associated with a particularly stable negative ion structure. But the conversion from positive to negative ion is very rapid;[12] hence, the corresponding positive ion must have essentially the same structure. Hence, only if the positively charged ion possesses a certain structure will an abundant negatively charged ion be observed. For example, the occurrence of $C_5H_5^-$ in high abundance in the anisole spectrum suggests that $C_5H_5^+$ is cyclic rather than linear, although more experiments, particularly with homologous ions, will be necessary to establish this conclusion firmly. The reverse procedure, inference of negative ion structures from well-established positive ion structures, should also be possible.

Acknowledgment. We wish to thank the National Science Foundation for generous support under Grant No. GP 32187 and Dr. J. H. Bowie for helpful discussions.

(12) For a one-step mechanism the relative velocity of the species is such that, for an ion of mass 100, 5 Å is covered in 10^{-13} sec.

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Photochemical Rearrangements of Pyrylium Cations[1]

Sir:

Photolysis of 2,6-disubstituted-4*H*-pyran-4-ones results in photoreactions typical of α,β-unsaturated carbonyl compounds. Thus, both 2,6-diphenyl- and 2,6-dimethyl-4*H*-pyran-4-one (I) undergo photodimerization, presumably *via* their n,π^* excited states, to yield their respective head-to-tail cage dimers.[2,3] Pyrone I has also been shown to undergo photoaddition reactions with alkynes to yield 1:1 cyclobutene adducts.[4] Recently, however, Ishibe and colleagues have reported that 2,6-disubstituted-3,5-diphenyl-4*H*-pyran-4-ones undergo photoisomerizations more characteristic of cross-conjugated cyclohexadienones to yield 3,6-diphenyl-4,5-disubstituted-2*H*-pyran-2-ones.[5] Lack of photodimerization in these latter cases was attributed to steric effects of the 3,5 substituents rather than to any change in the nature of the excited states involved in the reactions.

As part of our program to investigate the effects of protonation on the course of the photoreactions of carbonyl compounds, we wish to report that photolysis of 2,6-dimethyl-4-hydroxypyrylium ion (II), formed by protonation of I in 96% H_2SO_4, results in the formation of a mixture of 4,5-dimethyl-2-hydroxypyrylium ion (III) and 5,6-dimethyl-2-hydroxypyrylium ion (IV). Neutralization of the resulting solution converted ions III and IV to 4,5-dimethyl-2*H*-pyran-2-one (V) and 5,6-dimethyl-2*H*-pyran-2-one (VI), respectively. Subsequent experimental evidence showed that III was an intermediate in the photoisomerization of II to IV.

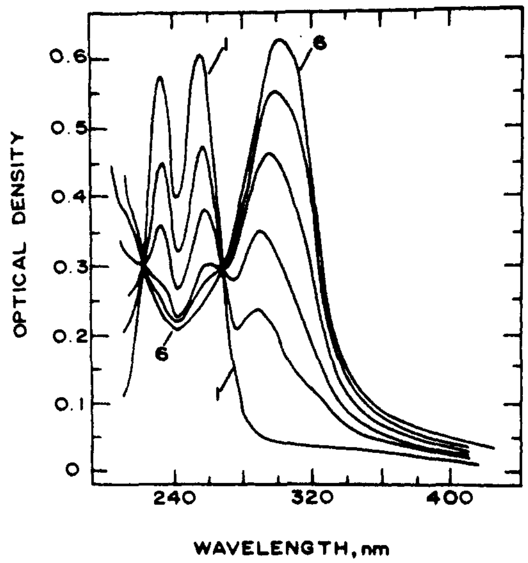
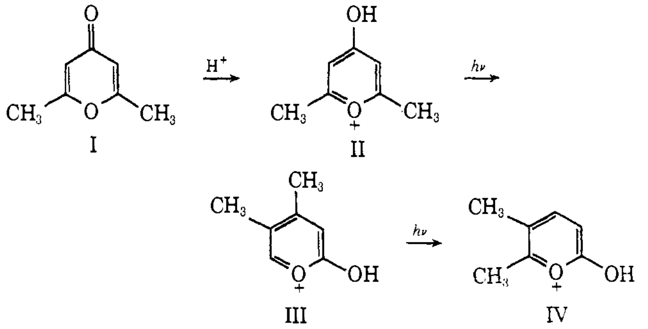


Figure 1. Ultraviolet absorption spectrum of II, 5×10^{-5} *M* in 96% H_2SO_4: 1, before irradiation; 2–6, after consecutive 15 min irradiations at 253.7 nm.



