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Heterocyclic Photochemistry. 1. Phototranspositions in Hydroxypyrylium Cations. Permutation Pattern Analysis and Mechanistic Studies[1]

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Abstract: A number of dialkyl-4-pyrones have been irradiated (as the corresponding 4-hydroxypyrylium cations) in sulfuric acid and the transposed 2-pyrones have been identified. A permutation pattern analysis of these and literature data shows that the photorearrangement follows a P_4 permutation pattern, thus defining the fate of all the ring atoms. This conclusion is supported by a total-labeling investigation: a study of the rearrangement of a ^{14}C-labeled 4-pyrone confirmed that the alkyl migrations are intramolecular, the alkyl groups remaining bonded to the ring atoms during the rearrangement. The irradiation of 3,5-dimethyl-4-pyrone in sulfuric acid led to the isolation of a new intermediate, the cyclic sulfate **22**, which in sulfuric acid is converted thermally or photochemically to the 2-pyrone **8**. In aqueous sulfuric acid, 2-acylfurans are also found as irradiation products. It is concluded that the excited 4-hydroxypyrylium cations relax to hydroxyoxabicyclohexenyl cations (**30**) as primary ground-state intermediates. A minor pathway of isomerization via a P_8 permutation pattern is also discussed. The photointerconversion of 2-hydroxypyrylium cations (e.g., eq 8) is shown to occur by a P_8 permutation pattern.

Introduction

Pyrones have displayed a wide variety of photochemical behavior[2] and a new facet was revealed when Pavlik reported the photoisomerization of 2,6-dimethyl-4-pyrone in sulfuric acid[3] (eq 1) in which solvent both 4- and 2-pyrones are protonated and are best described as hydroxypyrylium cations. Our interest in the photochemistry of pyrylium salts led us to consider these reactions, and, while not disputing Pavlik's postulated mechanisms, we recognized that they were based

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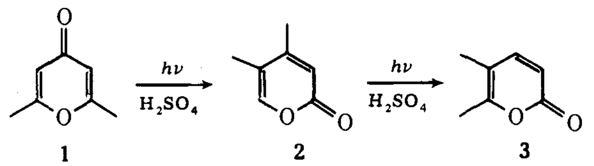
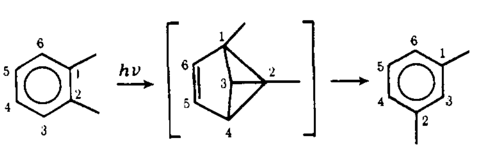


1 2 3 (1)

on unsubstantiated assumptions about the fate of the various ring atoms.

This deficiency is common to most studies in the area of aromatic phototransposition reactions[4] and can be illustrated by the *o*- to *m*-xylene reactions, which is commonly believed to proceed via a benzvalene intermediate (eq 2).[5] This mechanism implies that the single carbon atom between the *C*-methyl groups in the meta isomer was C-3 (or the symmetry-related C-6) of the ortho isomer, and that the other three atoms are in the same order in both. There is, however, no evidence that this is the case.



(2)

The important point is that, as a necessary preliminary to mechanistic speculation, the fate of each ring atom must be traced. This could, in principle, be done by studying molecules in which each ring atom is labeled distinctively, but the synthetic difficulties are obvious. This paper, however, includes the first such study.

We have used an alternative procedure, which depends on a study of more than one less-than-totally-labeled compound, and on making the assumption that alkyl groups act only as positional labels and do not perturb the system to a sufficient extent to change the reaction pathway. In order to handle the data obtained in this way, we have developed the idea of permutation patterns[4,6] (see Figure 1) where the lines inside the hexagons indicate the way in which the ring atoms are connected after the reaction. They provide a useful formalism which gives information about the fate of each ring atom in going from starting material to product. By way of illustration, the photoisomerization of the 4-hydroxypyrylium cation **1** into the 2-hydroxy isomer **2** can be represented by either of the permutation patterns P_4 and P_{10} as shown in Table II.

Discussing the hydroxypyrylium photochemistry in these terms and considering Tables II and III, we see that the reaction **1** → **2** can be accounted for by the permutation patterns P_4 and P_{10} and **2** → **3** can be accounted for by P_7, P_8, and two orientations of P_4. Our approach has been to study compounds with different labeling patterns and to compare the results, thereby establishing a unique permutation pattern common to all the compounds that undergo the same reaction.

Since our preliminary communication, Pavlik also has described[7] the photochemistry of some 2,3-dialkyl-4-hydroxypyrylium ions (see Table II). Together with his earlier results, these data would have sufficed to establish that P_4 is the permutation pattern involved in the 4-hydroxy- to 2-hydroxypyrylium reaction, but we present here a joint analysis of his and our results, and discuss mechanisms on the firm basis thus established.

Synthesis of Reactants. Some of the 2- and 4-pyrones required for this study were known and were synthesized by literature routes. 2,5-Dimethyl-4-pyrone (**4**) and 2-ethyl-3-methyl-4-pyrone (**5**) were synthesized by modifications of the procedure of Kuznetsov et al.[8] (eq 3). Various 2-pyrones became available from irradiation of 4-pyrones or other 2-pyrones.

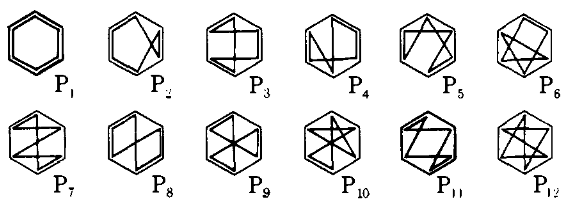
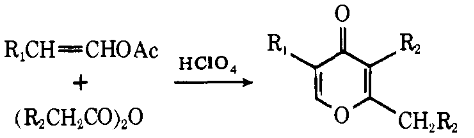


Figure 1. The permutation patterns of a six-membered ring.



(3)

4, R_1 = Me; R_2 = H
5, R_1 = H; R_2 = Me

Structure Assignments for Dialkyl-2-pyrones. Of the six isomeric dimethyl-2-pyrones, five were known. The sixth, 3,5-dimethyl-2-pyrone (**7**), was formed as a minor product from irradiation of 2,5-dimethyl-4-pyrone. Mass spectrometric analysis showed that it was isomeric with starting material. Three strong bands in the IR spectrum (1729, 1659, 1578 cm^{-1}) and two bands in the UV spectrum (221, 296 nm) are characteristic of a 2-pyrone. The NMR spectrum showed two one-proton signals at τ 2.91 and 3.11 and two three-proton signals at τ 7.97 and 8.08, showing it to be a dimethyl-2-pyrone. The absence of a large coupling between the two ring protons implies that they are nonadjacent. The compound is not identical with authentic samples of 4,5-[3] and 4,6-dimethyl-2-pyrone[9] so we assign the structure as 3,5-dimethyl-2-pyrone. This is supported by the observation that both ring protons are at τ <3.5 and both methyl groups are at τ >7.95.[10]

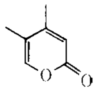
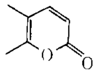
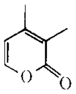
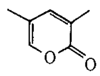
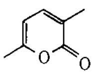
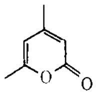
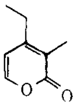
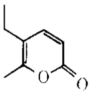
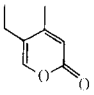
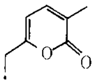
Pavlik reports the synthesis of 3,6-dimethyl-2-pyrone[7] (**8**) but gives no spectroscopic details. The photoproduct from 3,5-dimethyl-4-pyrone (**16**) was shown to be a dimethyl-2-pyrone by similar arguments to those above. The coupling constant between the ring protons was 6.5 Hz, which is appropriate[10] for J_{45} implying 3,6-dimethyl-2-pyrone (**8**).

Full spectroscopic data for all the dimethyl-2-pyrones are given in Table I. The NMR chemical shift assignments are, for the most part, made on the assumption that groups in the 3 and 5 positions resonate at higher field than those in the 4 and 6 positions. This difference is large and well established,[10] but careful examination of Table I reveals further small but consistent trends. A proton at the 6 position resonates at lower field than one at C(4) and a methyl group at C(3) resonates at lower field than one at C(5). On this basis, we are able to make a definite assignment of the spectrum of 3,5-dimethyl-2-pyrone (**7**). Also, a 6-methyl group is at lower field than one at C(4), enabling an assignment to be made for the methyl groups in 4,6-dimethyl-2-pyrone (**9**), but the differences are too small to permit a reliable assignment of the ring protons of this compound on this basis. However, the lanthanide-induced shifts described below make this possible.

A similar combination of spectroscopic and analytical data was used to establish the structure of the ethylmethyl-2-pyrones. In Table I, note, in particular, the similarity of the UV and IR data to those of the corresponding dimethyl homologues. The relative position on the ring of the two alkyl groups was assigned on the assumption that the chemical shift of the methyl group would be very close to that of the methyl group in the corresponding position in the dimethyl homologue.

