Photochemistry of Tetramethyl-4-pyrone in Alcohol Solvents

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Irradiation of tetramethyl-4-pyrone in alcohol solvents leads to the formation of tetramethyl-2-pyrone and to a variety of cyclopent-2-enone and cyclopent-3-enone solvent adducts. The structure and mode of product formation is consistent with photochemical generation of a short-lived 2,6-bridged oxabicyclohexenyl zwitterion which undergoes sigmatropic rearrangement to a longer-lived epoxycyclopentenone. Although the zwitterion is efficiently trapped by methanol solvent, in less nucleophilic alcohol solvents it rearranges to the epoxycyclopentenone which isomerizes to the 2-pyrone or reacts with the alcohol solvent to form the observed solvent adducts.

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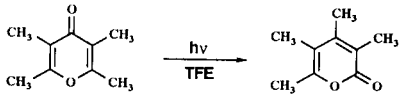
Introduction.

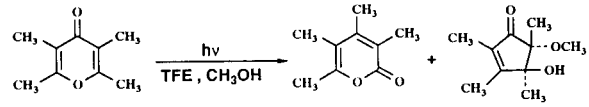
We have previously reported that tetramethyl-4-pyrone (**1**) undergoes photoisomerization in 2,2,2-trifluoroethanol (TFE) solvent to yield tetramethyl-2-pyrone (**2**) [1]. Furthermore, we presented evidence for the presence of at



1 2

least two thermally unstable intermediates on the 4-pyrone → 2-pyrone reaction coordinate. Accordingly, monitoring the photoreactions of **1** in TFE by uv-spectroscopy revealed that **2** is not a primary product in this transformation. Thus, when **1**, 1 x $10^{-4}M$ in TFE, was irradiated for 15 seconds, the absorbance due to **1** at 256 nm decreased from 1.42 to 0.47 while the absorbance at 305 nm due to **2** increased from 0.07 to 0.37. Although further irradiation caused a rapid additional increase in the absorbance due to **2**, the latter absorbance also continued to rise slowly in the absence of light until it reached a final value of 0.59 during a 5 hour dark period. This indicates that after short-duration irradiation, 2-pyrone **2** can be formed from a photochemically generated species with a half-life of ~50 minutes.

In addition to the evidence for this long-lived intermediate, our experimental results also suggested the presence of a shorter-lived intermediate earlier on the reaction pathway. Thus, when methanol (12.5 mole percent) was added to the TFE solution of **1** immediately after a 15 second irradiation, the absorbance of **2** at 305 nm again reached a value of 0.59 after the 5 hour dark period. This shows that methanol does not react with the immediate precursor of 2-pyrone **2** during the dark period. When the same amount of methanol was present in the TFE during the 15 second irradiation, the final yield of **2** was reduced



1 2 3

by ~25% with concomitant formation of methanol adduct **3**. This indicates that methanol is reacting with a species with a lifetime far shorter than that observed for the immediate precursor of **2**.

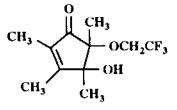
Subsequent experiments utilizing careful gas chromatography (gc) to monitor the photoreactions of **1** in various alcohol solvents have revealed the formation of a variety of additional minor products, some of which are formed during the dark period following the photolysis.

Results and Discussion.

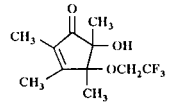
Irradiation of tetramethyl-4-pyrone (**1**) (2 x $10^{-2}M$) in TFE was monitored by capillary column gc. After 20 minutes of irradiation, analysis indicated 37% consumption of **1** and formation of **2** as the major product. The gc analysis also revealed the presence of three additional minor products **4**, **5**, and **6** at shorter retention times. After the irradiated solution was allowed to stand in the dark at room temperature for 24 hours, gc analysis revealed a 39% increase in the amount of **2** present. This is consistent with our earlier observation by uv-absorption spectroscopy. Interestingly, gc analysis also revealed that the peaks due to **5** and **6** also increased by 28 and 24% respectively while the peak due to **4** had totally disappeared.

