system, which numerically integrates by the Runge-Kutta method. We thank Professor Saunders and also Professor K. B. Wiberg for access to his PDP-1145 computer. (b) A. A. Frost R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 173.

(18) NATO Postdoctoral Fellow, sponsored by the Science Research Council of Great Britain, 1973-present.

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Photochemistry of Carbonyl Compounds through the Enol Form. Involvement of a Cyclopropanone Intermediate in the Photorearrangement of 4-Carbomethoxy-3-chromanone[1]

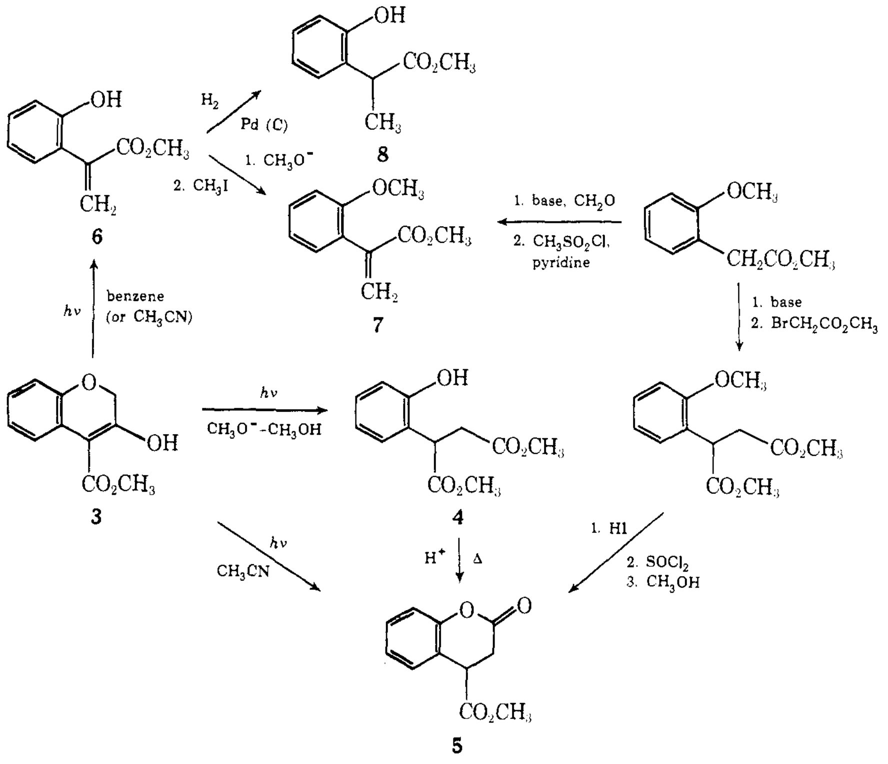
Sir:

Although the photochemical behavior of the carbonyl group has received much scrutiny in the past decade,[2,3] relatively little is known about the photochemistry of the small amount of enol tautomer which exists in equilibrium with the keto form.[4] In an earlier report[5] dealing with the photorearrangement of 4-phenyl-3-chromanone (**1**) to 4-phenyldihydrocoumarin (**2**),[6] evidence was presented which demonstrated that the enol content can be an overriding factor in determining the quantum efficiency of a photoreaction. As part of our continuing studies dealing with enol photochemistry,[7,8] we have undertaken an investigation of the excited state behavior of the 4-carbomethoxy-3-chromanone (**3**) system. We now report that in extending our studies to this system, we have discovered an unusual solvent effect which controls the product distribution. In addition, we have uncovered an unprecedented photodecarbonylation reaction which can best be explained by invoking the intermediacy of a transient cyclopropanone.