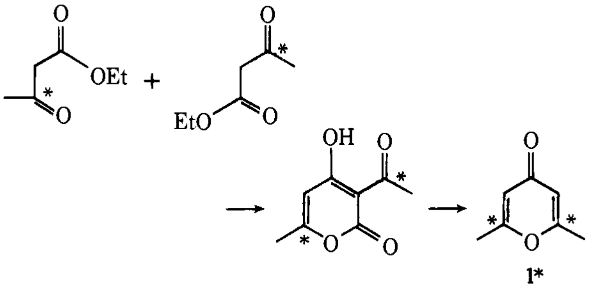
^{14}C-Labeling Experiment. Since our approach depended on the assumption that alkyl groups can act as positional labels for the ring atoms, it was important to rule out mechanisms in which these alkyl groups migrated round the ring independently of the ring atoms to which they were initially attached. To this end, 2,6-dimethyl-4-pyrone-*2,6*-^{14}*C* (**1***) was syn-

Table I. Spectroscopic Data for Dialkyl-2-pyrones

compd	UV[a] λ_{max}	UV[a] ϵ_{max}	IR,[b] cm^{-1}			NMR,[c] τ J, Hz	3H	4H	5H	6H	3Me	4Me	5Me	6Me	Et
 2	216 293	1780 5200	1738	1655	1555		4.05			2.78		7.92	8.11		
 3	219 308	2930 6590	1745	1651	1564	J_{34} = 9.4	4.06	2.85					8.06	7.84	
 6	224 287	1830 7350	1723	1649	1569	J_{56} = 5.4			3.99	2.74	8.04	7.90			
 7	221 296		1729	1659	1578			3.11		2.91	7.97		8.08		
 8	221 298	3100 8500	1729	1653	1591	J_{45} = 6.5		2.96	4.08		8.02			7.80	
 9	221 294	2570 7280	1733	1653	1571		4.23		4.17			7.92		7.82	
 10	223 287		1726	1644	1570				4.07	2.75	8.01				7.58 q 8.85 t
 11	221 307		1748	1649	1561		4.04	2.83						7.80	7.68 q 8.90 t
 12	217 306		1741	1646	1550		4.04			2.84		7.89			7.67 q 8.84 t
 13	223 294		1730	1649	1589	J_{45} = 6.3		3.10	4.27		7.99				7.52 q 8.76 t

[a] Ethanol. [b] CCl_4, 0.1-mm cell. [c] CCl_4.

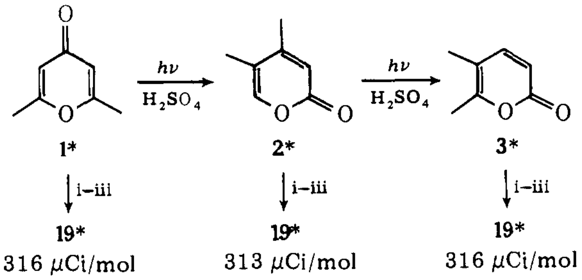
thesized from specifically labeled ethyl acetoacetate-*3*-^{14}C as indicated in eq 4.[11] On irradiation in sulfuric acid, the labeled 4-pyrone (1*) afforded the labeled 2-pyrones (2* and 3*). Kuhn-Roth degradation[12] of starting material and of both products independently gave acetic acid which was converted into its 4-bromophenacyl ester (19*) for counting (see Scheme I). The equality of the specific activities showed that the methyl groups do remain attached to the same ring atoms during both reactions.



(4)

Photochemical Results and Permutation Pattern Analysis. All pyrone primary photoproducts are listed in Tables II and III, which also include the results of Pavlik et al.[3,7] Details and yields are given in the Experimental Section. Gas chromatographic analysis of low-conversion irradiation mixtures showed that all three products from 4 and both products from 5 are primary. Irradiation of 6 also gave 2 as a second minor product but this was shown to be secondary, presumably derived from 3. It should be noted that acylfurans can also be formed in these irradiations—they are discussed later.

Scheme I



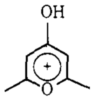
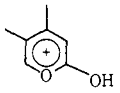
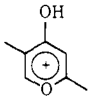
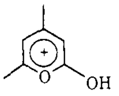
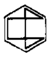
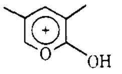
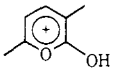
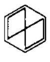
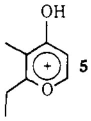
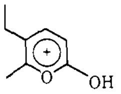
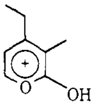
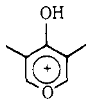
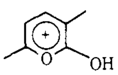
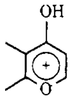
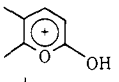
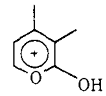
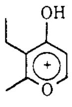
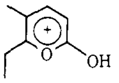
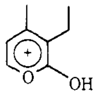
(i) Cr^{VI}; (ii) NaOH; (iii) $BrC_6H_4COCH_2Br$

Consider first the 4-hydroxy- to 2-hydroxypyrylium reaction in Table II. Looking first at the major product from each reactant, we see that the only pattern common to all of them is P_4. We note also that the minor products from **5, 17,** and **18** and one of the minor products from **4** (i.e., **7**) are derivable by a P_4 that is the mirror image of the major P_4, i.e., the same pattern, having the same orientation with respect to the heteroatoms, and differing only in its orientation with respect to alkyl substituents. Within our assumptions about the small effect of alkyl substituents, these are obviously equivalent.

The only exception to this P_4 generalization is one of the minor products from **4**, i.e., **8**, that cannot arise by a P_4 process.

Similar consideration of Table III shows that for the 2-hydroxypyrylium interconversion the only pattern common to all the major products is P_8, and the only exception to this is the minor product **3** formed from **6**.

Table II. Products and Permutation Patterns in the Photochemistry of 4-Hydroxypyrylium Cations

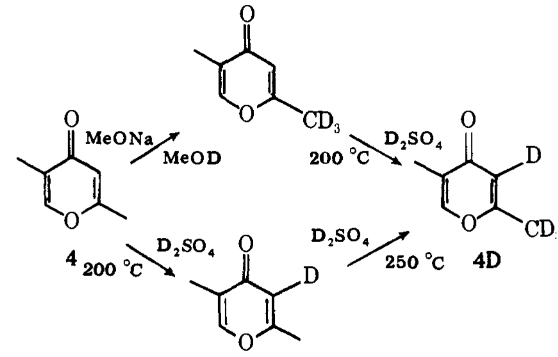
reactant	primary product (s) (yields, %)	possible permutation patterns	source
 1	 2	 P_4  P_{10}	*a*
 4	 9 (18.5) major	 P_4  P_3  $P_{4'}$  P_6	
	 7 (1.2) minor	 P_4  P_3  $P_{4'}$  P_8	
	 8 (0.4) minor	 P_8  P_{12}  P_7  $P_{7'}$	*b*
 5	 11 (23.9) major	 P_4  P_7	
	 10 (5.5) minor	 P_4  P_8	*c*
 16	 8 (69)	 P_4  P_{10}	*c*
 17	 3 major	 P_4  P_8  $P_{4'}$  P_7	
	 6 minor	 P_4  P_8  $P_{4'}$  P_7	*d*
 18	 15 major	 P_4  P_7	
	 14 minor	 P_4  P_8	*d*

[a] Reference 3. [b] This work. [c] Reference 1. [d] Reference 7.

Deuteration of Pyrones. The formation of the anomalous products (**8** from **4** and **3** from **6**) could not be investigated by our normal approach of studying a series of alkylated derivatives in order to determine which permutation pattern was, in fact, operating, since the reactions were already shown to be substituent dependent. We therefore resorted to a study of deuterated compounds, as this would minimize the perturbation of the system, and undertook the total labeling challenge which is necessary in order to determine the permutation pattern for a single compound.

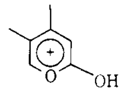
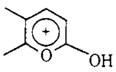
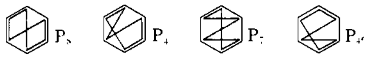
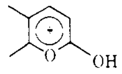
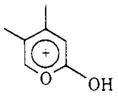
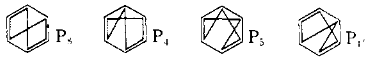
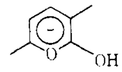
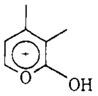
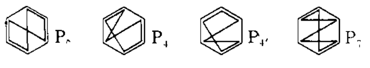
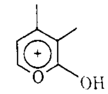
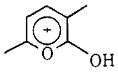
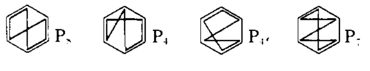
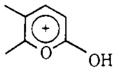
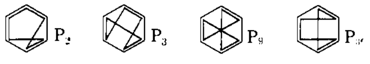
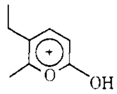
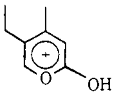
It was known[13] that the parent 4-pyrone undergoes deuteration at the 3 and 5 positions under basic conditions, presumably involving reversible conjugate addition of methoxide and protonation. Under the same conditions, pyrone **4** only incorporated deuterium into the 2-methyl group, presumably because steric effects favor conjugate addition at the 6 position rather than at 2. It was also known[14] that pyrylium salts undergo acid-catalyzed exchange at the 3 and 5 positions and heating **4** in D_2SO_4 at 200 °C did, indeed, result in exchange of the 3 proton. At even higher temperatures, the 2-methyl group was exchanged as well, but the two-step process, base followed by acid, was preferred (see Scheme II).

