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PHOTOISOMERIZATION OF 4-PYRONES. NUCLEOPHILIC TRAPPING OF REACTIVE INTERMEDIATES

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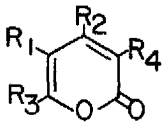
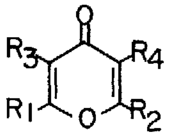
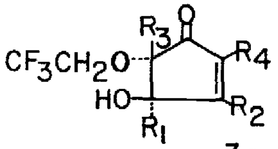
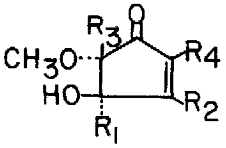
The photoisomerization of 4-pyrones is remarkably sensitive to substituent and solvent effects.[1,2] Thus although tetramethyl-4-pyrone **1a** undergoes photoisomerization to 2-pyrone **2a** in either acetonitrile or 2,2,2-trifluoroethanol (TFE),[3] 2,3,6-trimethyl-4-pyrone **1b** undergoes an analogous photorearrangement to 4,5,6-trimethyl-2-pyrone **2b** only in the more highly polar TFE.[4]


2a-d


1a-d


3a-d


4a-d

a: $R_1 = R_2 = R_3 = R_4 = CH_3$
b: $R_1 = R_2 = R_3 = CH_3$; $R_4 = H$
c: $R_1 = H$; $R_2 = CH_3$; $R_3 = OCH_3$; $R_4 = H$
d: $R_1 = CH_3$; $R_2 = H$; $R_3 = OCH_3$; $R_4 = H$

In the latter case, however, we wish to report the isolation of an additional minor product which has been assigned 4-hydroxycyclopentenone structure **3b** on the basis of its spectroscopic properties. Since it seemed likely that this minor product was formed by TFE trapping of a reactive precursor of 2-pyrone **2b**, a more thorough study of the photochemistry of 4-pyrones **1a**-**1d** in TFE and in the more nucleophilic methanol solvent was undertaken.

Although no product analogous to **3b** could be detected upon re-examination of the photoreaction of **1a** in TFE, photolysis[7] of disubstituted-4-pyrones **1c** and **1d** in TFE yielded hydroxycyclopentenone derivatives **3c** and **3d** as the only gc-volatile products.

The structural assignments of these products follow from their spectroscopic properties summarized in Table I. Thus while **3d** exhibits a pair of one-proton doublets at 6.2 and 7.5 ppm typical of vinyl protons in an α,β-unsaturated carbonyl system, **3b** and **3c** each show single α-vinyl proton absorptions at ∿6.0 ppm. This shows that substituents R_2 and R_4 in the original 4-pyrones have not interchanged during the ring contraction. Although the data for **3b** and **3d** do not allow distinction between the assigned structures and the isomeric 5-OH derivatives, the position of the OH group in **3c** is apparent from its nmr spectrum in DMSO-d_6. In particular, since the OH and C-4 protons appear as a pair of doublets, the OH group is unambiguously placed at C-4. Furthermore, upon addition of D_2O, both doublets collapse to a one proton singlet at 4.4 ppm confirming our spectral assignments. The *trans*-relationship between the OH and OCH_2CF_3 groups in **3b** is suggested by its infrared spectrum which exhibits strong absorption for a non-intramolecularly hydrogen bonded OH group.

Table I. Spectroscopic Properties of TFE-Adducts.

			NMR (δ in DMSO-d_6)[9]					
	M^+	$\nu^{CCl_4}_{C=O}$	R_1	R_2	R_3	R_4	OH	CF_3CH_2O[10]
3b	238	1716	1.2,s 3H	2.0,s 3H	1.2,s 3H	5.9,s 1H	5.5,s 1H	4.26,q 2H(9Hz)
3c	240	1730	4.4,d 1H(9Hz)	2.1,s 3H	3.3,s 3H	6.0,s 1H	5.85,d 1H(9Hz)	3.8-4.6,m 2H
3d	240	1737	1.3,s 3H	7.5,d 1H(7Hz)	3.3,s 3H	6.2,d 1H(7Hz)	5.7,s 1H	3.6-4.5,m 2H

4-Pyrones **1a**-**1c** behaved similarly when irradiated in methanol with the exception that they are more reactive with this more nucleophilic solvent. Thus whereas **1a** yielded 4-hydroxycyclopentenone **4a** and 2-pyrone **2a** in a gc-ratio of 16 to 1, 4-pyrones **1b** and **1c** gave 4-hydroxycyclopentenones **4b** and **4c** as the only gc-volatile products (Table II). Surprisingly, however, irradiation of **1d** in methanol did not result in the formation of any gc-volatile products. Failure to observe **4d** in this reaction is not due to its unique thermal or photochemical instability since when **1d** was irradiated in TFE containing 15 mole percent methanol, both **3d** and **4d** were formed in a ratio of 1 to 1.1.