Solution of I in 96% H_2SO_4 resulted in the formation of thermally stable II from which I could be quantitatively recovered by neutralization.[6] Figure 1 shows the successive changes in the absorption spectrum of II following short duration irradiations with light of 254 nm at ambient temperature.[7] The figure illustrates the gradual disappearance of II with the simultaneous increase in absorbance at longer wavelengths ultimately reaching a maximum at 304 nm. The final product (λ_{max} 304 nm) seems to be both thermally and photochemically stable under these conditions. The absorption spectrum of a solution of II irradiated to any per cent conversion remained unchanged after standing in the dark for extended times. This testifies that the changes in Figure 1 are photochemical with no interference from thermal reactions. Considering the three species present in the reaction solution, *i.e.*, II, III, and IV, the isosbestic points at 221 and 267 nm in Figure 1 indicate only a coincidental equality of their extinction coefficients at those wavelengths.

Preparative-scale photolysis[8] of II, 3.2×10^{-3} *M* in 96% H_2SO_4, followed by neutralization led to the isolation of V and VI, which were separated by preparative gas chromatography. Re-solution of V and VI in 96% H_2SO_4 regenerated III and IV, λ_{max} 287 and 304

(1) Presented in part at the Sixth Great Lakes Regional Meeting of the American Chemical Society, June 1972, Houghton, Mich., Abstract 43.

(2) P. Yates and M. J. Jorgenson, *J. Amer. Chem. Soc.*, **80**, 6150 (1958).

(3) N. Sugiyama, Y. Sato, and C. Kashirma, *Bull. Chem. Soc. Jap.*, **43**, 3205 (1970).

(4) J. W. Hanifin and E. Cohen, *J. Org. Chem.*, **36**, 910 (1971).

(5) N. Ishibe, M. Odani, and M. Sunami, *Chem. Commun.*, 1034 (1971).

(6) Cation II: λ_{max} 254 nm (ϵ 12,200), 232 nm (ϵ 11,600).

(7) Bausch and Lomb high intensity monochromater with 125-W high-pressure Hg arc.

(8) Preparative-scale photolyses were carried out under nitrogen in a 230-ml Pyrex vessel fitted around a quartz low-pressure Hg lamp with output of 2.5 W.

nm, respectively. V and VI had chemical and spectroscopic properties consistent with other known 2-pyrones.[9] Thus, both products were stable in acid solution, were rapidly degraded in alkaline solution, and reacted with maleic anhydride.[10] The positions of the methyl groups in V were unambiguously assigned on the basis of its 60-MHz nmr spectrum.[9] Lack of ring proton coupling clearly shows that the ring hydrogens are not on adjacent ring positions. Furthermore, consideration of the nmr spectra of other known 2 pyrones indicates that whereas protons on ring positions 3 and 5 absorb close to 6 ppm, protons on positions 4 and 6 absorb between 7 and 7.5 ppm.[11,12] Thus of the possible dimethyl-2-pyrone structures with nonadjacent ring hydrogens, *viz.* 3,5-dimethyl-, 4,6-dimethyl-, and 4,5-dimethyl-2*H*-pyran-2-one, only the latter is consistent with the observed spectrum.[13]

The coupling and chemical shift values of the ring protons in VI place these hydrogens on adjacent ring positions and are consistent with two possible structures, *viz.* 3,4-dimethyl- and 5,6-dimethyl-2*H*-pyran-2-one. Distinction between these two structures was based on chromatographic and spectroscopic comparison of VI with a sample of the 5,6-dimethyl isomer synthesized in this laboratory.[14]

Consideration of the per cent yield of V and VI after neutralization as a function of irradiation time (Table I) revealed an initial build-up and subsequent decrease in the yield of V accompanied by a continuous increase in the yield of VI. This suggests that both III and IV, the respective precursors of V and VI, are not both formed directly from II, but that III is a precursor of IV. Indeed, solution of pure V in 96% H_2SO_4 gave the thermally stable ion III (λ_{max} 287 nm), which was converted to VI by irradiation and neutralization.