Scheme II



The positions so deuterated were identified in several ways. (1) In the NMR spectrum, the low-field methyl signal (β to the carbonyl) and the high-field ring proton signal (α to the carbonyl, β on the enol ether) were reduced in intensity. (2) The unexchanged signals remained coupled (J = 1.3 Hz), implying that they were adjacent. (3) Literature analogy[13,14] and mechanistic arguments predict the positions of exchange indicated. (4) Comparison of the behavior of 4-pyrones (**4, 1,** and **16**) in D_2SO_4 under identical conditions showed that, whereas **1** underwent exchange at the 3 and 5 positions, **16** did

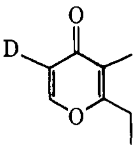
Table III. Products and Permutation Patterns in the Photochemistry of 2-Hydroxypyrylium Cations

reactant	product(s) (yields, %)	possible permutation patterns	source
 2	 3		*a*
 3	 (94.2) 2		*b*
 8	 (57.8) 6		*c*
 6	 (20.5) 8 (major)		*c*
	 (3.6) 3 (minor)		
 11	 (15.7) 12		*c*

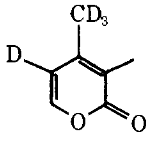
[a] Reference 3. [b] Reference 1. [c] This work.

not exchange at 2 and 6, whereas **4** exchanged only one of its protons—presumably therefore the 3 position.

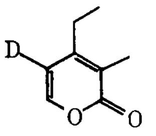
Similar treatment of **5** with D_2SO_4 led to **5D**, the structure being assigned on the basis of arguments similar to those given above.



5D



6D



10Da

The 5 position of **6** was readily deuterated in D_2SO_4 at 80 °C, but at higher temperatures the pyrone was destroyed without showing incorporation into either methyl group. The pyrone was also destroyed rapidly by methoxide in deuteriomethanol and slowly by sodium carbonate in D_2O, but in neither case did either methyl group show exchange.

However, the ethylmethyl-2-pyrone **10** was available from irradiation of **5** and treatment with D_2SO_4 at 140 °C afforded **10Da,** in the NMR spectrum of which the high-field ring proton signal was reduced in intensity, implying exchange at the 5 position as shown.

Total Labeling Studies. Products. Irradiation of **4D** in D_2SO_4 afforded three products (see Table IV). For **7D** and **8D,** the labeling pattern was readily established from the NMR spectrum and Table I. In the case of **7D** the signals at τ 2.91 and 8.08 were reduced in intensity, implying deuteration of the 6 position and in the 5-methyl group. In the case of **8D** the signals of reduced intensity were at τ 4.08 and 7.80, implying that the label was at the 5 position and in the 6-methyl group.

The labeled methyl group was shown to be in the 4 position in **9D** from the NMR spectrum and confirmation of this was found in the mass spectrum, which showed a base peak at *m/e* 43 (CH_3CO^+). To determine which of the ring protons was labeled, the lanthanide shift reagent $Eu(fod)_3$[15] was used. This, a Lewis acid, would be expected to coordinate to the electron-rich exocyclic oxygen atom, resulting in a strong downfield shift to a group in the 3 position. It was found that addition of the reagent to the partially labeled pyrone **9** resulted in the labeled ring proton shifting downfield, while the remaining signals were almost unchanged. We thus conclude that the label was in the 3 position as shown in Table IV.

Irradiation of **5D** in sulfuric acid afforded two 2-pyrones, shown to be deuterated derivatives of **10** and **11.** In both cases, the position of labeling was readily determined from the NMR spectrum. The signals of reduced intensity were at τ 4.04 and 2.75 for **11D** and **10Db**, respectively, implying the labeling patterns shown in Table IV. The deuterated derivative **10Db** differed from that obtained by acid-catalyzed exchange of **10** (i.e., **10Da**; see above). In particular, the signal for residual protium in **10Db** at τ 2.75 was a clean doublet showing the absence (<10%) of deuterium at the 5 position.

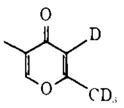
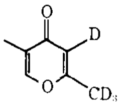
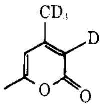
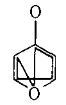
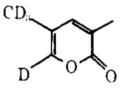
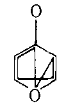
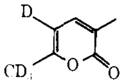
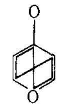
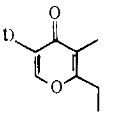
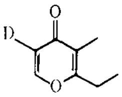
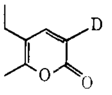
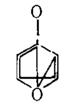
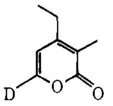
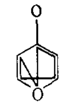
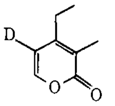
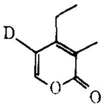
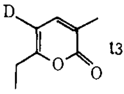
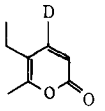
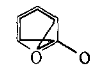
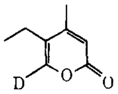
Irradiation of **10Da** in sulfuric acid afforded three products, two of which were shown to be deuterated derivatives of **11** and **12** while the third was a new compound obtained only in deuterated form, but its structure was established unambiguously by application of the spectroscopic arguments described above. It was shown in this way to be a 3,6-substituted ethylmethyl-2-pyrone. The chemical shift of the methyl group at τ 7.97 shows that this is on the 3 position. For all three compounds, the position of the label was determined from the NMR spectrum. The signals of reduced intensity were at τ 4.06, 2.83, and 4.27 for **11D, 12D,** and **13D,** respectively, implying the labeling patterns shown in Table IV.

Total Labeling Studies. Controls. In no case was total incorporation of deuterium achieved but not only is this unimportant since label is lost during irradiation, it is, in fact helpful since the presence of residual protium in the labeled positions aids structural assignments from the NMR spectra.

The loss of label on irradiation cannot be thermal in view of the great difference in temperature between the exchange process and the irradiation, but control experiments with various pyrones show that the photochemical reaction has the same positional specificity as the thermal, and cannot affect the results. The loss of label in the products is most probably due to thermal exchange in the intermediates.

A New Intermediate. Irradiation of 3,5-dimethyl-4-pyrone (**16**) in sulfuric acid (ca. 10^{-4} M, λ_{max} 253 nm) at 254 nm in a UV cell was found to give absorption (λ_{max} 304 nm) corre-

Table IV. Percentage[a] Deuteration of Pyrones and Permutation Patterns

substrate	products	% D at CH	% D at CH_3	permutation	pattern
 **4D**	 **4D**	85^b 68^c	77^b 62^c		
	 **9D**	77	62		P_4
	 **7D**	88	58		P_4
	 **8D**	68	65		P_6
 **5D**	 **5D**	61^b			
	 **11D**	23			P_4
	 **10Db**	56			P_4
 **10Da**	 **10Da**	64^b 14^c			
	 **13D**	20			P_5
	 **11D**	25			P_2
	 **12D**	40-20			

[a] By NMR integrating ±5% except where indicated. The mass spectra are in agreement. [b] Before irradiation. [c] Recovered starting material.

sponding to 3,6-dimethyl-2-hydroxypyrylium cation (**21**) known to be the product of the reaction. Interruption of the irradiation earlier showed that an intermediate (λ_{max} 232 nm) had been formed which, on further irradiation or on standing in the dark, was converted into the species absorbing at 304 nm.

Irradiation of **16** in sulfuric acid (ca. 0.3 M) in a quartz NMR tube showed, in addition to a decrease in the signals due to the 4-hydroxypyrylium (**20**) and an increase in those due to 2-hydroxypyrylium cation (**21**), the appearance of other signals which initially increased and then, on further irradiation, or on standing in the dark, decreased, with a corresponding increase in the signals due to **21**.

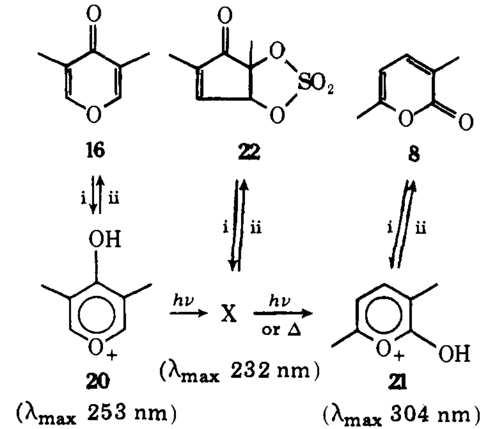
The half-life for the dark reaction of the intermediate at room temperature was ca. 2 days and was the same for both the UV and NMR runs. It was concluded that the intermediate was the same in both cases, and an attempt was made to isolate it.

We found that in order to achieve high steady-state concentrations of intermediate in preparative irradiations (initially ≥0.1 M in pyrone) it was necessary to stir the solution, presumably because with an optical density in our 2-cm diameter tubes, $>10^3$, 99% of the light is absorbed in the first 0.1 mm and all the reaction occurs near the walls. The photochemically labile intermediate is then destroyed before it can diffuse away from the walls, in the very viscous solvent. The problem is obviously an extreme one in this case, with high optical densities and high viscosities, but it may in many such cases result in measured steady-state concentrations of photolabile species being much less than these calculated from extinction coefficients and bulk concentrations.

Even when there was spectroscopic evidence for the presence of the intermediate, only starting material and 2-pyrone (**8**) could be isolated under our normal workup condition, but injection of the sulfuric acid solution through a fine needle into vigorously stirred saturated aqueous sodium bicarbonate solution, ether extraction, and PLC on silica gel afforded a 43% yield of crystalline product (mp 73-74 °C).