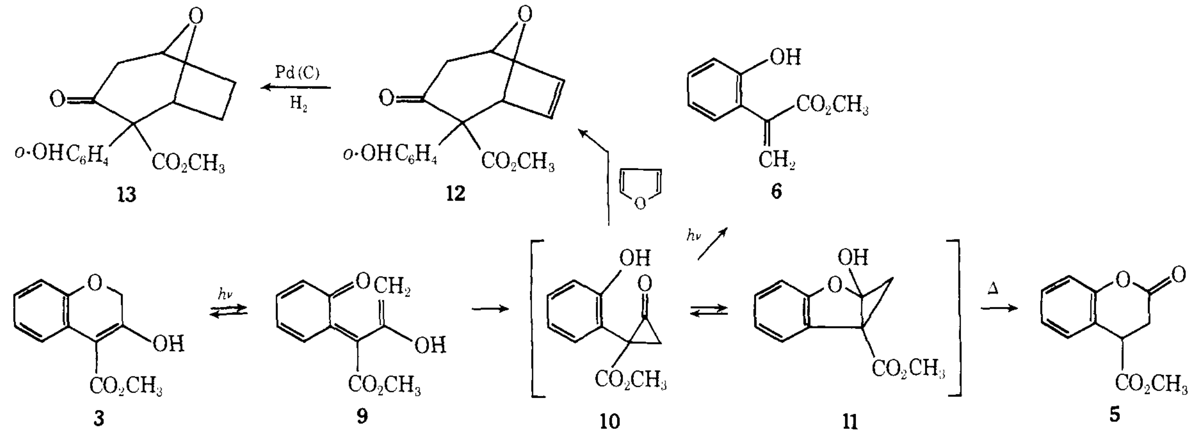
Using procedures similar to those descried for the preparation of other chromanones,[9] 4-carbomethoxy-3-chromanone (**3**), mp 35-36°, was prepared in high yield. The nmr spectrum of **3** indicates that this β-ketoester exists predominantly (>98%) in the enol form (τ 5.98 (*s*, 3 H), 5.24 (*s*, 2 H), 2.0-3.1 (*m*, 4 H), and −3.0 (*s*, 1 H, exchanged with D_2O)). When a thoroughly deaerated methanolic solution of **3** was treated with sodium methoxide and then irradiated with light of wavelength >300 nm,[10] an extremely rapid and clean conversion to methyl 3-(*o*-hydroxyphenyl)-3-carbomethoxypropanoate (**4**), mp 101-102°, was observed. The identity of **4** was determined by its straightforward spectral characteristics (nmr (100 MHz), τ 7.26 (dd, 1 H, J = 16.0 and 7.0 Hz), 6.68 (dd, 1 H, J = 16 and 9.0 Hz), 6.32 (s, 3 H), 6.28 (s, 3 H), 5.70 (dd, 1 H, J = 9.0 and 7.0 Hz), 2.6-3.3 (m, 4 H)) as well as its facile conversion to 4-carbomethoxydihyrocoumarin (**5**), mp 79-80°, on heating in the presence of a trace of acid. The structure of dihydrocoumarin **5** (nmr (100 MHz), τ 7.18 (dd, 1 H, J = 17.0 and 6.0 Hz), 6.84 (dd, 1 H, J = 17.0 and 3.0 Hz), 6.28 (s, 3 H), 6.05 (dd, 1 H, J = 6.0 and 3.0 Hz), 3.0-3.6 (m, 4 H)) was established by comparison with an independently synthesized sample.

Irradiation of **3** in acetonitrile at 25° for 14 hr under a nitrogen atmosphere with Pyrex-filtered light gave a 3:1 mixture of 4-carbomethoxydihydrocoumarin (**5**) and *o*-hydroxy-α-carbomethoxystyrene (**6**) (Scheme I). The two components could be easily separated by thick-layer chromatography. Elemental analysis, the ultraviolet spectrum (methanol, 295, 263, 252, and 243 nm (ϵ 4700, 4700, 6300, and 6500)), and the nmr spectrum (100 MHz, τ 6.12 (s, 3 H) 4.05 (d, 1 H, J = 1.2 Hz), 3.55 (d, 1 H, J = 1.2 Hz), 2.70-3.20 (m, 4 H), and 2.50 (s, 1 H, exchanged with D_2O)) suggested *o*-hydroxy-α-carbomethoxystyrene (**6**), mp 76-77°, as the structure of the minor photoproduct. Chemical confirmation was obtained by (a) catalytic reduction to methyl 2-(*o*-hydroxyphenyl)propanoate (**7**) and (b) conversion to *o*-methoxy-α-carbomethoxystyrene (**8**), which was, in turn, independently synthesized. It is interesting to note that when the irradiation of **3** was carried out

