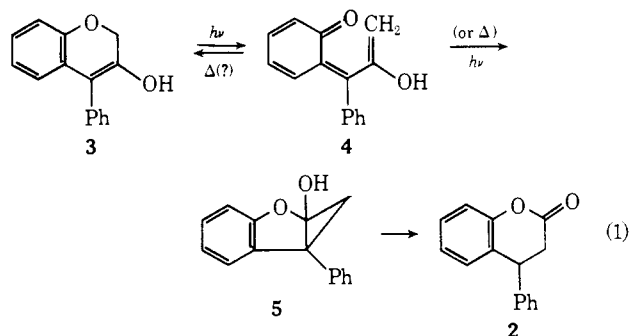
(3) H. Nazaki, M. Kurita, T. Mori, and R. Noyori, *Tetrahedron*, **24**, 1821 (1968).

whether it is possible to observe photochemistry from an excited enol (or enolate) when the carbonyl tautomer is the absorbing species. The need for understanding the behavior of excited enols has further increased the significance of this area of photochemistry.

A recent communication⁷ on the photoisomerization of 4-phenyl-3-chromanone (**1**) to 4-phenyldihydrocoumarin (**2**) prompts us to report results pertinent to



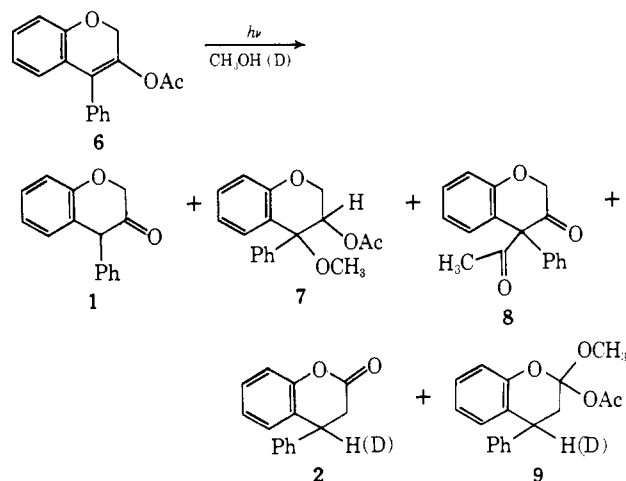
the mechanism of this unique rearrangement. The authors proposed a mechanism in which two critical steps involved an intramolecular hydrogen abstraction through a five-membered transition state.⁷ It seemed to us that a more viable explanation involved the prior enolization of chromanone **1** into its enol tautomer **3**, which upon photoexcitation underwent ring opening to the *o*-quinoneallide **4**. Closure of **4** either by photochemical⁸ or thermal means would give 1-hydroxy-5-phenyl-2-oxabenzobicyclo[3.1.0]hex-3-ene (**5**) which



would be expected to ring open to the observed dihydrocoumarin **2** (eq 1).⁹ In this communication we describe evidence for a path from **1** → **2** which implicates the existence of intermediates **3**–**5**.

Since it was the 4-phenyl-3-hydroxychromene (**3**) tautomer of **1** which was suspected of giving rise to dihydrocoumarin **2**, we sought to permanently lock **1** into its enol form (*i.e.*, **3**) and examine the behavior of the resulting system. This was accomplished by synthesizing the corresponding enol acetate (**6**),¹⁰ mp 72–73°, and studying its photochemical behavior. Irradiation of a methanolic solution of **6** with Corex-filtered light produced a mixture of five components which could be readily separated by preparative vapor-phase chromatography. Three minor products obtained from the photolysis of **6** were identified as **1** (3%), 3-acetoxy-4-methoxy-4-phenylchroman (**7**) (8%), and 4-acetyl-4-phenyl-3-chromanone (**8**) (10%) while the two major

products were identified as **2** (18%) and 2-acetoxy-2-methoxy-4-phenylchroman (**9**) (30%).¹¹ The structures of **7**, **8**, and **9** are based on the following observa-



tions. The nmr spectrum of **8** consisted of two singlets at δ 1.98 (3 H) and 4.26 (2 H) in addition to the aromatic multiplet at δ 7.2 (9 H). Treatment of **8** with methanolic sodium methoxide afforded 4-phenyl-3-chromanone (**1**) in high yield. Structure **7** showed peaks at δ 2.50 (s, 3 H), 2.95 (2 H, d, $J = 8.0$ Hz), 3.52 (s, 3 H), 4.64 (1 H, t, $J = 8.0$ Hz), and 7.15 (m, 9 H) in the nmr spectrum and was readily converted to **2** when exposed to a slightly acidic aqueous solution. Structure **9** was assigned on the basis of its spectral properties: ir (CCl₄) 5.68 μ ; m/e 298 (M^+); nmr (100 MHz) δ 2.55 (s, 3 H), 3.04 (2 H, dd, $J = 8.0$ Hz), 3.53 (s, 3 H), 4.92 (1 H, t, $J = 8.0$ Hz), and 7.2 (m, 9 H).

