almost 1 order (Table I). Since macrocycle **3a** showed no sign of complexation with any guest molecules, the complexation between **3b** and the aromatic guests must occur in the cavity. Naphthalene derivatives such as *N*-(2-naphthyl)acetamide, a good guest for **4**, were hardly bound with **3b**, possibly due to their steric demand.[11] In addition to the good fit of the cavity size, *the specific recognition of electron-rich benzene derivatives is apparently ascribable to the electronic environment in the cavity surrounded by tetrafluorophenylene and coordinated pyridyl groups, both of which are extremely electron-deficient.*

Supplementary Material Available: A procedure for the preparation of **2b**, physical data of **2b** and **3a,b**, FAB mass spectrum of **3a,b**, X-ray crystallographic data for **3a**, details on the computer modeling of **3b**, and details on the NMR determination of the host-guest association constants (15 pages). Ordering information is given on any current masthead page.

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[11] *N*-(1-Naphthyl)acetamide and 1,4- and 1,5-dimethoxynaphthalenes were not complexed with **3b**.

Solution Photochemistry of 2*H*-Pyran-2-one: Laser Flash Photolysis with Infrared Detection of Transients[1]

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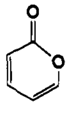
The photochemistry of 2*H*-pyran-2-one (**1**) and its derivatives has been a source of continued interest for more than 30 years. Its complexity is perfectly suited for demonstrating the usefulness of laser flash photolysis with infrared detection (LFP-TRIR) to obtain mechanistic information and kinetic details in a situation where other techniques are difficult or impossible to apply.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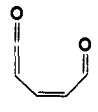
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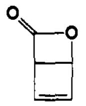
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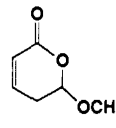
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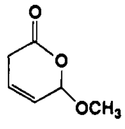
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The formation of methyl ester products during the photolysis of an alkylated derivative of **1** in methanol led de Mayo to postulate the existence of a ketene intermediate.[3,4] While ketene **2** was later characterized in a glass at low temperature by infrared spectroscopy,[5-8] its intermediacy in the ester formation was put in serious doubt.[9]

It has been shown that **2** is formed reversibly from **1** upon irradiation and that a photostationary state between the ketene and pyrone is rapidly reached. Continued irradiation leads to the slow buildup of bicyclic lactone **3**.[6,7,10] The possibility that the lactone is not a direct photoproduct from **1** but is instead produced from the ketene either thermally or photochemically cannot be addressed by matrix experiments.

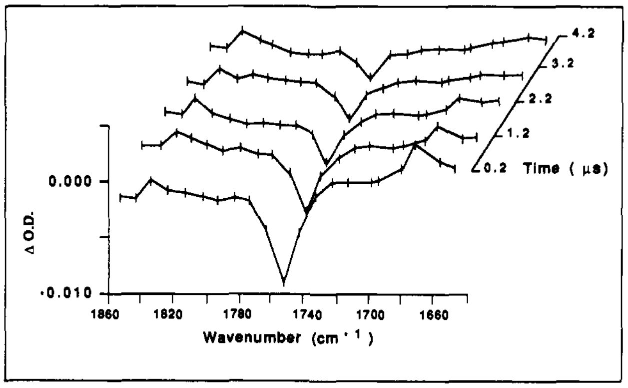

Figure 1. 3D representation of LFP-TRIR spectra showing the bleaching and partial recovery of **1** and the formation of the photoproducts **2** and **3** (see text).