Scheme I



Scheme II

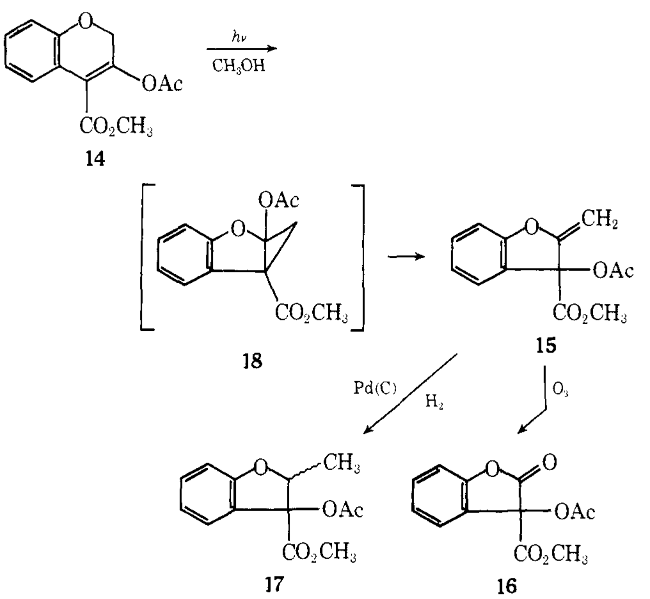


in benzene, the only product detected was o-hydroxy-α-carbomethoxystyrene (**6**).[11]

The formation of these products (see Scheme II) is readily explicable in terms of a photoinduced ring opening of chromanone **3** to an o-quinoneallide intermediate (*i.e.*, **9**). Closure of **9** by either photochemical or thermal means would give 2-carbomethoxy-2-(o-hydroxyphenyl)cyclopropanone (**10**) as a transient intermediate. This species would exist in tautomeric equilibrium with 1-hydroxy-5-carbomethoxy-2-oxabenzobicyclo[3.1.0]hex-3-ene (**11**). In polar solvents such as methanol or acetonitrile, the oxabicyclohexene (**11**) is rapidly opened to give the observed dihydrocoumarin.[12,13] Opening of the cyclopropanol ring would be expected to proceed at a much slower rate in benzene, however, since the developing charges are not significantly solvated in this medium. Consequently, the tautomeric mixture of **10** and **11** can exist for a sufficient period of time in benzene[14] to allow the system to absorb another photon of light and thereby extrude carbon monoxide.[15]

Supporting evidence for the above scheme was obtained by carrying out the irradiation of **3** in benzene which contains an excess of furan. Turro and coworkers had previously demonstrated that cyclpropanones undergo facile (3 + 4 → 7)cycloadditions with furan.[16,17] Under these conditions, the only product obtained from the irradiation of **3** was methyl 2-(o-hydroxyphenyl)-3-oxo-8-oxabicyclo[3.2.1]oct-6-ene-2-carboxylate (**12**), mp 66–69° (Scheme II). The nmr spectrum of **12** was very similar to related cycloadducts[17] and showed signals at τ 7.60 (2 H, d), 6.08, (s, 3 H), 5.02 (m, 1 H), 4.85 (d, 1 H, *J* 2.0 Hz), 4.65 (dd, 1 H, *J* = 6.0 and 2.0 Hz), 3.82 (dd, 1 H, *J* = 6.0 and 2.0 Hz), 2.6–3.4 (m, 4 H). Addition of incremental amounts of Eu(fod)$_3$[18] to solutions of adduct **12** caused a downfield shift of the signal at τ7.60 and its conversion into an AB quartet (J_{AB} = 14.5 Hz, low field half split *J* = 4.5 Hz, high field half split *J* = 1.2 Hz). Cycloadduct **12** was also characterized by catalytic hydrogenation to oxabicyclo[3.2.1]octane **13**, mp 113–114°. The isolation of cycloadduct **12** and the complete absence of **5** and **6** provides compelling evidence for the intermediacy of a cyclopropanone in the photolysis of **3**.