Compounds **5** and **6** were isolated by preparative gc. Compound **5** was obtained as a white crystalline solid, mp 106-108°. The mass spectrum exhibited a molecular ion at m/z 252 consistent with a molecular formula of $C_{11}H_{15}O_3F_3$. This corresponds to a 1:1 addition adduct of **1** and TFE. The mass spectrum of **5** also exhibits an intense peak (87% of the base peak) at m/z 153, corresponding to the loss of CF_3CH_2O. Ring contraction is supported by the infrared spectrum which exhibits a carbonyl absorption at

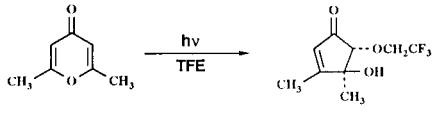
1715 cm^{-1}, consistent with other cyclopent-2-enone solvent adducts derived from photo-ring contraction of 4-pyrones [1]. The ^1H nmr spectrum exhibits four 3-proton singlets at 1.25, 1.45, 1.80, and 2.00 ppm and a 2-proton multiplet at 3.67-3.86 ppm. The ^{19}F nmr spectrum shows a triplet 1.9 ppm downfield from TFE. These spectral data are consistent with either 4-hydroxy or 5-hydroxycyclopentenone structures **5a** or **5b**. Although the cyclopentenone-TFE adduct **8**, derived from 2,6-dimethyl-4-pyrone (**7**) was unambiguously identified as a 4-hydroxycyclopentenone adduct [2], the thermal origin of **5** and the structural difference between the photochemically and thermally generated methanol adducts discussed later lead us to suggest that **5** is a 5-hydroxyisomer, **5b**.



5a

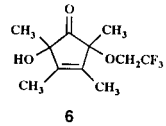


5b



7 **8**

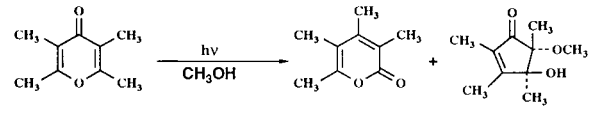
The second product **6**, which was collected as a colorless oil, exhibited a molecular ion at m/z 252, also consistent with a molecular formula of $C_{11}H_{15}O_3F_3$. Although **5** and **6** are isomeric, their mass spectral splitting patterns are quite different. Thus, in the case of **6**, the peak at m/z 153 is very small indicating that loss of a CF_3CH_2O group is a minor fragmentation pathway. Comparison of the ^1H nmr and infrared spectra of **5** and **6** also reveals important structural differences. Thus the α and β methyl groups in **5** absorbing at 1.80 and 2.00 ppm have been replaced in **6** by methyl groups absorbing at 1.74 and 1.84 ppm. This indicates that the allylic methyl groups in **6** are more nearly identical and not part of an α,β-unsaturated system. Furthermore, although the infrared spectrum of **6** confirms the presence of hydroxyl, ethylenic, and carbonyl functional groups, the carbonyl absorption frequency is displaced to 1755 cm^{-1}, consistent with a non-conjugated carbonyl group. Based on these spectroscopic data, the structure 2-hydroxy-5-(2,2,2-trifluoroethoxy)-2,3,4,5-tetramethylcyclopent-3-enone has been assigned to **6**.



6

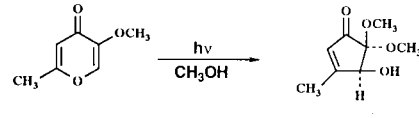
Although **4** was not sufficiently stable for isolation, gc-mass spectral analysis revealed that it was not a solvent adduct. Thus, the molecular ion at m/z 152 showed that **4** was isomeric with 4- and 2-pyrones **1** and **2**.

The irradiation of tetramethyl-4-pyrone (**1**) (2 x $10^{-2}M$) in methanol was also monitored by capillary column gc. After 20 minutes of irradiation, analysis indicated 16% consumption of **1** and formation of **2** and **3** in a ratio of 1:16. Products **4**, **5**, and **6** were not observed. Furthermore, continued analysis during the subsequent 24 hour dark period revealed neither a change in the concentration of **2** and **3** nor the formation of any additional products. Methanol adduct **3**, isolated by preparative gc as a



1 **2** **3**

colorless oil, exhibited a molecular ion in the mass spectrum at m/z 184, consistent with the molecular formula $C_{10}H_{16}O_3$. The infrared spectrum, which exhibits ethylenic and carbonyl absorptions at 1660 and 1715 cm^{-1} respectively, is typical of other cyclopent-2-enone solvent adducts and also exhibits free and concentration dependent intermolecular hydrogen-bonded O-H absorptions at 3620 and 3480 cm^{-1}, consistent with a *trans*-relationship between the OH and OCH_3 groups [3]. Also, as expected for the assigned structure, the ^1H nmr spectrum exhibits 3-H singlets (dimethyl sulfoxide-d_6) at 1.20, 1.23, 1.98, and 2.48 ppm and a deuterium oxide exchangeable 1-H singlet at 5.12 ppm. These spectral data are insufficient to distinguish between the suggested 4-hydroxycyclopentenone structure suggested and the alternate 5-hydroxycyclopentenone structure in which the OH and OCH_3 groups are transposed. In this case the structural assignment is based on the analogous methanol adduct **10** derived from photo-ring contraction of 2-methyl-5-methoxy-2-pyrone (**9**) [1]. In