Elemental and mass spectrometric analysis showed it to be a formal adduct of starting material and sulfur trioxide. Hy-

Scheme III

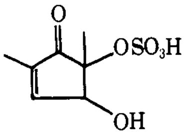


(i) H_2SO_4
(ii) aq Na_2CO_3

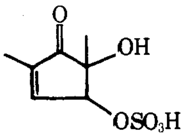
drogenation over palladium on barium sulfate gave 2,5-dimethylcyclopentanone as a mixture of cis and trans isomers identical with an authentic mixture synthesized independently by the method of House and Trost,[16] thus establishing the carbon skeleton. The IR (1744 and 1641 cm^{-1}) and UV [223 nm (ϵ 8440) and 339 (42.3)] spectra implied a conjugated cyclopentenone. The NMR spectrum confirms the cyclic sulfate structure **22** as the only possibility (cf. analogous compounds[2]). The presence of bands at 1416 and 1217 cm^{-1} confirms the sulfate structure.[17]

The relationship between the various compounds is indicated in Scheme III.

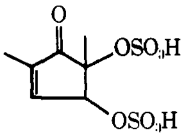
We turn now to the structure of the intermediate (X) in sulfuric acid, and the question whether it is the same as in deuteriochloroform. A solution of the cyclic sulfate **22** redissolved in sulfuric acid showed the same spectroscopic, chemical, and photochemical properties as the intermediate, so X is obviously related to **22** by some readily reversible process. The similarity of the NMR coupling pattern in neutral and acid solution suggests preservation of the 4,5-dioxygenated cyclopentenone skeleton while the downfield shifts in acid suggest protonation. There cannot be a proton on the carbonyl oxygen since O-protonation of α,β-unsaturated ketones shifts the UV absorption about 50 nm to the red,[18] whereas the shift in this case is only 9 nm. We thus suggest protonation on the sulfate ring, with or without ring opening to **23, 24,** or **25.**



23



24



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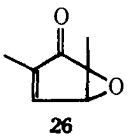
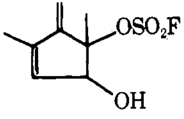


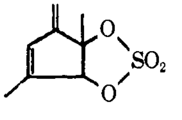
26

A conceivable precursor to the sulfate adduct is epoxide **26.** Since this was available from other work,[2] we investigated its behavior in sulfuric acid. Extraction of the epoxide from solution in carbon tetrachloride into sulfuric acid showed, in the NMR spectrum of the acid layer, signals corresponding to a ca. 1:1 mixture of X and 2-pyrone (**8**).

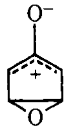
Transient signals have also been observed when irradiations of other systems have been monitored by UV or NMR spectroscopy. Thus 3,5-dimethyl-4-pyrone in fluorosulfonic acid shows transient NMR signals at τ 1.79, 4.11, 7.82, and 8.06 which decay with a half-life of ca. 1 h and which are attributable to a species such as **27.** 2,5-Dimethyl-4-pyrone (**4**) in sulfuric acid shows NMR signals at τ 3.08, 4.29, 7.38, and 8.23 and UV absorption ca. 240 nm which decay with a half-life of ca. 3 h, and which are attributable to a species related to **28.**



27



28



29

In neither case has the species responsible proved isolable. It does seem, however, that compound **22** is not unique but that sulfate participation is a general feature of 4-hydroxypyrylium photochemistry in sulfuric acid.

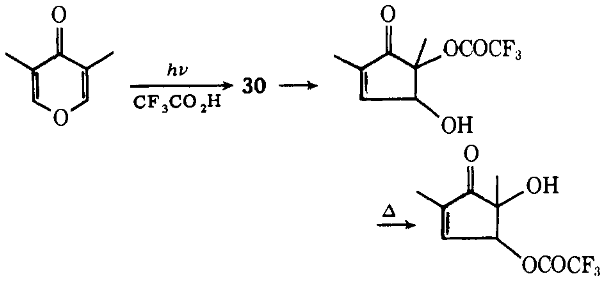
Irradiation of 3,5-dimethyl-4-pyrone in fluorosulfonic acid at −78 °C in an NMR tube followed by rapid transfer to a spectrometer probe precooled to −70 °C resulted in detection of no intermediates other than that described above and assigned as **27.**

Discussion

Major Pathways. The ^{14}C-labeling experiment has ruled out any mechanism in which the alkyl groups become detached from the ring and migrate independently, and the total labeling study has confirmed our inference from the permutation pattern analysis that the major processes involve P_4 and P_8 permutation patterns.

The accompanying paper establishes that oxabicyclohexenyl zwitterions (**29**) are the key intermediates in the photochemistry of 4-pyrones in neutral solvents.[2] By analogy, irradiation of 3,5-dimethyl-4-pyrone under acidic conditions would be expected to give the hydroxyoxabicyclohexenyl cation (**30**). This entity, after nucleophilic attack by bisulfate ion, would give rise to the cyclic sulfate (**22**) as shown in Scheme IV.

Sulfate ester migrations such as those postulated in Scheme IV are reasonable in view of the results in carbohydrate chemistry[19] and a similar migration of trifluoroacetate observed in our own work (eq 5).

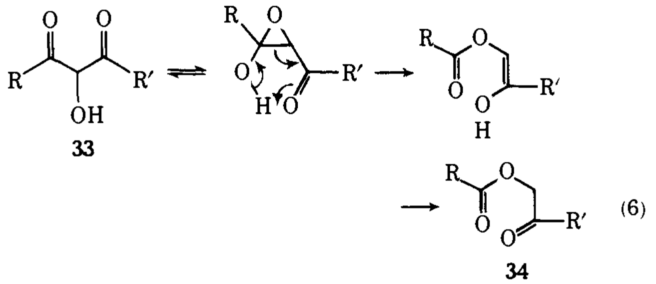


(5)

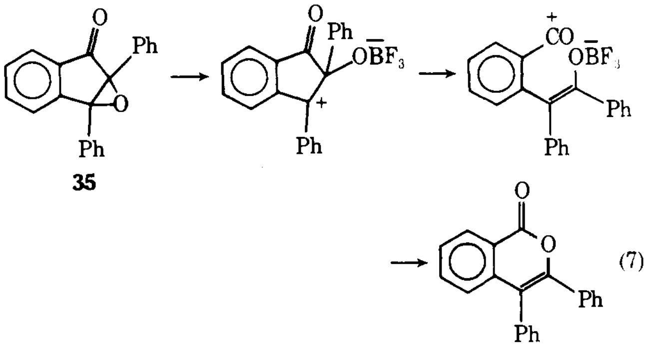
Of course, the cation **30** could rearrange to the epoxide **26**—the rearrangement of the corresponding zwitterion (cf. **29**) to the epoxide has been actually observed in the irradiation of 4-pyrones in neutral solution. However, this compound has been shown to react with sulfuric acid to give an approximately 1:1 mixture of the sulfate adduct (X) and 2-hydroxypyrylium cation (**21**), whereas, in the early stages of the irradiation of **20** in sulfuric acid, the ratio of X to 2-pyrone is much larger than 1. Thus, if it participates at all, the role of the epoxide is a minor one.

The sulfate adduct rearranges photochemically and also (but very slowly) thermally to the 2-pyrone. Scheme V outlines two possible mechanisms for this transformation starting from the 4-sulfate **24,** which is presumed to be in equilibrium with **22** in sulfuric acid solution.

Analogues can be found for these processes. A hydroxyoxirane like **31** is the suggested intermediate in the conversion of hydroxy diketone **33** to ester **34** (eq 6).

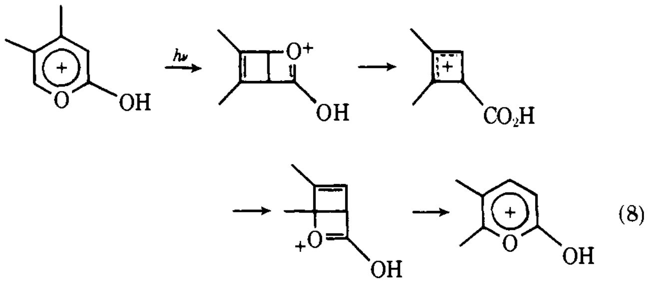


While we have shown that the epoxide itself is not significantly involved in the rearrangement, the carbonium ion **32** is analogous to that formed by the acid-catalyzed ring opening of α,β-epoxy ketones.[21] An acyl shift to oxygen via an acylium ion is postulated for the rearrangements of the indenone oxide **35**, eq 7. In contemplating the route via **32**, it should be borne in mind that there we have no evidence for the participation of two photons in the rearrangement, nor for the existence of **32** as a discrete intermediate; the fragmentation of **24** into the hydroxyacylium cation could well be concerted.

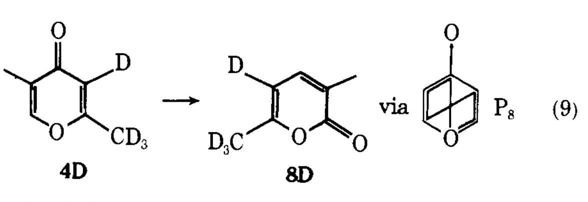


It thus seems that the broad sequence of events in the photoisomerization of 4-pyrones in sulfuric acid to 2-pyrones is [4-hydroxypyrylium]* → hydroxyoxabicyclohexenyl cation → sulfate adduct → 2-pyrone.