Scheme III



Additional support for the mechanism outlined in Scheme II was obtained by studying the photochemistry of the related 3-acetoxy-4-carbomethoxychromene (**14**).[19] Irradiation of **14** in methanol under a nitrogen atmosphere with Pyrex-filtered light gave a single compound whose structure was identified as 2-methylene-3-acetoxy-3-carbomethoxydihydrobenzofuran (**15**); nmr τ 8.04 (s, 3-H), 6.04 (s, 3 H), 5.68 (d, 1 H, *J* = 3.0 Hz), 5.46 (d, 1 H, *J* = 3.0 Hz), and 2.5–3.2 (m, 4 H). Chemical confirmation was obtained by ozonization to 3-acetoxy-3-carbomethoxybenzofuranone (**16**) and by catalytic reduction to 2-methyl-3-acetoxy-3-carbomethoxydihydrobenzofuran (**17**)[20] (Scheme III). The formation of benzofuran **15** from the photolysis of enol acetate **14** is another unique process and can also be explained in terms of an oxabenzobicyclo[3.1.0]hexene intermediate (*i.e.*, **18**). In this case, the oxabicyclohexene does not open to a dihydrocoumarin but instead undergoes further reaction *via* a tight ion pair to give the observed product (*i.e.*, **15**). Further work on the quantitative aspects of these systems and on additional photoreactions of carbonyl compounds which proceed through the enol form is in progress and will be reported at a later date.

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(10) Irradiation of **3** in the presence of methanol afforded a rather complex mixture of photoproducts. The photoreaction was found to be remarkably clean, however, when a small amount of sodium methoxide was added to the methanolic soluton. Control experiments showed that chromanone **3** was stable to these basic conditions in the dark.
(11) A control experiment clearly demonstrated that dihydrocoumarin **5** was stable to extended irradiation, both in benzene and acetonitrile.
(12) For ring opening reactions of cyclopropanols see C. H. Depuy, *Accounts Chem. Res.*, **1**, 33 (1968).
(13) Control experiments show that when trace amounts of sodium methoxide were added to a methanolic solution of **5** in the dark, diester **4** was formed in quantitative yield.
(14) To date, all attempts to detect cyclopropanone **10** by infrared spectroscopy at room temperature have failed. This may be due to the low concentration of this tautomer or to a ring opening reaction which occurs during our experimental manipulations.
(15) Cyclopropanones are known to lose carbon monoxide on exposure to ultraviolet light, see N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers, and G. F. Vesley, *J. Amer. Chem. Soc.*, **87**, 2613 (1965).
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(19) 3-Acetoxy-4-carbomethoxychromene (**14**), mp 72–73°, was conveniently prepared by treating **3** with acetic anhydride: nmr τ 7.82 (s, 3 H), 6.22 (s, 3 H), 5.38 (s, 2 H), and 2.7–3.4 (m, 4 H).
(20) Complete spectroscopic details of all new compounds will be given in our full manuscript.

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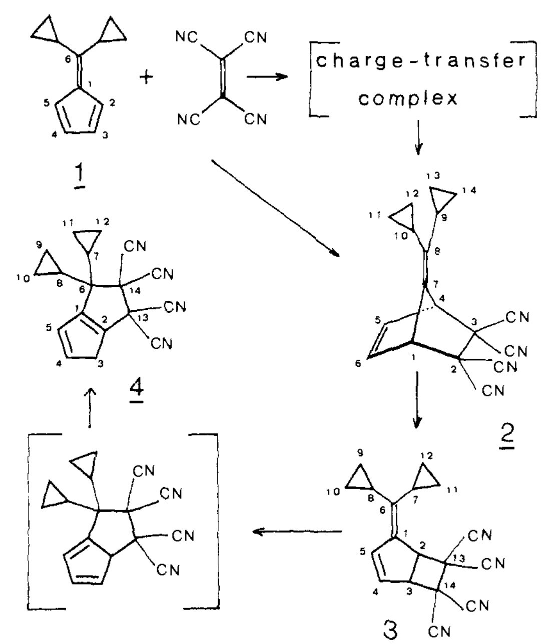
A Reactional Cascade. Addition of Tetracyanoethylene to Dicyclopropylfulvene[1]

Sir:

Fulvenes[2] confront the prospective 2π addend with a multifarious choice: [2 + 2] cycloaddition on the exocyclic 1,6 double bond or [2 + 2] with one of the endocyclic double bonds, [2 + 4] with the whole cyclopentadiene moiety or yet [2 + 6] encompassing atoms 2 and 6 at the termini of the (formally) π system.[3] With dicyclopropylfulvene[4] (**1**), the difficulty of predicting theoretically the outcome of an addition is compounded by the near-degeneracy of the a_2 (A) and b_1 (S) which are the two highest occupied molecular orbitals.[3] We have discovered that **1** adds to tetracyanoethylene with consecutive formation of [2 + 4], [2 + 2], and [2 + 6]cycloadducts (Scheme I). They interconvert through zwitterionic intermediates, the evidence for which will now be delineated.

Scheme I



Reaction of **1** (10 mmol) with TCNE (10 mmol) in ether solution, at 0°, gave the expected[2] [4 + 2] Diels-Alder cycloadduct[5] in nearly quantitative yield. As gauged by the cmr shifts,[5] the exocyclic double bond is electron-depleted *both* by the homoconjugative interaction with the endocyclic 5,6 double bond and by attachment of the cyclopropane rings at C-8; its polarization is weak compared to other 7-methylene norbornenes.[6] The activation energy for this first step is not high. This cycloaddition is either concerted, with the predominant interaction connecting the LUMO of TCNE with the a_2 MO of **1**, both antisymmetric, or proceeding *via* an intermediate; the experimental evidence currently available does not allow us to settle this point.

At slightly higher temperatures, **2** decays by clean first-order kinetics into the [2 + 2] adduct **3**.[7] The rate constant determined by nmr for the transformation of **2** into **3** displays pronounced solvent dependence (Figure 1), with an activation energy $\Delta G^*_{273} = 20.7$ kcal mol^{-1} in pure acetone. The extensive evidence by Huisgen, *et al.*,[9,10] has provided elegant proof for the intermediacy of a zwitterion in the [2 + 2] cycloadditions between TCNE and enol ethers. The analogous zwitterion formed by heterolytic cleavage of the 1,2 bond in **2** is strongly resonance stabilized. A plot of ln k_1 against the dielectric function $(\epsilon - 1)/(2\epsilon + 1)^9$ is linear (Figure 1; $\rho > 0.98$), and indicates an increase in the dipole moment by *ca.* 12 D in going from **2** to the more polar transition state. Observation of a strong dependence of the reaction rate upon the solvent polarity also serves to rule out a 1,3 sigmatropy for the **2** → **3** process.[11]

That is not the end of the story! The [2 + 2] cyclobutane derivative **3** has considerable strain, as implied, *e.g.*, by the

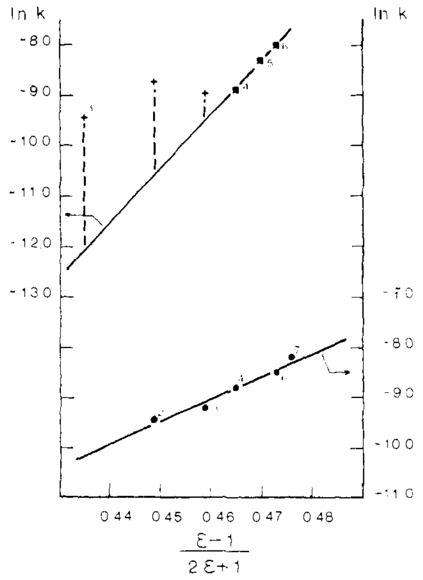


Figure 1. Plots of ln k_{obsd} for decomposition of **2** at 0° (bottom) and of **3** at 50° (top) against the dielectric function $(\epsilon - 1)/(2\epsilon + 1)$. Numbers refer to the solvent systems used (v/v): 1, diethyl ether 60:acetone 40; 2, diethyl ether 40:acetone 60; 3, diethyl ether 20:acetone 80; 4, acetone; 5, acetone 80:acetonitrile 20; 6, acetone 60:acetonitrile 40; 7, acetone 40:acetonitrile 60. The significantly greater slope for the top solid line implies a larger dipole moment for the second zwitterionic intermediate (see text). The dashed segments have lengths approximately proportional to the diethyl ether concentration.