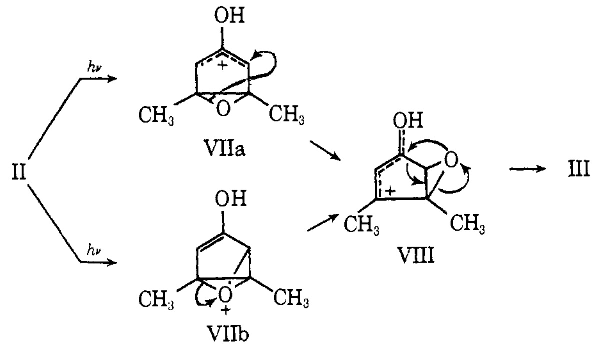
Table I. Product Distribution as a Function of Irradiation Time

Time, hr	I[a,b]	V, % yield[c]	VI, % yield
3.0	65	27	7.6
7.5	18	54	24
11.0	3	39	58

[a] Refers to the per cent of I recovered from solution. [b] Analysis was performed by glpc on a 4 ft × 0.25 in. column packed with 2% Carbowax 20M on Chromosorb G. Retentions of V and VI relative to I at 170° are 1.44 and 0.83, respectively. [c] Yields given refer to the per cent of volatiles recovered after neutralization and ether extraction of photolyzed solutions. More accurate yields for the overall reaction II → IV were calculated from extinction coefficients of II and IV to be 72% of theoretical.

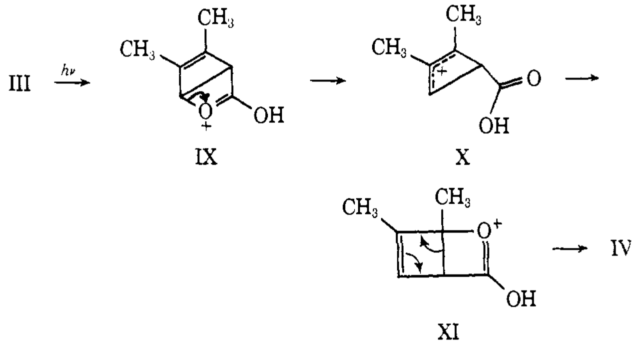
The rearrangement of II → III can be viewed (Scheme I) as taking place by way of thermal conversion of oxabicyclohexenyl cation VIII in a manner similar to the known acid-catalyzed rearrangements of 4,5-epoxy-2-cyclopentenones to 2-pyrones.[15,16] As in the present case, substituents originally in the 3 and 4 positions of the cyclopentenone ring are found in the 4 and 5 positions of the 2-pyrone ring. Two pathways, perforce originating in $\pi \rightarrow \pi^*$ excitation of II, are possible for the formation of VIII. Thus VIIa, formed by symmetry allowed 2,6 bridging in the first excited state of II, could undergo 1,2 migration of the epoxide ring to yield VIII. Such a pathway is mechanistically similar to that proposed for the photoisomerization of hydroxycyclohexadienyl cations.[17,18] Alternatively, oxybenzvalene VIIb is also a plausible precursor of VIII. Analogously, benzvalene type intermediates have also been implicated in the photoreactions of pyridinium cations.[19] As in the latter case, there is no indication that VIIb has any appreciable lifetime under present conditions but is rather converted to VIII by opening of the 1,2 bond.

Scheme I



To explain the formation of IV from III we have evoked the intermediacy of protonated bicyclo-β-lactone IX and carboxylcyclobutenyl cation X (Scheme II). Bicyclo-β-lactones have previously been established as primary photoproducts of the photolysis of 2-pyrones[20–22] and have been shown to be an excellent source of carboxylcyclobutenyl cations.[22] Although it has been suggested that in the presence of external nucleophiles carboxylcyclobutenyl cations do not usually regenerate lactones,[22] it is plausible that in the

Scheme II



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(9) V: ir (CCl_4) 2970, 1750, 1450, 1410, 1650, 1210, 1050 cm^{-1}; nmr ($CDCl_3$) δ 7.23 (s, 1 H), 6.26 (s, 1 H), 2.31 (s, 3 H), 2.19 (s, 3 H). VI: ir (CCl_4) 3040, 2940, 1750, 1650, 1450, 1420, 1295, 1085 cm^{-1}; nmr ($CDCl_3$) δ 7.20 (d, J = 9.5 Hz, 1 H), 6.15 (d, J = 9.5 Hz, 1 H), 2.23 (s, 3 H), 2.00 (s, 3 H).