For the 2-hydroxypyrylium interconversions we have no reason, at this stage, to question Pavlik's mechanism, involving 3,6 bonding in the excited state (eq 8).[3]

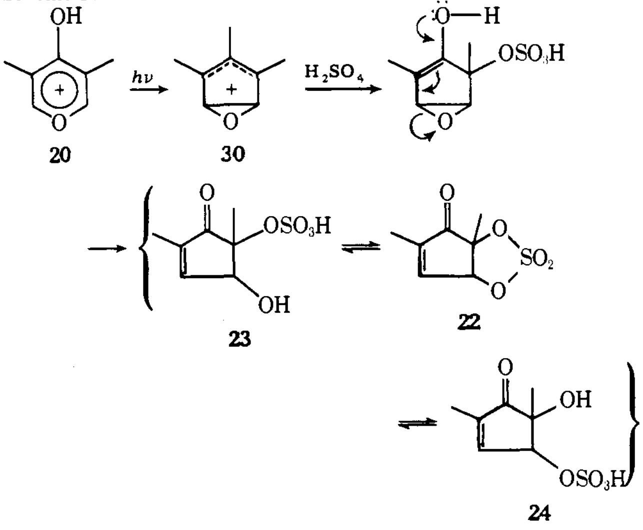


Minor Pathways. The reaction **4D** → **8D** shows that the minor process for 4-hydroxypyryliums is a P_8 process (eq 9).

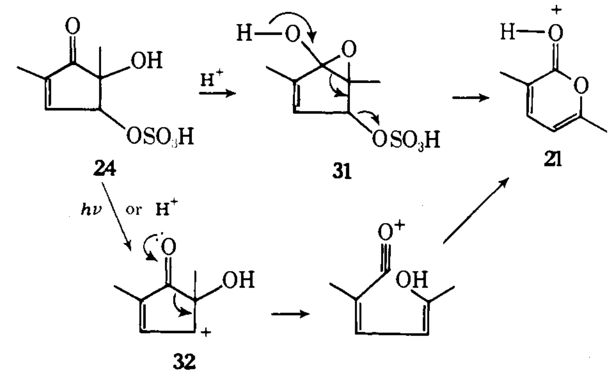


Within the limits of our GC analysis (ca. 1%), we can say that products derived by the P_8 process were absent from the other 4-pyrones studied. A possible exception is the formation of **10** from **5**, where the P_8 product is the same as the P_4 product. However, **5D** would give rise to different products by the two processes (see Scheme VI). The observation that **5D** gave **10Db** in which all the label (>90%) was at the 6 position showed that this product was formed by a P_4 process. The reaction **4** → **8** is indeed unique.

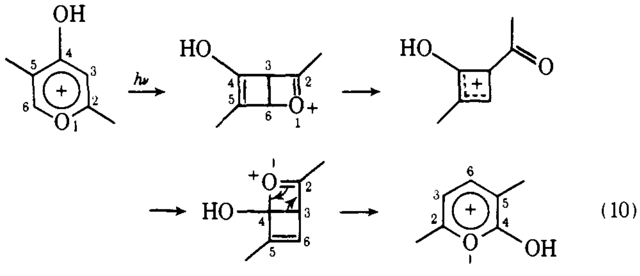
Scheme IV



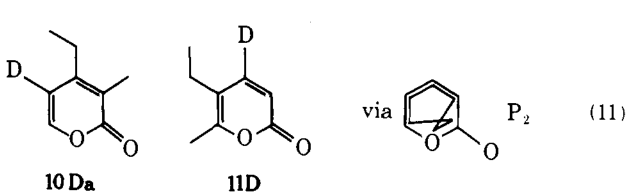
Scheme V



With the permutation pattern established and the fate of each ring atom defined, we are in a position to discuss mechanistic possibilities. Consideration of the pattern P_8 shows that new bonds are present in the product between atoms 1 and 4 and between 3 and 6. Formation of the latter bond may then be reasonably proposed to initiate the reaction, followed by the rearrangement indicated in eq 10.

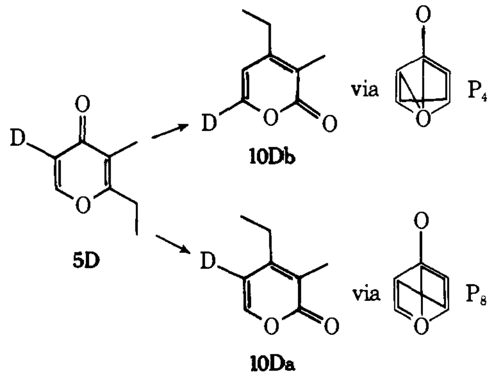


The reaction of **10Da** to give **11D** shows that the minor pathway for the 2-hydroxypyryliums is a P_2 process (eq 11).

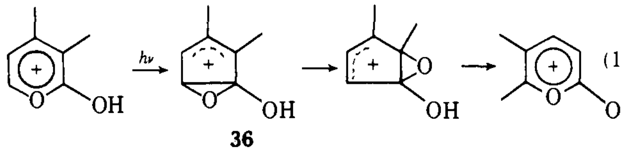


Consideration of the pattern P_2 suggests that the reaction may be initiated by 2,6 or 1,3 bonding. The former seems more

Scheme VI

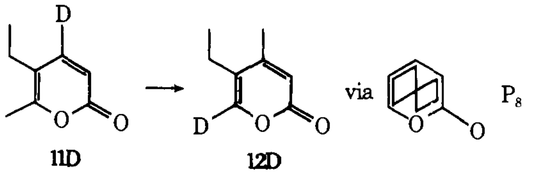


reasonable as the first step since it would give rise to a species (**36**) which could rearrange as shown in eq 12.



(12)

The labeling pattern in **12D** is quite consistent with its formation in a second photochemical step from **11D** by a normal P$_8$ process (eq 13).



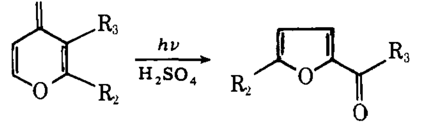
(13)

Generalization. MO Rationale. We thus see, in the case of the 4-hydroxypyrylium cations, a strong preference for 2,6 bonding with occasional 3,6 (or the equivalent 2,5) bonding, while for 2-hydroxypyrylium cations the preference is for 3,6 bonding with occasional 2,6 bonding. The preference for these two types of bonding can be nicely rationalized in terms of the molecular orbitals of the parent pyrylium cation.

Consider first the six π-molecular orbitals of benzene and then the effect of introducing an electronegative endocyclic oxygen atom as a first-order perturbation. All the orbitals are lowered in energy except for ψ_3 and ψ_5, which have a node through the heteroatom and, to first order, are unchanged in energy as shown in Figure 2.

$\pi \rightarrow \pi^*$ excitation involves promotion of an electron from ψ_3 which is 2,6 and 3,6 antibonding to ψ_4 which is 2,6 and 3,6 bonding. Thus we might expect a tendency for these processes to occur in the lowest $\pi \rightarrow \pi^*$ excited state.

Furan Derivatives. In addition to the two isomeric 2-pyrones (**10** and **11**) isolated from irradiation of **5**, in sulfuric acid a third product was formed which was identical with 2-acetyl-5-ethylfuran (**37a**), eq 14, synthesized by the published procedure.[22] Pavlik has recently reported similar reactions for **17** and **18**.[7]



(14)

5 **37a**, R$_2$ = Et; R$_3$ = Me
17 **b**, R$_2$ = Me; R$_3$ = Me
18 **c**, R$_2$ = Me; R$_3$ = Et

The yield of **37a** was found to depend markedly on the concentration of acid used. Thus, in 90% sulfuric acid, it was formed almost to the exclusion of the 2-pyrones; in nominally 98% acid it was formed in ca. 40% yield; its formation was almost suppressed by the addition of 5% of 20% oleum and it was absent when fluorosulfonic acid was used as solvent.

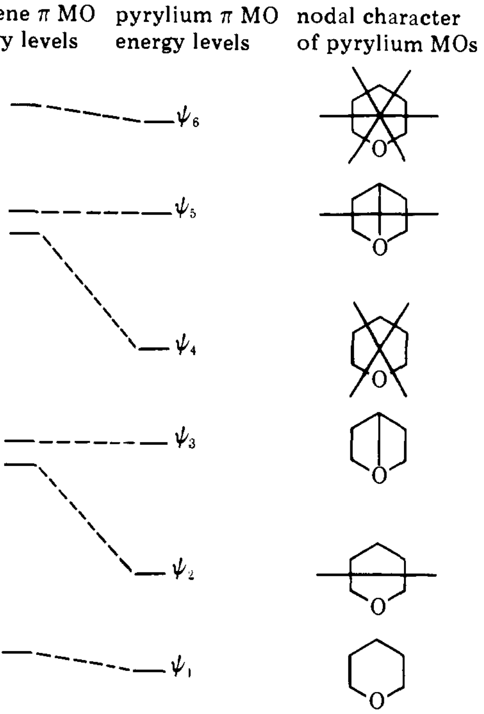
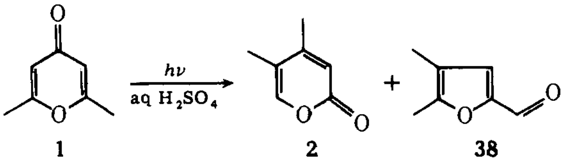
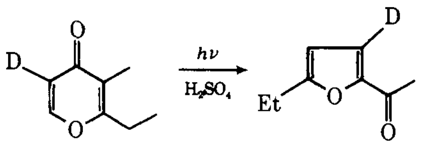


Figure 2. Nodal properties of the π molecular orbitals of pyrylium cations.