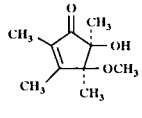
9 **10**

this case, since in dimethyl sulfoxide-d_6 the O-H and C-4 protons appeared as two doublets (J = 9 Hz) at 5.5 and 4.3 ppm respectively, the O-H is unambiguously placed at C-4. Furthermore, upon addition of deuterium oxide, both doublets collapsed to a one proton singlet at 4.3 ppm confirming these spectral assignments. Considering the similarity of the photoreactions of **1** and **9** in methanol solvent, *i.e.*, neither ring contracted product exhibits any thermal formation after cessation of irradiation, this structural analogy between **3** and **10** seems reasonable.

When **1** was irradiated in TFE containing 9% methanol, gc analysis revealed that methanol adduct **3** was also formed at the expense of the formation of **2**, and the cyclopentenone-TFE adducts **5** and **6**. Methanol adduct **3** was not observed if the methanol was added to the TFE so-

lution immediately after irradiation. This supports our original conclusion that **3** is formed by methanol trapping of a short-lived intermediate.

Whether the methanol was added before or after irradiation, continued monitoring of the solution during the subsequent dark period did reveal the additional formation of tetramethyl-2-pyrone (**2**) and cyclopentenone-TFE adducts **5** and **6**. Interestingly, although this analysis did not reveal continued formation of cyclopentenone-methanol adduct **3**, the formation of two new products, **11** and **12**, were observed whether the TFE solution of **1** was spiked with methanol before or after irradiation. These new products were isolated by preparative gc. Compound **11** was collected as an oil that subsequently crystallized whereas **12** remained an oil. Both compounds exhibited spectral properties consistent with those expected for a hydroxycyclopentenone-methanol adduct. Thus both exhibited absorption in the ultraviolet at 234 nm, infrared absorptions at 1715-1720 (C=O) and 1650-1660 (C=C) cm^{-1}, identical to **3**, and both exhibited molecular ions in their mass spectra at m/z 184, also consistent with a molecular formula of $C_{10}H_{16}O_3$. Unlike **3**, however, the mass spectra of **10** and **11** exhibited base peaks at m/z 153, indicating that in these isomers, loss of CH_3O is enhanced relative to **3**. This enhanced loss of the alkoxyl group was also observed in the case of the thermally generated TFE adduct **5**. These thermally generated methanol adducts **11** and **12** have thus been assigned *cis*- and *trans*-4-methoxy-5-hydroxycyclopentenone structures respectively.



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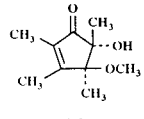
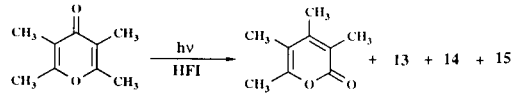


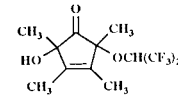
12

The photochemistry of **1** was also investigated in 1,1,1-3,3,3-hexafluoroisopropyl alcohol (HFI) solvent. Upon irradiation of **1** (2×10^{-2} *M*) in HFI, gc analysis showed that **2** was formed as the major product along with three additional minor products, **13**, **14**, and **15**. Monitoring the irradiated solution by gc analysis during the subsequent 24 hour dark period showed neither an increase in the



quantities of these products nor the formation of any additional new products. Of these three products detected, **13** and **14** were formed in sufficient quantity to allow collection by preparative gc.