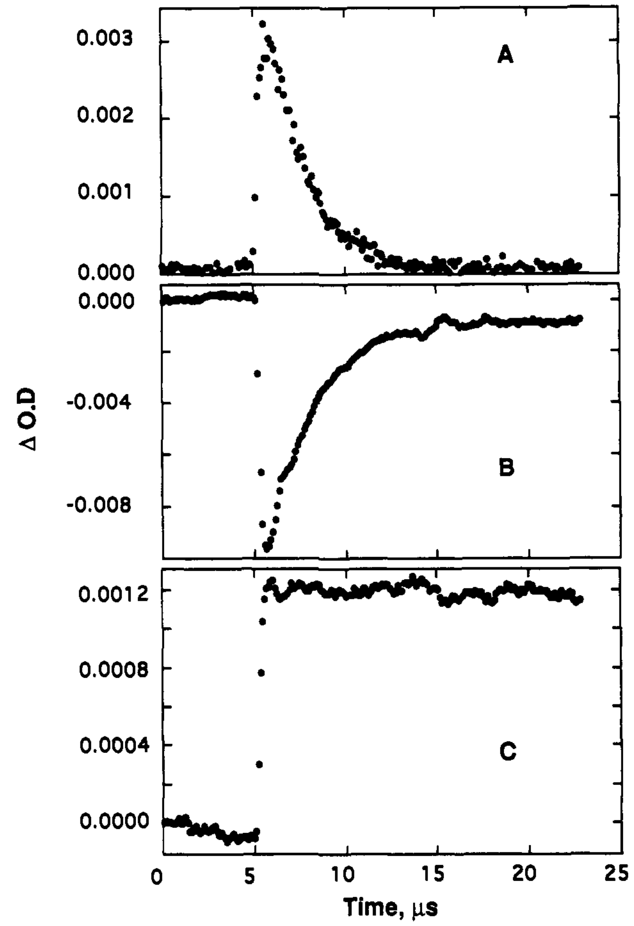

Figure 2. Kinetic traces of the transient absorptions observed after irradiation of **1**: (A) decay at 1690 cm^{-1} (aldehyde stretch of the ketene, **2**); (B) bleaching and partial recovery of **1** at 1750 cm^{-1} (carbonyl stretch); (C) absorption at 1850 cm^{-1} (carbonyl stretch of lactone, **3**).

While extensive studies of **1** and its derivatives have been carried out under matrix isolation conditions, the intermediates, including the excited states of the pyrone, have never been characterized in solution. Further, the mechanism of their interconversion is unknown and information concerning their reactivity is scarce. The present study was undertaken to address these questions.

Our preliminary studies indicating that **1** and **2** absorb in similar regions of the ultraviolet (λ_{max} = 300 and 295 nm, respectively) combined with the fact that **3** shows only end absorption (λ_{max} < 250 nm)[10] convinced us that unraveling the mechanistic and kinetic information by means of laser flash photolysis with UV-

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[1] Issued as NRCC No. 35237.
[2] NRCC Research Associate 1989-1992.
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visible detection would be difficult. Laser flash photolysis with infrared detection on the other hand does not suffer from the same disadvantages in that strong IR bands corresponding to carbonyl stretching transitions are accessible for all of the species involved with no overlap of the expected absorbances, i.e., for **1**, 1750 cm^{-1}; for **2**, 2129 and 1690 cm^{-1}; and for **3**, 1850 cm^{-1}.[7] LFP-TRIR experiments[11] were carried out using 308-nm excitation on a 3×10^{-3} M solution of **1** in cyclohexane. LFP-TRIR spectra, obtained 200 ns after the 308-nm laser pulse and every 1.0 μs thereafter for 4.2 μs, are shown in a 3D representation in Figure 1. Three distinct transient features are observable in these spectra, formation of two new absorbances and the bleaching of the precursor. The kinetic traces associated with each of the phenomena are shown in Figure 2. Panel A depicts the kinetic trace recorded at 1690 cm^{-1}, monitoring the absorption that we assign to the aldehyde stretch of **2**.[15] It decays with first-order kinetics with a lifetime of 2.9 μs. Similarly, panel B shows the bleaching and partial recovery of **1** monitored at 1750 cm^{-1}. The rate of the recovery is consistent with the rate of decay of **2**. The short ketene lifetime and the extent to which the bleaching recovers suggests that the thermal reversion of **2** back to **1** is both rapid and efficient. Finally, panel C shows the kinetic trace obtained at 1850 cm^{-1} corresponding to an absorption that is assigned to **3**. There is no doubt that **3** is formed instantaneously on our time scale, eliminating the possibility that it is formed thermally from **2**. The intensities of the absorptions at 1690 and 1850 cm^{-1} (as well as that of the bleaching at 1750 cm^{-1}) increase linearly with the laser flux, proving that both **2** and **3** are primary photoproducts from **1**. The quantum yields for their formation were determined to be $\Phi_2 = 0.52 \pm 0.1$ and $\Phi_3 = 0.09 \pm 0.1$, respectively, by comparing the intensity of the bleaching at 1750 cm^{-1} with the intensity of the absorption obtained for a standard reaction under otherwise identical conditions.[16]