The effect of added water on the photochemistry of 2,6-dimethyl-4-pyrone (**1**) was also studied in the range 20–98% sulfuric acid. The detailed results will be reported elsewhere but the same pattern as for **5** emerged, in that increasing concentration of water increased the yield of 4,5-dimethylfurfural (**38**) (eq 15). In the deuterium labeling study, **5D** gave **37aD** in which the label was in the 3 position (eq 16). In the product, the CH and the CEt are adjacent, suggesting the involvement of 2,6 bonding in the mechanism and therefore a close relationship to pyrone formation.

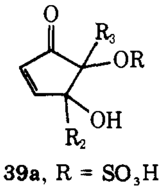


(15)



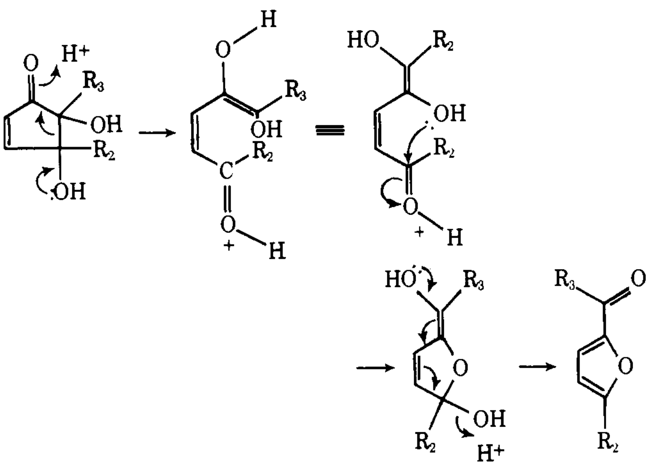
(16)

Pavlik has considered the possibility that these compounds are derived from a sulfate adduct of type **39a** but presented evidence against this. In view of the water dependence, we thought that the related water adduct **39b** was a reasonable



39a, R = SO$_3$H
b, R = H

Scheme VII



precursor. **39b** (R_2 = Et; R_3 = Me) was available from irradiation of the 4-pyrone **5** in water and on treatment with sulfuric acid gave furan **37a**. A possible mechanism is outlined in Scheme VII. This mechanism should be regarded as tentative, for, as a referee has kindly pointed out, since there can be little neutral water in 98% sulfuric acid, there may be doubt as to the intervention of a water adduct in the production of the furan **37a**. More experimentation is necessary.

Experimental Section

Unless otherwise stated, the following procedures apply. Gas chromatography was carried out using one of the following columns: A, 20% Carbowax 20M; B, 10% PEGS; C, 30% Apiezon L. Preparative thin layer chromatography (PLC) was carried out using 200 × 200 × 1 mm layers of Kieselgel, eluting with the indicated percentage of ether in petroleum ether (bp 30–40 °C), the indicated number of times. Bands absorbing 254-nm light are recorded in order of decreasing R_f. Sulfuric acid refers to AR sulfuric acid, nominally 98%. Petrol refers to petroleum ether (bp 40–60 °C). Melting points were measured on a Kofler block and are uncorrected.

2,5-Dimethyl-4H-pyran-4-one. A mixture of 1-propenyl acetate (5.0 g, 0.06 mol) and acetic anhydride (60 mL) was stirred in an ice bath and 60% perchloric acid (5 mL) was added dropwise. The solution was heated at 70 °C for 1.5 h and cooled, and ether (300 mL) was added. A black tar settled, the ether layer was decanted, and the tar was extracted with hot water which was cooled and ether extracted. The combined ether extracts were dried and concentrated in vacuo to give a brown oil which was chromatographed on silica gel. Elution with ether gave 2,5-dimethyl-4-pyrone (1.4 g, 19%), which crystallized on standing. Recrystallization from petrol gave mp 38–39 °C. The spectral data follow: NMR (CCl_4) τ 2.46 (q, 1 H, J = 1.3 Hz, H_6), 4.01 (q, 1 H, J = 0.7 Hz, H_3), 7.78 (d, 3 H, J = 0.7 Hz, Me_2), 8.17 (d, 3 H, J = 1.3 Hz, Me_5); UV λ_{max} (EtOH) 211 nm (ϵ 10 020), 252 (13 400); IR (CCl_4) 1670 (s), 1642 (s) cm^{-1}; mass spectrum m/e 124 (100), 96 (13), 95 (31), 84 (12), 83 (9), 69 (53), 56 (28), 43 (89), 39 (53). Anal. ($C_7H_8O_2$) C, H.

In an improved procedure, the reaction mixture was diluted with water and continuously extracted with petrol which was dried and concentrated in vacuo. The residue was distilled to afford the pyrone.

2-Ethyl-3-methyl-4*H*-pyran-4-one. A mixture of vinyl acetate (40.4 g, 0.47 mol) and propionic anhydride (500 mL) was stirred in an ice bath and 60% perchloric acid (37.5 mL) was added dropwise. The solution was heated at 70 °C for 1.5 h and cooled, and ether (1.2 L) was added. A black tar settled, the ether layer was decanted, and the tarry layer was extracted with hot water which was cooled and ether extracted. The combined extracts were dried and concentrated in vacuo to give a black oil, from which material boiling below 100 °C (30 mm) was removed by distillation. The residue was chromatographed on silica gel. Elution with ether gave a brown oil which was distilled to give 2-ethyl-3-methyl-4-pyrone (7.0 g, 10.8%, bp 119–120 °C, 5 mm) which crystallized on standing (mp 25–30 °C). The spectral data follow: NMR (CCl_4) τ 2.33 (d, 1 H, J = 5.7 Hz, H_6), 3.98 (d, 1 H, J = 5.7 Hz, H_5), 7.44 (q, 2 H, J = 7.5 Hz, CH_2CH_3), 8.18 (s, 3 H, CH_3), 8.81 (t, 3 H, J = 7.5 Hz, CH_2CH_3); UV λ_{max} (EtOH) 210 nm (ϵ 9310), 255 (13 600); IR (CCl_4) 1660 (s), 1630 (m) cm^{-1}; mass spectrum m/e 138 (98), 137 (100), 123 (12), 110 (8), 109 (13), 95 (40), 83 (9), 82 (15), 71 (77), 69 (16), 67 (33), 53 (40). Anal. ($C_8H_{10}O_2$) C, H.

In an improved procedure, the reaction mixture was diluted with water and continuously extracted with petrol, which was dried and concentrated in vacuo. The residue was distilled.

Irradiation Procedures. Solutions of the pyrones in sulfuric acid (0.02–0.2 M) in test tubes were irradiated under various conditions: A, Rayonet RPR-100 reactor fitted with 254-nm lamps and quartz tubes; B, the same reactor fitted with 300-nm lamps and quartz tubes; C, Hanovia 450-W medium-pressure mercury lamp in water-cooled housing and Pyrex tubes held close to the housing. In suitable cases, the reaction was monitored by diluting an aliquot to ca. 10^{-4} M and measuring the UV spectrum. After irradiation, the acid solution was added with stirring to ice/water (ca. 10 g/ml of acid). Anhydrous sodium carbonate (ca. 2 g/ml of acid) was added to the stirred solution until the pH rose above 6, when the solution was ether extracted. The extract was dried and concentrated in vacuo to yield the crude photolysate.

Irradiation of 3,5-Dimethyl-4-pyrone. The pyrone (1.00 g) in sulfuric acid (50 ml) was irradiated (conditions A) for 33 h, when the absorption shifted from 253 to 304 nm. Normal workup gave an oil (690 mg 69%) which crystallized on standing (mp 45–47 °C). Recrystallization from petrol gave 3,6-dimethyl-2*H*-pyran-2-one[7] as almost colorless crystals. The spectral data follow: NMR, IV, UV (Table I); mass spectrum m/e 124 (43), 96 (29), 95 (18), 81 (16), 53 (25), 43 (100). Anal. ($C_7H_8O_2$) C, H.

Irradiation of 2,5-Dimethyl-4-pyrone. The pyrone (1.00 g) in sulfuric acid (90 mL) was irradiated (conditions A) for 27 h. Normal workup gave a brown oil (0.35 g) which was subjected to PLC (25% ether, four times) which gave four bands. Band 1 (24 mg) was unidentified. Band 2 (42 mg) was rechromatographed on alumina (20% ether, four times), which gave two bands. Band 2a (3.8 mg) contained 3,6-dimethyl-2-pyrone. Band 2b (10.7 mg) contained 3,5-dimethyl-2*H*-pyran-2-one. The spectral data follow: NMR, IR, UV (Table I); mass spectrum m/e 124 (100), 96 (66), 95 (22), 68 (21), 67 (63), 53 (26), 43 (19), 41 (36), 39 (44). Band 3 (173 mg) contained 4,6-dimethyl-2-pyrone.[9] Band 4 (67 mg) contained recovered starting pyrone.