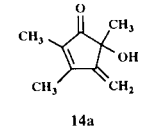
Product **13** was collected as an oil which crystallized upon standing in the freezer. The mass spectrum of this compound exhibited a molecular ion at m/z 320 consistent with the formula $C_{12}H_{14}O_3F_6$ required for a 1:1 addition adduct of **1** and HFI and a weak signal (6% of the base peak) at m/z 153, indicating that loss of $OCH(CF_3)_2$ is a minor fragmentation pathway. This suggests that HFI-adduct **13** is structurally analogous to TFE-adduct **6**. Other spectral properties are consistent with this suggestion. Thus, in addition to absorption at 1755 cm^{-1}, indicative of a non-conjugated carbonyl group, the ^1H nmr spectrum is also consistent with a cyclopent-3-enone structure for the adduct. Thus, as was observed in the case of **6**, the spectrum of **13** exhibits singlets at 1.33 and 1.40 ppm for the methyl groups α to the carbonyl groups and two singlets at 1.81 and 1.85 ppm for the nearly identical allyl methyl groups at C-3 and C-4. In addition, as demanded by the hexafluoroisopropoxyl side chain, the ^1H nmr spectrum also exhibits a one-proton septet at 4.75 ppm ($J \sim 6$ Hz). Accordingly, the structure 2-hydroxy-5-(1,1,1,3,3,3-hexafluoro-2-propoxy)-2,3,4,5-tetramethylcyclopent-3-enone has been assigned to **13**.



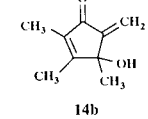
13

Compound **14** was also collected as an oil that crystallized upon standing in the freezer. The mass spectrum of this compound exhibited a molecular ion at m/z 152 indicating that this product is isomeric with the starting 4-pyrone **1**. The infrared spectrum of this compound revealed a conjugated carbonyl absorption at 1705 cm^{-1} and a C=C absorption at 1635 cm^{-1}, characteristic of a cyclopent-2-enone ring structure, and an additional C=C absorption at 1605 cm^{-1}, suggestive of a terminal alkene. The ^1H nmr spectrum supports these structural suggestions. Thus, in addition to revealing the presence of only three methyl signals at 1.15, 1.71, and 2.01 ppm, the ^1H nmr spectrum of **14** in anhydrous DMSO-d_6 revealed two one-proton signals at 5.25 and 5.29 ppm characteristic of a terminal methylene unit formed from one of the original methyl groups, and also a one-proton, deuterium oxide exchangeable resonance at 5.20 as required for a hydroxyl proton.

Taken together these spectral properties are consistent with either structure **14a** or **14b**. Although these spectral data do not allow unambiguous distinction between the

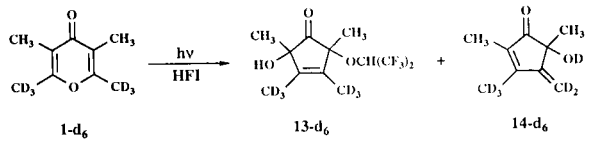


14a



14b

two structural possibilities, this distinction was made possible by analysis of the corresponding product isolated from irradiation of 2,6-di(methyl-d_3)-3,5-dimethyl-4-pyrone (**1**-d_6) in HFI. In this case ^1H nmr analysis of the isolated



1-d_6 13-d_6 14-d_6

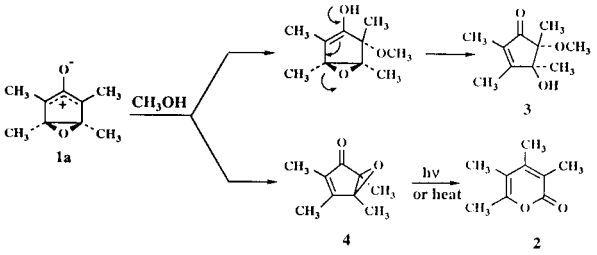
product revealed the presence of signals at 1.15 and 1.71 ppm for the methyl groups located α to the carbonyl functional group and the absence of the β-methyl signal at 2.01 ppm and the methylene unit absorptions at 5.25 and 5.29 ppm, confirming that the latter group is located at C-4 in **14**-d_6. The ^{1}H nmr spectrum of **13**-d_6 isolated from this reaction is also consistent with the assigned structure. Thus, as demanded by the cyclopent-3-enone structure, the ^{1}H nmr spectrum of **13**-d_6 exhibited two singlets at 1.33 and 1.40 ppm for the two methyl groups α to the carbonyl, and an absence of the allyl methyl group singlets observed at 1.81 and 1.85 ppm in the spectrum of **13**.