(10) M. J. Goldstein and G. L. Thayer, Jr., *J. Amer. Chem. Soc.*, **87**, 1925 (1965).

(11) A. Padwa, *Tetrahedron Lett.*, 813 (1964).

(12) P. Beaks and G. A. Carls, *J. Org. Chem.*, **29**, 2678 (1964).

(13) Ring hydrogens in the 3,5-dimethyl isomer would both appear between 7.0 and 7.5 ppm while those in the 4,6-dimethyl isomer are equivalent in $CDCl_3$ and appear at 5.92 ppm.

(14) 5,6-Dimethyl-2*H*-pyran-2-one was synthesized independently starting with the monocyanoethylation of methyl ethyl ketone according to a modification of the procedure given by N. P. Shusherina, R. Ya. Levina, and Z. S. Sidenko, *Zh. Obshch. Khim.*, **29**, 398 (1959).

(15) R. Pütter and W. Dilthey, *J. Prakt. Chem.*, **119**, 183 (1937); **150**, 40 (1938).

(16) E. F. Ullman, *J. Amer. Chem. Soc.*, **85**, 3529 (1963).

(17) N. Filipescu and J. W. Pavlik, *ibid.*, **92**, 6062 (1970).

(18) B. Parrington and R. F. Childs, *Chem. Commun.*, 1581 (1970).

(19) L. Kaplan, J. W. Pavlik, and K. E. Wilzbach, *J. Amer. Chem. Soc.*, **94**, 3283 (1972).

(20) E. J. Corey and J. Streith, *ibid.*, **86**, 950 (1964).

(21) J. P. Guthrie, C. L. McIntosh, and P. deMayo, *Can. J. Chem.*, **48**, 237 (1970).

(22) W. H. Pirkle and L. H. McKendry, *J. Amer. Chem. Soc.*, **91**, 1179 (1969).

absence of such nucleophiles X undergoes intramolecular cyclization at the tertiary ring position to yield XI. A similar rearrangement has also been used to explain the photochemical formation of β-methylglutaconic anhydride from triacetic acid lactone.[23] Electronic rearrangement in XI leads directly to IV.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research and to the Wisconsin State Universities Board of Regents for Research Grant No. RF-5-71.

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[23] C. T. Bedford, J. M. Forrester, and T. Money, *Can. J. Chem.*, **48**, 2645 (1970).

[24] ACS-PRF Undergraduate Research Participant, 1971–1972.

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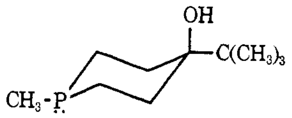
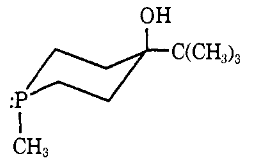
Investigation of the Conformational Equilibrium of 1-Methylphosphorinane by Low-Temperature ^{31}P and ^{1}H Nuclear Magnetic Resonance Spectroscopy[1]

Sir:

Substantial differences are known to exist in the ^{31}P and ^{1}H nmr spectra of the conformationally biased phosphorinane derivatives I and II[2] [respectively, δ(^{31}P) +57.7 and +64.6 ppm; δ(PCH$_3$) 0.95 ($^{2}J_{\mathrm{PH}}$ = 2.1) and 0.89 ppm ($^{2}J_{\mathrm{PH}}$ = 4.0 Hz)], whose structures are known with certainty from X-ray analysis.[3] In the absence of a *tert*-butyl group, *P*-methylphosphorinanes should undergo rapid equilibration between conformers with axial and equatorial methyl and give nmr spectra at room temperature that are time averaged. At very low temperatures, however, it would be expected that equilibration would be so slow that the conformers could be detected by the same ^{31}P and ^{1}H nmr differences seen for I and II. This has proved to be the case and has led to the first determination of some of the energetic parameters for conformational equilibration in a phosphorinane. Qualitative indications[2] that 1,3-nonbonded interactions involving the *P*-methyl group are weak and do not result in a strong preference by the substituent for the equatorial position are confirmed.[4–9]

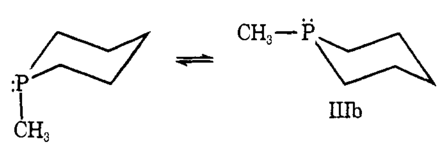


I (cis)



II (trans)