Irradiation of 2-Ethyl-3-methyl-4-pyrone. Run 1. The pyrone (1.00 g) in sulfuric acid (100 mL) was irradiated (conditions A) for 30 h. Normal workup and PLC (50% ether, three times) gave four bands. Band 1 (221.9 mg) contained 2-acetyl-5-ethylfuran, identical with independently synthesized material.[22] The spectral data follow: NMR (CCl_4) τ 3.02 (d, 1 H, J = 3.3 Hz, H_4), 3.90 (br d, 1 H, J = 3.3 Hz, H_3), 7.32 (q, 2 H, J = 7.5 Hz, CH_2CH_3), 7.70 (s, 3 H, CH_3), 8.77 (t, 3 H, J = 7.5 Hz, CH_2CH_3); IR (CCl_4) 1680 (s), 1590 (m), 1515 (s) cm^{-1}; UV λ_{max} (EtOH) 222 nm (ϵ 2190), 283 (14 700); mass spectrum m/e 138 (24), 124 (14), 123 (100), 95 (10), 81 (12), 43 (19). Anal. ($C_8H_{10}O_2$) C, H. Band 2 (55.0 mg) contained 4-ethyl-3-methyl-2*H*-pyran-2-one. The spectral data follow: NMR, IR, UV (Table I); mass spectrum m/e 138 (55), 110 (39), 95 (100), 81 (15), 67 (18), 53 (18), 43 (10). Anal. ($C_8H_{10}O_2$) C, H. Band 3 (238.5 mg) contained 5-ethyl-6-methyl-2*H*-pyran-2-one. The spectral data follow: NMR, IR, UV (Table I); mass spectrum m/e 138 (49), 123 (18), 110 (40), 95 (86), 77 (45), 67 (29), 43 (100), 41 (19), 39 (19). Anal. ($C_8H_{10}O_2$) C, H. Band 4 contained recovered starting pyrone.

Run 2. The pyrone (33 mg) in sulfuric acid (5 mL) was irradiated (conditions A) for 21 h. Normal workup and analysis of the crude photolysate by NMR and GC (column A, 184 °C) showed that the predominant product was 2-acetyl-5-ethylfuran (ca. 75%) and that the two 2-pyrones were minor (15 and 10%).

Irradiation of 5,6-Dimethyl-2-pyrone. The pyrone[3] (100 mg) in sulfuric acid (10 mL) was irradiated (conditions C) for 46 h, when the absorption shifted from 308 to 299 nm. Normal workup and PLC (50% ether, four times) gave two bands. Band 1 contained recovered starting pyrone (49 mg) and band 2 contained 4,5-dimethyl-2-pyrone[3] (48 mg).

Irradiation of 3,6-Dimethyl-2-pyrone. The pyrone (1.00 g) in sulfuric acid (75 mL) was irradiated (conditions C) for 6 days, when the absorption shifted from 304 to 292 nm. Normal workup and PLC (40% ether, three times) gave two bands. Band 1 (377 mg) contained recovered starting pyrone and band 2 (360 mg) contained 3,4-dimethyl-2*H*-pyran-2-one,[7] which crystallized on standing (mp 58–60

°C) and was recrystallized from petrol (mp 60–61 °C). The spectral data follow: NMR, IV, UV (Table I); mass spectrum *m/e* 124 (54), 96 (100), 95 (66), 81 (61), 68 (20), 67 (33), 53 (27), 51 (20), 41 (28), 39 (42). Anal. ($C_7H_8O_2$) C, H.

Irradiation of 3,4-Dimethyl-2-pyrone. The pyrone (450 mg) in sulfuric acid (50 mL) was irradiated (conditions B) for 4 days. Normal workup and PLC (40% ether, four times) gave four bands. Band 1 (63 mg) contained 3,6-dimethyl-2-pyrone. Band 2 (143 mg) contained recovered starting pyrone. Band 3 (11 mg) contained 5,6-dimethyl-2-pyrone.[3] Band 4 (12 mg) contained 4,5-dimethyl-2-pyrone.[3]

Irradiation of 5-Ethyl-6-methyl-2-pyrone. The pyrone (630 mg) in sulfuric acid (80 mL) was irradiated (conditions B) for 7 days. Normal workup and PLC (25% ether, four times) gave two bands. Band 1 (312 mg) contained recovered starting pyrone. Band 2 (50 mg) contained 5-ethyl-4-methyl-2*H*-pyran-2-one. The spectral data follow: NMR, IR, UV (Table I); mass spectrum *m/e* 138 (42), 110 (45), 95 (100), 67 (65), 53 (32), 43 (30), 41 (45), 39 (55).

$[^{14}\mathrm{C}]$Dehydroacetic Acid. Ethyl $[3\text{-}^{14}\mathrm{C}]$acetoacetate (5 mCi/mmol, 250 μCi) was diluted to 101.3 g with inactive material and converted to dehydroacetic acid (17.85 g, 30.6%, specific activity 640 μCi/mol) by the published procedure.[11] Recovered ethyl acetoacetate (44.1 g, 43.6%) was recycled.

$[2,6\text{-}^{14}\mathrm{C}]$-2,6-Dimethyl-4-pyrone. $[^{14}\mathrm{C}]$Dehydroacetic acid (25 g) was converted to 2,6-dimethyl-4-pyrone (8.76 g, 23%, specific activity 638 μCi/mol) by the published procedure.[11]

Irradiation of $[2,6\text{-}^{14}\mathrm{C}]$-2,6-Dimethyl-4-pyrone. The labeled pyrone (4.00 g, specific activity 638 μCi/mol) in sulfuric acid (120 mL) was irradiated (conditions A) for 6 days. Normal workup gave a yellow oil (2.87 g). A portion of the crude photolysate (1.5 g) was subjected to PLC, which gave two bands. Band 1 (0.64 g) contained 5,6-dimethyl-2-pyrone, which was recrystallized from petrol (specific activity 633 μCi/mol). Band 2 (0.45 g) contained 4,5-dimethyl-2-pyrone, which was distilled (bp 130–140 °C, 10 mm). Two fractions were collected (specific activity 635 and 621 μCi/mol).

Degradation of Labeled Pyrones.[12] Portions of each pyrone (ca. 1 mmol) were dissolved in sulfuric acid (7.5 mL). Chromic acid (5 M, 30 ml) was added dropwise over 20 min and the solution was heated under reflux for 1.5 h, then steam distilled. The distillate was neutralized by titration with 5×10^{-3}M sodium hydroxide, concentrated to ca. 15 mL, and treated with 1 equiv of 4-bromophenacyl bromide in ethanol (10 mL). The mixture was heated under reflux for 0.5 h, water (80 mL) was added, and the suspension was concentrated to ca. 60 mL and ether extracted. The extract was dried, concentrated, and subjected to PLC (50% ether, once) which gave 4-bromophenacyl acetate (mp 84–85 °C) which was recrystallized to constant specific activity from aqueous ethanol.

2,6-Dimethyl-4-pyrone gave acetic acid (64%) and 4-bromophenacyl acetate (25%, specific activity 316 μCi/mol). 4,5-Dimethyl-2-pyrone gave acetic acid (41%) and 4-bromophenacyl acetate (55%, specific activity 313 μCi/mol). 5,6-Dimethyl-2-pyrone gave acetic acid (75%) and 4-bromophenacyl acetate (65%, specific activity 316 μCi/mol).

Deuteration of 2,5-Dimethyl-4-pyrone. The pyrone in methanol-*O-d*[22] containing a trace of sodium methoxide was allowed to stand for 5 days, diluted with ether, dried, filtered, and concentrated in vacuo. The residue was dissolved in deuteriosulfuric acid and heated at 200 °C for 24 h. Normal workup and vacuum sublimation of the crude product gave mp 25–31 °C.

Deuteration of 2,6- and 3,5-Dimethyl-4-pyrones. The pyrones (25 mg) in deuteriosulfuric acid (0.5 mL) in NMR tubes were heated at 190–200 °C for 2 h. The 2,6-dimethyl-4-pyrone sample showed 70% deuteration at the 3 and 5 positions; 3,5-dimethyl-4-pyrone was unchanged.

Deuteration of 2-Ethyl-3-methyl-4-pyrone. The pyrone (7.54 g) in deuteriosulfuric acid (10 mL) was heated at 180–200 °C for 24 h. Normal workup and NMR analysis showed 30% deuteration at H_5. This material was recycled to give 0.90 g with 75% deuteration.

Deuteration of 4-Ethyl-3-methyl-2-pyrone. The pyrone (110 mg) in deuteriosulfuric acid (3 mL) was heated at 130 °C for 24 h. Normal workup and NMR analysis indicated 68% deuteration at H_5.

Deuteration of 5-Ethyl-6-methyl-2-pyrone. The pyrone in deuteriosulfuric acid was heated at 80–85 °C for 15 h. Normal workup and NMR analysis indicated 90% deuteration at H_3.

Irradiation of Deuterated 2,5-Dimethyl-4-pyrone. The labeled pyrone (0.87 g) in sulfuric acid (105 mL) was irradiated (conditions A) for 30 h. Normal workup and PLC (15% ether, three times) gave three bands. Band 1 (24.3 mg) contained deuterated 3,5- and 3,6-dimethyl-2-pyrones. This was combined with the corresponding bands from other irradiations and resubjected to PLC on alumina (15% ether, five times), which gave two bands. Band 1a contained deuterated 3,6-dimethyl-2-pyrone. Band 1b contained deuterated 3,5-dimethyl-2-pyrone. Band 2 (85.6 mg) contained deuterated 4,6-dimethyl-2-pyrone. Band 3 (58.2 mg) contained recovered starting pyrone.