4-Pyrone **1** was also irradiated in HFI to which 9% TFE was added either before or immediately after a 20 minute irradiation. The gc analysis immediately after irradiation, or immediately after irradiation and addition of TFE, and after allowing the solutions to stand in the dark for 24 hours revealed that the added TFE had no effect on the reaction. In both cases gc analysis revealed the formation of 2-pyrone **2**, HFI adduct **13**, and methylenecyclopentenone **14** as was observed upon irradiation of **1** in HFI without added TFE.

When **1** was irradiated in TFE to which 9% HFI was added before or immediately after a 20 minute irradiation period, in addition to the formation of **2**, both HFI adduct **13** and methylene-cyclopentenone **14**, as well as TFE adducts **5** and **6** were observed by gc analysis and the concentration of all of these products were observed to increase upon standing in the dark after photolysis. Furthermore, formation of **13** and **14**, due to the addition of HFI, is accompanied by a decrease in the quantities of **5** and **6** formed in the absence of added HFI. This indicates the TFE adducts **5** and **6** are being formed thermally from the same intermediate species as are **13** and **14**.

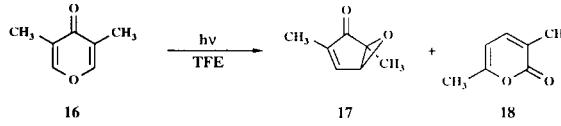
These results can be rationalized in terms of the mechanism outlined in Scheme 1. Thus, electrocyclic ring closure is envisioned as the primary photochemical process

Scheme 1



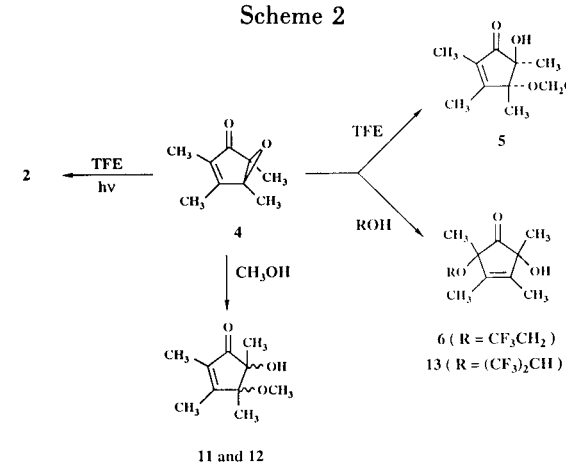
yielding oxabicyclic zwitterion **1a**. Bicyclic zwitterions were first suggested as primary photoproducts from 4-pyrones by Ishibi and colleagues [4]. Such intermediates, photochemically generated from a variety of 4-pyrones, have been captured by inter or intra molecular trapping by nucleophiles [1,2,5-7] while the oxabicyclohexenyl zwitterion derived from 3,5-dimethyl-4-pyrone (**16**) has been trapped as a [4+3] cycloadduct [8].

In the case of tetramethyl-4-pyrone (**1**), oxabicyclohexenyl zwitterion **1a** is suggested to be the short-lived intermediate previously observed on the 4-pyrone → 2-pyrone reaction coordinate [1]. In methanol, **1a** is either efficiently captured by intermolecular nucleophilic attack on the oxyallyl system by methanol to eventually yield *trans*-4-hydroxy-5-methoxy-2,3,4,5-tetramethylcyclopent-2-enone (**3**), or in the absence of a suitable external nucleophile, **1a** undergoes [1,3]-sigmatropic shift of the epoxide ring (*i.e.*, intramolecular nucleophilic attack) to provide epoxycyclopentenone **4**. This epoxide is postulated to be the long-lived [$t_{1/2}$ (TFE) ~50 minutes] intermediate observed by both uv spectroscopy and gc. The intermediacy of epoxycyclopentenones in the photoisomerization of 4-pyrones was first suggested by Yates and Still [9] and later confirmed by Barltrop and Day who reported that 3,5-dimethyl-4-pyrone (**15**) undergoes photoisomerization in TFE to yield 2,5-dimethyl-4,5-epoxycyclopent-2-enone (**16**) [18]. Although **16** is photochemically converted to 3,6-dimethyl-2-pyrone (**17**), it is of sufficient thermal stability in TFE to allow isolation. In methanol solvent the concentration of **4** is never large due to efficient trapping of the bicyclic zwitterion precursor **1a** and because of its efficient photoisomerization to 2-pyrone **2**. TFE is apparently not sufficiently nucleophilic to trap **1a** and in this solvent the concentration of **4** becomes appreciable. In TFE (Scheme 2), **4** is photochemically or thermally converted to 2-pyrone **2**, or