The salient features of our data indicate that three distinct transformations occur on irradiation of **1**. The two minor paths involve (1) a 1,3-acyl shift of enol acetate **6** to give **8**,¹² and (2) addition of methanol across the C–C double bond of **6**. Both of these paths are well documented in the literature.^{13,14} The major photochemical route, which ultimately leads to the formation of **2** and **9**, can be readily understood on the basis of an oxabicyclohexene (**5**) intermediate (see eq 1). This transient species collapses to **2** and **9** on reaction with methanol. Examination of the reaction as a function of time demonstrated that dihydrocoumarin **2** was also derived, in part, from the hydrolysis of **9** on workup.

Additional evidence for the mechanism outlined in eq 1 was obtained by studying the photochemistry of **6** in deuteriomethanol. Nmr analysis of products **2** and **9** obtained from this reaction clearly indicates that one atom of deuterium has been exclusively incorporated into the 4-position of both products. This is to be expected for an intermediate corresponding to **5**.⁹ It should be pointed out that a similar result was obtained when chromanone **1** was irradiated in deuteriomethanol. In this case, dihydrocoumarin **2** contained

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

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

(6) A. Padwa and G. A. Lee, *J. Amer. Chem. Soc.*, **95**, 6147 (1973).

(7) P. K. Grover and N. Anand, *Chem. Commun.*, 982 (1969).

(8) For a related photochemical reaction see D. A. Seeley, *J. Amer. Chem. Soc.*, **94**, 4378 (1972), and references cited therein.

(9) For ring opening reactions of cyclopropanols see C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968).

(10) P. K. Grover and N. Anand, *Indian J. Chem.*, **7**, 196 (1969).

(11) Enol acetate **6** can be recovered unchanged from a methanolic solution which has been allowed to stand in the dark for 12 hr.

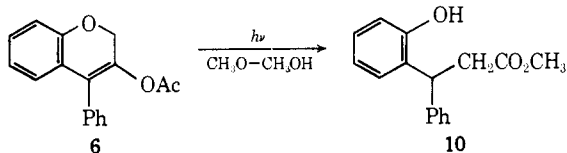
(12) The small quantities of chromanone **1** obtained from the irradiation of **6** can be attributed to partial hydrolysis of **6** or **8** on workup.

(13) D. Bellus, *Advan. Photochem.*, **8**, 146 (1971).

(14) For a related case of photoaddition of methanol across a carbon-carbon double bond see S. S. Hixson, *Tetrahedron Lett.*, 4211 (1971); A. Padwa and G. A. Lee, *J. Chem. Soc., Chem. Commun.*, 795 (1972).

one deuterium atom in the 4-position of the coumarin ring.

Based on the results obtained with enol acetate **6**, we propose that the photoisomerization of **1** → **2** proceeds *via* photoreaction of the enol (or enolate) tautomer of **1**. To test this conclusion, we have studied the photochemistry of the corresponding enolate anion. Addition of sodium methoxide to a methanolic solution of **1** caused a very rapid change in the absorption spectrum with new maxima appearing at 314 and 239 nm. The extinction coefficients for these new maxima were on the order of $\epsilon \sim 10^4$. The sodium enolate of **1** could also be generated by addition of sodium methoxide to solutions of **6**. When a thoroughly deaerated methanolic solution of **6** was first treated with sodium methoxide and then irradiated with light of wavelength >300 nm, an extremely rapid and clean conversion to methyl 3-(2-hydroxyphenyl)-3-phenylpropionate (**10**) was observed. The identity of **10** was



determined by its straightforward spectral characteristics as well as its facile conversion to **2** on heating. Structure **10** is not the primary photoproduct of the reaction but rather is derived by attack of methoxide on dihydrocoumarin **2**. A control experiment clearly demonstrated that when trace amounts of sodium methoxide were added to a methanolic solution of **2**, ester **10** was formed in quantitative yield.