Irradiation of Deuterated 2-Ethyl-3-methyl-4-pyrone. The labeled pyrone (1.40 g) in sulfuric acid (130 mL) was irradiated (conditions A) for 22 h. Normal workup and PLC (8% ether, once) gave four bands. Band 1 (82 mg) was unidentified. Band 2 (23 mg) was unidentified. Band 3 (99 mg) contained deuterated 2-acetyl-5-ethylfuran. Band 4 was resubjected to PLC (10% ether, five times), which gave three bands. Band 4a (40 mg) contained deuterated 4-ethyl-3-methyl-2-pyrone. Band 4b (55 mg) contained deuterated 5-ethyl-6-methyl-2-pyrone. Band 4c (52 mg) contained recovered starting pyrone.

Irradiation of Deuterated 4-Ethyl-3-methyl-2-pyrone. The pyrone (0.50 g) was deuterated under the above conditions to give 64% 5-*d*, material which was dissolved in sulfuric acid (180 mL) and irradiated (conditions B) for 5 days. Normal workup and PLC (20% ether, four times) gave three bands. Band 1 contained deuterated 6-ethyl-3-methyl-2*H*-pyran-2-one. The spectral data follow: NMR, IR, UV (Table I). Band 2 contained recovered starting pyrone. Band 3 was resubjected to PLC (25% ether, four times) to give two bands. Band 3a contained deuterated 5-ethyl-6-methyl-2-pyrone. Band 3b contained deuterated 5-ethyl-4-methyl-2-pyrone.

Lanthanide-Induced Shift Studies. Incremental quantities of $Eu(fod)_3$[15] were added to various pyrones and the following molar shifts (ppm per mol/mol ratio) were observed: 5,6-dimethyl-2-pyrone, H_3 (13.8), H_4 (5.1), Me_5 (3.3), Me_6 (4.6); 3,4-dimethyl-2-pyrone, Me_3 (7.6), Me_4 (2.8), H_5 (1.7), H_6 (3.2); deuterated 4,6-dimethyl-2-pyrone, unlabeled ring proton (5.9), labeled ring proton (19.1), unlabeled methyl group (2.1), labeled methyl group (1.3).

5,7-Dimethyl-2,4-dioxa-3-thiabicyclo[3.3.0]oct-7-en-6-one 3,3-Dioxide. 3,5-Dimethyl-4-pyrone (1.00 g) in sulfuric acid (25 mL) was irradiated (conditions A) for 7 h, with efficient stirring. The acid solution was injected over the course of 1 h through a fine syringe needle with the tip below the surface into rapidly stirred saturated sodium bicarbonate solution. Ether extraction, drying, concentration in vacuo, and PLC (10% ether, four times) gave three bands. Band 1 (246.3 mg) contained 3,6-dimethyl-2-pyrone. Band 2 (407.8 mg) was the cyclic sulfate, which crystallized on standing. Trituration with petrol gave 388.7 mg (21.9%, mp 72.5–73.5 °C). Recrystallization from petrol/chloroform gave mp 73.5–74 °C. The spectral data follow: NMR ($CDCl_3$) τ 2.69 (dq, 1 H, $J = 2.6, 1.5$ Hz), 4.57 (dq, 1 H, $J = 2.6, 1.3$ Hz), 8.03 (dd, 3 H, $J = 1.5, 1.3$ Hz), 8.28 (s, 3 H); UV λ_{max} (EtOH) 223 nm (ϵ 8440), 339 (42.3); IR (CCl_4) 1744 (s), 1641 (w), 1416 (s), 1217 (s) cm^{-1}; mass spectrum *m/e* 204 (4), 124 (21), 109 (11), 96 (100), 95 (38), 81 (35), 53 (26), 43 (39), 39 (19). Anal. ($C_7H_8O_5S$) C, H, S. Band 3 (214.8 mg) contained further cyclic sulfate, together with recovered starting pyrone.

Hydrogenation of the Cyclic Sulfate. The sulfate (90.9 mg) in methanol was hydrogenated, under ambient conditions, for 15 h, over 10% palladium on barium sulfate (82.4 mg), when ca. 2.7 equiv was taken up. Filtration and concentration in vacuo gave a residue which was identical in spectroscopic (NMR and IR) and chromatographic (GC on column C) behavior with authentic 2,5-dimethylcyclopentanone.[16]

Irradiation of the Cyclic Sulfate. The cyclic sulfate in sulfuric acid (3 mL, ca. 10^{-4} M), in a quartz UV cell, was irradiated (conditions A) for 15 min, during which time the initial absorption at 232 nm had shifted to 304 nm.

Thermal Reaction of the Cyclic Sulfate. The cyclic sulfate in sulfuric acid (3 mL, ca. 10^{-4} M), in a quartz UV cell, was allowed to stand at room temperature. The absorption maximum shifted from 232 to 304 nm with a half-life of ca. 40 h.

Reaction of the Epoxide with Sulfuric Acid. Sulfuric acid (0.5 mL) was added to a solution of the epoxide (10 mg) in carbon tetrachloride (0.5 mL) in an NMR tube. The tube was shaken and the NMR spectrum of the lower (acid) layer was measured. It showed signals appropriate to 3,6-dimethyl-2-pyrone and the cyclic sulfate in the ratio ca. 1:1.

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Heterocyclic Photochemistry. 2. 4-Pyrones. A Mechanistic Study

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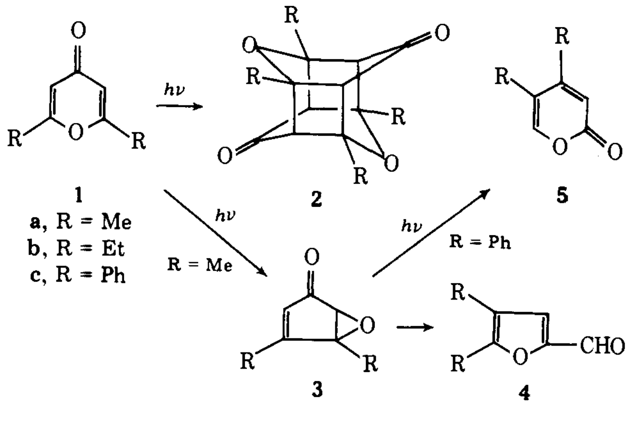
Abstract: The phototransposition of 4-pyrones into 2-pyrones in neutral solvents is shown to follow the sequence (4-pyrone)* → oxabicyclohexenyl zwitterion (e.g., **14**) → cyclopentadienone epoxide (e.g., **15**) + $h\nu$ → 2-pyrone. The oxabicyclohexenyl zwitterion derived from 3,5-dimethyl-4-pyrone has been trapped as a [4 + 3] cycloadduct with furan and the corresponding cyclopentadienone epoxide has been isolated and shown to rearrange photochemically to 2-pyrone. The zwitterion also reacts with hydroxylic solvents to give derivatives of cyclopentenone-4,5-diols and of furfuraldehyde. The effect of substituents in the 4-pyrone and of solvents on the photochemical behavior is rationalized.

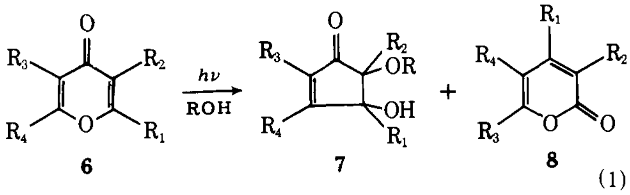
Introduction

The history of pyrone photochemistry is a long one, dating back to the early days of photochemistry when Paterno in 1914 reported a photodimer of 2,6-dimethyl-4-pyrone (**1a**).[2] The structure of this dimer was not correctly assigned,[3] however, until 1958, when Yates and Jorgenson[4] showed it to have the head-to-tail cage structure (**2a**). Under conditions of low concentration, chosen to retard dimerization, Yates and Still[5] observed the first monomeric product, finding that irradiation of **1a** in water afforded ca. 1% yield of 4,5-dimethylfurfuraldehyde (**4a**) which they suggested was formed via an epoxide (**3a**).



Padwa and Hartman showed that 2,6-diphenylpyrone (**1c**) gave a photodimer, to which they assigned a similar cage structure (**2c**), but no monomeric photoproducts. However, they did show that epoxide (**3c**), synthesized independently, gave **4c** on treatment with acid and the transposed **5c** on irradiation.[6]

More recently, appropriately substituted 4-pyrones have been found to rearrange photochemically to 2-pyrones,[7,8] and, again, epoxides such as **3** have been postulated as intermediates. In concentrated sulfuric acid, where pyrones are protonated and are best described as hydroxypyrylium cations, this rearrangement to 2-pyrones occurs almost regardless of substitution pattern;[8,9] our studies of this system are described in the accompanying paper.[10] Since we began this work, reports have appeared of solvent adducts (**7**) formed in competition with 2-pyrones (**8**) in alcoholic solvents (eq 1).[11,12]



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Further studies on the photodimerization have appeared, including reports of the dimer of 2,6-diethyl-4-pyrone (**1b**)[13]

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