16 17 18

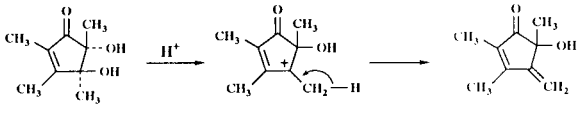
Scheme 2



11 and 12

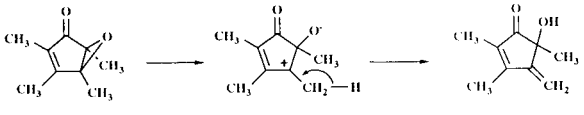
it reacts thermally with TFE either *via* an Sn2 or an Sn2' type attack at C-4 or C-2 of the hydrogen bonded epoxycyclopentenone to yield the two observed TFE adducts **5** and **6**. Alternatively, 9% methanol present in the TFE solution during the irradiation reduces the yields of 2-pyrone **2** and TFE adducts **5** and **6** as a result of methanol trapping of bicyclic zwitterion **1a** to form methanol adduct **3** and as a result of methanol reacting with epoxycyclopentenone **4** to form **11** and **12**, the only observed methanol adducts.

HFI is also not sufficiently nucleophilic to capture bicyclic zwitterion **1a** and in this solvent this intermediate is converted to epoxycyclopentenone **4**, which isomerizes to 2-pyrone **2** or methylenecyclopentenone **14**, or reacts with HFI to yield adduct **13**. Reaction of 4,5-dihydroxy-2,3,4,5-tetramethylcyclopent-2-enone (**18**) with 50% sulfuric acid has previously been observed to yield methylene cyclo-



18 19 14

pentenone **14**, presumably by deprotonation of carbocation **19** [10]. Formation of **14** from **4** suggests that a similar intermediate, **20**, is also formed in HFI *via* opening of the



4 20 14

epoxide ring in **4**. Unlike the situation in TFE, **4** appears to have no appreciable lifetime in the significantly more acidic HFI.

EXPERIMENTAL

Melting points were determined on a Mel Temp capillary melting point apparatus and are uncorrected. The ^{1}H nmr spectra were recorded at 60 MHz on a Hitachi Perkin-Elmer (PE) R-24B spectrometer. Chemical shifts were measured relative to internal tetramethylsilane. Infrared spectra were recorded on a PE-683 spectrometer. Gas Chromatography was performed on either a PE-8500 FID instrument equipped with a 30 m x 0.25 mm i.d. fused silica column coated with 0.25 μ Supelcowax 10 bonded phase (Column A) or on a PE-3920 FID instrument using 6 ft. x 1/8 in. (Column B) or 6 ft. x 1/4 in. (Column C) columns packed with 2% Carbowax 20 M-TPA on Chromosorb G (80-100 mesh). Mass spectra were recorded on a Dupont 21-491 spectrometer. All irradiations were carried out in a Rayonett reactor equipped with eight 2537 Hg-arc lamps. Elemental analysis was determined by MicAnal, Tucson, AZ.

Tetramethyl-4-pyrone **1**.

This compound [mp 92-93° (lit [11] mp 92°)] was prepared by allowing 3-pentanone to condense with acetic acid in the presence of polyphosphoric acid according to the procedure developed by Letsinger [12].

Irradiation and Analysis Procedures.

To monitor analytical-scale reactions, a solution of **1** in the appropriate solvent (3.0 ml, 2.0 x $10^{-2}M$) was placed in a quartz tube (7 mm i.d. x 13 cm long), sealed with a rubber septum, and purged with nitrogen for 5 minutes prior to irradiation. Preparative-scale reactions were carried out by irradiating a nitrogen-purged solution (12.0 ml, 2.0 x $10^{-2}M$) in the appropriate solvent in a quartz tube (14 mm i.d. x 13 cm long). Analytical reactions were monitored by gc without concentration. The retentions of all products are given relative to 4-pyrone **1**. Solutions resulting from preparative-scale reactions were concentrated to less than 0.5 ml. Products were collected by preparative gc at the temperatures indicated.

Irradiation of **1** in TFE.

The gc analysis (Column A, 190°) after 20 minutes of irradiation showed 37% consumption of **1** and the formation of the following products (relative retention, peak area): **2** (2.3, 0.3989), **4** (0.39, 0.5772), **5** (0.87, 0.4212), and **6** (0.48, 3.0375). The gc analysis after this irradiated solution remained in the dark at room temperature for 24 hours showed only **2** (2.3, 0.6562), **5** (0.87, 0.4212), and **6** (0.48, 3.0375).