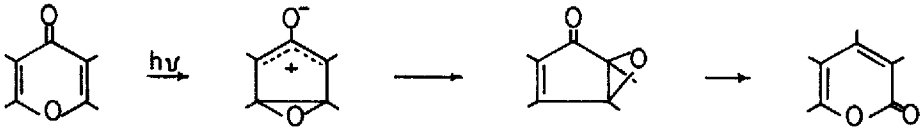
This observation that small amounts of methanol could compete with TFE as a trapping agent led us to examine the photochemistry of other 4-pyrones in this solvent mixture. Of particular mechanistic significance is the effect of added methanol on the photoreaction of **1a** in TFE. Thus although **1a** gave only **2a** upon irradiation in TFE, addition of 8.3 or 15.4 mole percent methanol

Table II. Spectroscopic Properties of Methanol-Adducts.

	M^+	$\nu_{C=O}^{CCl}$	NMR (δ in DMSO-d_6)					
			R_1	R_2	R_3	R_4	OH	CH_3O
4a	184	1710	1.23,s 3H	1.98,s 3H	1.20,s 3H	1.62,s 3H	5.12,s 1H	3.48,s 3H
4b	170	1715	1.19,s 3H	2.00,s 3H	1.15,s 3H	5.77,s 1H	5.23,s 1H	3.26,s 3H
4c	172	1730	4.3,d 1H(9Hz)	2.10,s 3H	3.30,s 3H	6.0,s 1H	5.5,d 1H(9Hz)	3.25,s 3H
4d	172	1735	1.40,s 3H	7.45,d 1H(7Hz)	3.40,s 3H	6.10,d 1H(7Hz)	5.5,s 1H	3.30,s 3H

resulted in the formation of both 2a and 4a in relative ratios of 1 to 4.2 or 1 to 7.7 respectively. These relative yields show that 4a is being formed at the expense of 2a and is consistent with the notion that 4a is being formed by reaction of methanol with a reactive precursor of 2-pyrone 2a.

Although no intermediates have previously been detected in the photoisomerization of 4-pyrones to 2-pyrones, a pathway involving zwitterionic species 5 and epoxycyclopentenone 6 has been postulated.[2,8]



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Consistent with this mechanism, monitoring of the photoreaction of 1a in TFE by uv-spectroscopy revealed that 2a is not a primary product in this transformation. Thus when 1a, 1×10^{-4}M in TFE, was irradiated for 15 sec, the absorbance due to 1a at 256 nm decreased from 1.42 to 0.47 while the absorbance at 305 nm due to 2-pyrone 2a increased from 0.07 to 0.37. Although further irradiation caused a rapid additional increase in the absorbance due to 2a, 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 hr. dark period. This indicates that after short-duration irradiation, 2-pyrone 2a can be formed thermally from a photochemically generated species with a half-life of ∿50 min.

Although at this point we have not been able to identify this labile intermediate, we postulate its structure as epoxycyclopentenone 6a. While such epoxides are known to undergo efficient photoisomerization to 2-pyrones,[11-12] their rate of thermal conversion to 2-pyrones is quite dependent upon the extent of ring substitution.[13]

Whereas in the presence of methanol 6a is a plausible intermediate common to both 2-pyrone 2a and 4-hydroxycyclopentenone 4a, our experimental evidence does not support this view. Thus when methanol (12.5 mole percent) was added to the TFE solution of **1a** immediately after a 15 sec irradiation, the absorbance of **2a** at 305 nm again reached a value of 0.59 after the 5 hr. dark period. This shows that methanol is not reacting with the immediate precursor of 2-pyrone **2a** during the dark period. Conversely, when the same amount of methanol was present in the TFE solution during the 15 sec irradiation, the final yield of **2a** was reduced by ∿25 percent. This indicates that methanol is reacting with a species with a lifetime far shorter than that observed for the immediate precursor of **2a**. These observations are consistent with methanol trapping of zwitterion **5a**. Further work on the mechanisms and electronic details of these reactions is currently in progress.

References

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4. The photoisomerization of **1b** ⟶ **2b** has not been previously reported. Distinction between the two possible trimethyl-2-pyrones, *viz.* 3,4,5-trimethyl and 4,5,6-trimethyl-2-pyrone was unambiguously achieved from the nmr[5] and mass spectral[6] properties. This regiospecificity is an intriguing aspect of this photoisomerization and is under further study.
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9. NMR spectra of **3b**-**d** and **4c**-**d** were recorded at 60MHz while **4a**-**b** were recorded at 100MHz.
10. With the exception of **3b**, the two-proton signals for the CF_3CH_2O did not appear as a quartet but as an unsymmetrical complex resembling the AB portion of an ABX_3 spin system. This would require nonequivalence of the methylene protons due to lack of free rotation or due to their proximity to the nearby asymmetric center.
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