In addition to being a cleaner reaction than that observed with either **1** or **6**, the base-catalyzed photolysis of **6** proceeded with a much higher quantum efficiency (*i.e.*, $\Phi(6 \rightarrow 1)^{\text{base}} = 0.24$, $\Phi(1 \rightarrow 2) = 0.007$). The difference in reaction efficiency can be readily attributed to the high concentration of the reactive enolate tautomer present in solution during the photolysis of **6** in basic methanol. Further work on the photochemistry of carbonyl compounds which proceed through the enol form is in progress and will be reported at a later date.

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

(16) National Institutes of Health Postdoctoral Fellow, 1971–1972.

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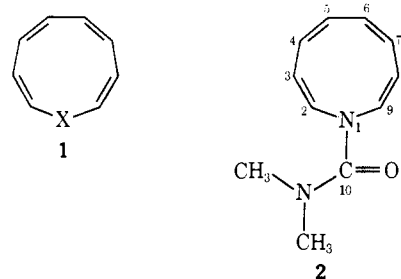
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Molecular Structure of an N-Substituted Azonine. Demonstration of Polyenic Character in a Member of This Class of Compounds

Sir:

Among π -excessive heteromonocycles, the 10π -electron heteronins (**1**) are deemed potentially aromatic by

Hückel's $4n + 2$ rule. A group of heteronins¹ has recently been synthesized and studied by Anastassiou and collaborators.^{2–4} The thermodynamic stability and spectral characteristics suggest that some of the N-substituted azonines (**1**; X = NR) be considered polyenic,⁵ and it is expected that reducing the availability of the electron pair on the heteroatom will result in a gradual transition from aromatic to polyenic character. In an effort to elucidate the detailed molecular geometry of the nitrogen-containing or azonine nine-membered ring, we have carried out a three-dimensional X-ray study on *N*-(*N,N*-dimethylcarbamyl)azonine (**2**).¹



The crystals of **2** belong to the monoclinic system with $a = 11.119(3)$, $b = 6.499(1)$, $c = 16.617(5)$ Å, and $\beta = 118^\circ 14'(1')$. There are four molecules of $C_{11}H_{14}N_2O$ in the unit cell, and the space group is $P2_1/c$. A total of 853 independent nonzero ($2\theta \leq 90^\circ$) values was measured on a Picker FACS-1 diffractometer using Cu $K\alpha$ radiation. The crystals are quite stable at 0° but decompose over a period of a few days at room temperature.⁶ The structure was solved by the symbolic addition method and has been refined by full-matrix least-squares procedures to an R factor of 0.061 on all observed data. Anisotropic temperature factors were included for the carbon, nitrogen, and oxygen atoms, while the hydrogen atoms were refined with isotropic temperature factors. See paragraph at end of paper regarding supplementary material.

The molecular structure of **2** in the crystal is shown in Figure 1. Some molecular dimensions are shown in Figure 2. The molecule is significantly nonplanar and exists in a boat conformation relative to the reasonably good plane (maximum deviation 0.046 Å) through the four atoms C(2), C(3), C(6), and C(7), with C(4), C(5), C(8), C(9), and N(1) lying 0.918, 0.955, 0.826, 1.352, and 1.178 Å, respectively, from this plane. The double bond lengths, 1.301–1.334 Å, are definitely localized at C(2)–C(3), C(4)–C(5), C(6)–C(7), and C(8)–C(9), while the C(3)–C(4), C(5)–C(6), and C(7)–C(8) lengths (1.460–1.469 Å) are in the range expected for C(sp²)–C(sp²) single bonds.^{7–9} This bond alternation is in contrast to

(1) A. G. Anastassiou, *Accounts Chem. Res.*, **5**, 281 (1972).

(2) A. G. Anastassiou and J. H. Gebrian, *J. Amer. Chem. Soc.*, **91**, 4011 (1969).

(3) A. G. Anastassiou and R. P. Cellura, *Chem. Commun.*, 903 (1969).

(4) A. G. Anastassiou and J. H. Gebrian, *Tetrahedron Lett.*, 5239 (1969).

(5) A. G. Anastassiou, S. W. Eachus, R. P. Cellura, and J. H. Gebrian, *Chem. Commun.*, 1133 (1970).

(6) Two crystals were used to accumulate the data. The first crystal was discarded after the standards fell to 75% of their initial value and the second when they fell to 85% of their initial value. We did not attempt to collect data beyond this point as we found that the high order reflections began to lose intensity quite soon after a crystal was irradiated and thus we felt that little increase in precision would be obtained due to crystal decomposition and the uncertainties in scaling additional decomposing crystals.

(7) J. Bordner, R. G. Parker, and R. H. Stanford, Jr., *Acta Crystallogr., Sect. B*, **28**, 1069 (1972).