Preparative-scale reactions were monitored until gc analysis revealed greater than 85% consumption of **1**. The solutions were allowed to stand in the dark for 24 hours and concentrated under reduced pressure. Samples **2**, **5**, and **6** were collected by preparative gc on Column C at 140°.

3,4,5,6-Tetramethyl-2-pyrone **2**.

This compound was collected as an oil that rapidly crystallized (mp 47-48°) and was identified by comparison of its chromatographic and spectroscopic properties with those of an authentic sample of this compound previously synthesized in this laboratory [13].

trans-5-Hydroxy-4(2,2,2-trifluoroethoxy)-2,3,4,5-tetramethylcyclopent-2-enone **5**.

This compound was collected as an oil that crystallized to a colorless solid (mp 106-108°); ^{1}H nmr (deuteriochloroform): δ 1.25 (s, 3H), 1.45 (s, 3H), 1.80 (s, 3H), 2.00 (s, 3H), 3.67-3.86 (m, 2H); ^{19}F nmr (deuteriochloroform): δ 1.9 (t) downfield from TFE; ir (carbon tetrachloride): 3560 (O-H), 1715 (C=O), 1650 (C=C) and 1290 (CF_3) cm^{-1}; uv (methanol): λ max 244 nm; ms: m/z (%) 252 (2), 237 (5), 153 (87), 109 (14), 81 (13), 43 (100).

2-Hydroxy-5-(2,2,2-trifluoroethoxy)-2,3,4,5-tetramethylcyclopent-3-enone **6**.

This compound was collected as a colorless oil; ^{1}H nmr (deuteriochloroform): δ 1.34 (s, 3H), 1.37 (s, 3H), 1.74 (s, 3H), 1.84 (s, 3H), 3.43-3.67 (m, 2H); ^{19}F nmr (deuteriochloroform): δ 1.4 (t) downfield from TFE; ir (carbon tetrachloride): 3530 (O-H), 1755 (C=O), 1660 (C=C), 1300 (CF_3) cm^{-1}; ms: m/z (%) 252 (2), 234 (10), 224 (7), 181 (7), 153 (11), 136 (15), 123 (15), 109 (11), 93 (16), 91 (15), 81 (15), 67 (23), 43 (100).

Irradiation of **1** in Methanol.

The gc analysis immediately after 20 minutes of irradiation showed 16% consumption of **1** and the formation of **2** and **3** with

relative retentions of 2.3 and 1.3 respectively. No change was detected after the solution remained in the dark at room temperature for 24 hours.

trans-4-Hydroxy-5-methoxy-2,3,4,5-tetramethylcyclopent-2-enone **3**.

This compound was isolated by preparative gc in 21% yield as a colorless oil; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 1.20 (s, 3H), 1.23 (s, 3H), 1.62 (s, 3H), 1.98 (s, 3H), 3.48 (s, 3H), 5.12 (s, 1H, exchangeable with deuterium oxide); ir (carbon tetrachloride): 3610 (free O-H), 3480 (intermolecular H-bonded O-H), 1715 (C=O) and 1660 (C=C) cm^{-1}; uv (methanol): λ max 234 nm; ms: m/z (%) 184 (14), 169 (18), 154 (11), 153 (40), 152 (42), 139 (14), 136 (14), 109 (14), 93 (14), 81 (11), 55 (13), 43 (100).

Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.17; H, 8.76. Found: C, 64.92; H, 8.74.

Irradiation of **1** in TFE.

(a) Containing 9% methanol, the gc analysis (Column B: 130° (16 minutes), 130-167° (2° per minute)) immediately after irradiation revealed the formation of 3,4,5,6-tetramethyl-2-pyrone **2**, *trans*-4-hydroxy-5-methoxy-2,3,4,5-tetramethylcyclopent-2-enone **3**, *trans*-5-hydroxy-4-(2,2,2-trifluoroethoxy)-2,3,4,5-tetramethylcyclopent-2-enone **5**, 2-hydroxy-5-(2,2,2-trifluoroethoxy)-2,3,4,5-tetramethylcyclopent-3-enone **6**, *cis*-5-hydroxy-4-methoxy-2,3,4,5-tetramethylcyclopent-2-enone **11**, and *trans*-5-hydroxy-5-methoxy-2,3,4,5-tetramethylcyclopent-2-enone **12** with relative retentions of 1.80, 1.50, 1.16, 0.69, 0.53, and 1.46 respectively. The gc analysis after the solution remained in the dark at room temperature for 24 hours showed an increase in the concentrations of **2**, **5**, **6**, **11**, and **12**. (b) 9% Methanol added immediately after irradiation, the gc analysis (as above) showed the formation of **2**, **5**, **6**, **11**, and **12** with the relative retentions given above. The gc analysis after the solution remained in the dark at room temperature for 24 hours showed an increase in the concentration of all products. Products **11** and **12** were collected by preparative gc.