The addition of small quantities of methanol leads to a decrease in the observed optical density of the 1690-cm^{-1} absorption assigned to **2**, but its rate of decay remains unchanged. This type of behavior is characteristic of the scavenging of an early intermediate, which in this case must be the singlet excited state of **1**.[17] The LFP-TRIR spectrum obtained for a cyclohexane solution containing sufficient methanol to completely inhibit formation of **2** shows only instantaneous permanent bleaching of the absorption assigned to **1** and the instantaneous formation of a new absorption that does not decay within the time scale of our experiment. This absorption, at 1715 cm^{-1}, is assigned to the cyclic addition product **4** on the basis of the reported carbonyl stretching frequencies of the dimethyl derivative.[9] The other expected product, **5**, should absorb at ~1755 cm^{-1}, which is close to where bleaching of **1** occurs. A ~10-cm^{-1} shift to lower wavenumber in the bleaching maximum and its much smaller intensity compared with that observed in the absence of methanol indicate that **5** is indeed formed but its absorbance is masked by the bleaching of **1**. The open ester product, $CH_3OC(O)CH_2CH{=}CHCHO$, expected if **2** were to react with methanol, has two carbonyl stretching vibrations at 1733 (ester) and 1686 cm^{-1} (aldehyde).[5] These absorptions are absent in our experiment. This indicates that, in solution, methanol quenches the singlet excited state of **1** in preference to reacting with **2**.

In summary, we have unequivocally shown that ketene **2** and the lactone **3** are both primary products of the photochemical reaction of 2*H*-pyran-2-one (**1**). Furthermore, we have provided strong evidence that the excited singlet state of **1**, and not ketene, is responsible for the observed photoreactivity with methanol. The ketene has a lifetime of only 2.9 μs in solution at 25 °C, and it reverts efficiently back to the starting pyrone in an energy-wasting process.

These studies show the versatility of infrared detection of transients since vibrational transitions are more sensitive to molecular structure than are electronic transitions. Further studies concerning the reactivity of 2*H*-pyran-2-one and similar sources of ketenes are planned.

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[11] The LFP-TRIR apparatus used has been described elsewhere.[12-14] Further experimental details will be published with the full report of this work.

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[15] The absorption at 2129 cm^{-1}, attributable to $C{=}C{=}O$ stretch of **2**, and the UV band at 295 nm are also observable in solution and display similar kinetics.

[16] We have chosen the decarbonylation of diphenylcyclopropenone as our standard reaction, which was itself calibrated against the benzophenone/piperylene actinometer using 308-nm laser pulses from a Lumonics EX-500 excimer laser. The quantum yield for the decarbonylation was determined to be $\Phi = 1.00 \pm 0.03$. Product formation and starting material depletion were followed using GC analysis. Extinction coefficients were determined using a Nicolet 20DBX FTIR spectrometer. The relative values reported for the quantum yields are known much more accurately than the reported error limits imply. The large error in the absolute values is due to uncertainties in the infrared extinction coefficients and the determination of the observation wavelength, as well as the usual errors associated with quantum yield determinations using lasers as radiation sources. Experimental details will be published with the full report of this work.

[17] The yield of the ketene is not affected by addition of typical triplet quenchers, such as biacetyl.

Alkene Reactivities toward a Strongly Electrophilic Radical. First Absolute Rate Constants for Some Reactions of Perfluoro-*n*-alkyl Radicals in Solution[1]

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The absolute reactivities of alkyl and perfluoroalkyl radicals are expected to differ significantly since the former are electron-rich, planar π-radicals, whereas the latter are electron-poor, nonplanar σ-radicals. Direct, time-resolved methods have been extensively employed to obtain absolute kinetic data for a wide variety of alkyl radical reactions in the liquid phase,[3] but no such measurements have been made for perfluoroalkyl radicals. Indeed, even relative rate data for fluoroalkyl and other electrophilic radicals in solution are sparse.[3,4] Since the effective use of fluoroalkyl radicals in organic synthesis requires a proper understanding of their reactivity vis-à-vis the reactivity of structurally related alkyl radicals, we have begun a program to measure the absolute kinetics of prototypical fluoroalkyl radical reactions by a combination of laser flash photolysis (LFP), product analyses, and conventional competitive kinetics. The stereoelectronic factors governing the reactivity of nucleophilic alkyl radicals, particularly in addition reactions, have been extensively examined.[5-8] There

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