The proton-decoupled ^{31}P nmr signal for neat 1-methylphosphorinane (III, bp 144–147°; prepared from methylphosphonous dichloride and BrMg(CH$_2$)$_5$MgBr and analyzed as the methiodide, decomposition without melting) was a sharp singlet at room temperature at +53.7 ppm. In a vinyl chloride solution prepared at −40°, the singlet was also present. On lowering the temperature, the peak broadened and finally at −80° separated into two sharp signals spaced 3.1 ppm apart. In accord with I and II, the upfield signal is assigned to the axial conformer (IIIa) and the downfield signal to the equatorial conformer (IIIb). The sharpness of the proton-decoupled signals permitted estimation of the equilibrium composition by peak height measurement.[10] At the lowest temperature reached (−130°), the equatorial conformer predominated over the axial (2.0 to 1). This is a remarkably low equatorial preference when compared to methylcyclohexane (99% equatorial at −110° [11]) or *N*-methylpiperidine (95% or more equatorial at −150° [12]), but this result nevertheless suggests that repulsive 1,3 interactions do prevail in the phosphorinane system. The variation in the peak height ratio with temperature gave the following additional vaues for *K*: −125°, 1.8; −120°, 1.7; −115°, 1.5; −110°, 1.5; −105°, 1.4. A plot of log *K* against 1/*T* was linear (Figure 1) and on extrapolation gave a constant for the conformational equilibrium at 25° of 0.56. Thus, *the axial form predominates at room temperature.*



IIIa

IIIb

We believe this to be the first instance of the use of ^{31}P nmr spectroscopy to explore conformational equilibration in a cyclic system. The technique offers considerable advantage over the use of proton spectra (*vide infra*); the signals are clearly separated and sharp even at very low temperatures. That they are of quite different chemical shift causes coalescence to be reached at higher temperatures.

The methyl proton signal for III, a doublet ($^{2}J_{\mathrm{PH}}$ = 3.0 Hz) at room temperature for the averaged conformation, broadened into a single peak at −100° in either trimethylethylene or vinyl chloride; in the latter, it was possible to lower the temperature further, whereupon the singlet separated into two doublets, somewhat broad and in slight overlap. That the two signals were indeed due to the two P–CH$_3$ doublets was established by decoupling ^{31}P from the protons, which caused the two doublets to collapse to two singlets. At −144°, the upfield doublet had *J* = 1.8, the lowfield 3.2 Hz, with separation of 8 Hz (0.09 ppm). Based on *J* values for

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[1] Supported by Public Health Service Research Grant CA-05507, National Cancer Institute. Purchase of the Bruker spectrometer was made possible in part by a grant from the National Science Foundation (Grant No. GP-10301).

[2] L. D. Quin and J. H. Somers, *J. Org. Chem.*, 37, 1217 (1972).

[3] A. T. McPhail, P. A. Luhan, S. I. Featherman, and L. D. Quin, *J. Amer. Chem. Soc.*, **94**, 2126 (1972).

[4] Related systems have also shown some unusual conformational properties. Single-crystal X-ray analysis reveals that 1-phenyl-4-phosphorinanone[5] and its dimethyl ketal[6] have the phenyl group axially oriented. Nmr studies show the same preference for the proton of phosphorinane at −50°[7] and for P substituents of dioxa-[8] and dithiaphosphorinanes.[9]

[5] A. T. McPhail, J. J. Breen, and L. D. Quin, *J. Amer. Chem. Soc.*, **93**, 2574 (1971).

[6] A. T. McPhail, J. J. Breen, J. H. Somers, J. C. H. Steele, Jr., and L. D. Quin, *Chem. Commun.*, 1020 (1971).

[7] J. B. Lambert and W. L. Oliver, Jr., *Tetrahedron*, 27, 4245 (1971).

[8] W. G. Bentrude, K. C. Yee, R. D. Bertrand, and D. M. Grant, *J. Amer. Chem. Soc.*, **93**, 797 (1971).

[9] R. O. Hutchins and B. E. Maryanoff, *ibid.*, **94**, 3266 (1972).

[10] The equilibrium constants and thermodynamic values are subject to refinement with the use of more accurate peak measuring techniques.

[11] F. A. L. Anet, C. H. Bradley, and G. W. Buchanan, *J. Amer. Chem. Soc.*, **93**, 258 (1971).

[12] J. B. Lambert, W. L. Oliver, Jr., and B. S. Packard, *ibid.*, **93**, 933 (1971).