cis-5-Hydroxy-4-methoxy-2,3,4,5-tetramethylcyclopent-2-enone **11**.

This compound was collected as a colorless oil that crystallized upon standing in the freezer; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 1.12 (s, 3H), 1.22 (s, 3H), 1.57 (s, 3H), 1.89 (s, 3H), 3.30 (s, 3H), 5.28 (s, 1H, exchangeable with deuterium oxide); ir (carbon tetrachloride): 3420 (broad intermolecular H bonded O-H), 1715 (C=O), 1650 (C=C) cm^{-1}; uv (methanol): λ max 234 nm; ms: m/z (%) 184 (15), 169 (29), 154 (13), 153 (100), 152 (10), 123 (11), 109 (16), 81 (15), 43 (89).

trans-5-Hydroxy-5-methoxy-2,3,4,5-tetramethylcyclopent-2-enone **12**.

This compound was collected as a colorless oil; ^{1}H nmr (deuteriochloroform): δ 1.20 (s, 3H), 1.32 (s, 3H), 1.72 (s, 3H), 1.95 (s, 3H), 3.17 (s, 3H); ir (carbon tetrachloride): 3430 (broad intermolecular H bonded O-H), 1720 (C=O), 1650 (C=C) cm^{-1}; ms: m/z (%) 184 (13), 169 (28), 154 (16), 153 (100), 152 (20), 136 (22), 124 (22), 123 (20), 109 (30), 93 (20), 91 (15), 81 (22), 43 (100).

Irradiation of **1** in HFI.

The gc analysis [Column B: 130° (16 minutes), 130-167° (2° per minute)] immediately after irradiation revealed the formation of 3,4,5,6-tetramethyl-2-pyrone **2**, 2-hydroxy-5-(1,1,1,3,3,3-hexafluoro-2-propoxy-2,3,4,5-tetramethylcyclopent-3-enone **11**, and 4-hydroxy-2,3,5-trimethyl-4-methylenecyclopentenone **12** with relative retentions of 1.81, 0.47, and 1.12 respectively. The gc analysis after the solution remained in the dark at room temperature for 24 hours showed no change in the composition of the mixture. Products **13** and **14** were collected by preparative gc.

2-Hydroxy-5-(1,1,1,3,3,3-hexafluoro-2-propoxy)-2,3,4,5-tetramethyl-cyclopent-3-enone **13**.

This compound was collected as an oil that crystallized in the freezer; ^{1}H nmr (deuteriochloroform): δ 1.33 (s, 3H), 1.40 (s, 3H), 1.81 (s, 3H), 1.85 (s, 3H), 4.75 (septet, ^{1}H, J ~ 6 Hz); ir (carbon tetrachloride): 3460 (O-H), 1755 (C=O), 1660 (C=C) cm^{-1}; uv (methanol): λ max 232 nm; ms: m/z (%) 320 (2), 288 (21), 247 (10), 153 (6), 141 (31), 125 (10), 123 (15), 109 (10), 94 (8), 82 (15), 81 (18), 67 (31), 43 (100).

4-Hydroxy-2,3,5-trimethylcyclopentenone **14**.

This compound was collected as an oil that crystallized in the freezer; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 1.15 (s, 3H), 1.71 (s, 3H), 2.01 (s, 3H), 5.20 (m, 3H, one of these protons is exchangeable with deuterium oxide leaving two one-proton singlets at δ 5.25 and 5.29); ir (carbon tetrachloride): 3390 (O-H), 1705 (C=O), 1635 (C=C), 1605 (C=CH$_2$) cm^{-1}; uv (methanol): λ max 285 nm; ms: m/z (%) 152 (8), 151 (36), 124 (16), 123 (13), 109 (54), 93 (10), 91 (11), 81 (52), 79 (20), 53 (23), 51 (17), 43 (100).

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