

## NMR Spectra of 2-Pyrone and 2-Pyrone Derivatives

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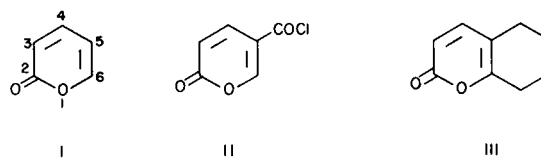
An analysis of the complex NMR spectrum of 2-pyrone is presented and the spectra of a series of variously substituted 2-pyrones and 5,6-dihydro-2-pyrones are discussed. It is demonstrated that NMR spectroscopy affords a convenient and reliable method of assigning the position of substituents on the 2-pyrone nucleus.

During the course of an investigation of the chemistry of 2-pyrone (I) (1) it was found that the nature of substituents on the pyrone ring have little effect upon the remaining proton-proton coupling constants and that, by this means alone, the position(s) of substitution upon the ring can be determined with relative confidence.

In both its 60 and 100 MHz NMR spectra, 2-pyrone exhibits two very complex multiplets of equal area centered at *ca.* 6.28 and 7.50 ppm downfield from internal TMS. While the complex spectra cannot be simply analyzed, they have been analyzed with the aid of an IBM 7094 computer (2). Figure 1 shows the correspondence between the calculated and observed 60 MHz spectra of 2-pyrone. The parameters used in the calculation appear in Table I. Chemical shift assignments were initially made from the magnitudes of the spin-spin coupling constants observed and from simple valence bond considerations.

The availability of the 3-, 5-, and 6-deuterio-2-pyrones, prepared from the corresponding halopyrones *via* zinc dust-deuterioacetic acid reduction, allowed independent corroboration of the 2-pyrone spectral assignments (*c.f.* Table I). Also appearing in Table I are the tabulated NMR spectra of the previously known coumaly chloride (II) (4), 6-chloro-2-pyrone (5), 3,5-dichloro-2-pyrone (6) and 5,6,7,8-tetrahydrocoumarin (III) (7), all of which were found to be analyzable by inspection. As can be seen, the

position of substituents about the 2-pyrone ring is easily discerned from the characteristic coupling constants (and to a lesser extent, the chemical shifts) observed for the remaining ring hydrogens.



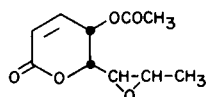
In the NMR spectra of all 5,6-dihydropyrones investigated, the coupling between  $H_3$  and  $H_4$  is *ca.* 10 Hz. Because of the long-range coupling observed (*i.e.*  $J_{H_4-H_6}$  2 Hz) the configuration of the 5 and 6 substituents in 5,6-dibromo-5,6-dihydro-2-pyrone, 5-bromo-6-fluoro-5,6-dihydro-2-pyrone, 5-bromo-6-acetoxy-5,6-dihydro-2-pyrone, 3,5,6-tribromo-5,6-dihydro-2-pyrone and 3,5-dibromo-6-fluoro-5,6-dihydro-2-pyrone is thought in all cases to be *trans* diaxial since this places  $H_4$ ,  $C_4$ ,  $C_5$ ,  $C_6$  and  $H_6$  in a near planar situation. Such a planar "W" arrangement often leads to observable four-bond coupling (8) and the long-range coupling is thus rationalized. Further, it is noted that no long-range coupling between  $H_4$  and  $H_6$  is observed for *cis*-5,6-dihydro-2-pyrone (IV) (9).

TABLE I

## NMR Parameters of 2-Pyrones (a)

	Chemical Shifts ( $\delta$ )				Coupling Constants (Hz)					
	H <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>	J <sub>34</sub>	J <sub>35</sub>	J <sub>36</sub>	J <sub>45</sub>	J <sub>46</sub>	J <sub>56</sub>
2-Pyrone (1) (b)	6.38	7.56	6.43	7.77	9.4	1.5	1.25	6.3	2.4	5.0
2-Pyrone-3- <i>d</i>	—	7.48	6.45	7.67	—	—	—	6.3	2.4	5.0
2-Pyrone-5- <i>d</i>	6.38	7.60	—	7.76	9.5	—	1.2	—	2.4	—
2-Pyrone-6- <i>d</i> (c)	6.30	7.50	6.38	—	9.5	(d)	—	6.3	—	—
2-Pyrone-3,5- <i>d</i> <sub>2</sub>	—	7.47	—	7.62	—	—	—	—	2.36	—
3-Bromo-2-pyrone	—	7.56	6.23	7.77	—	—	—	6.8	2.0	5.0
5-Bromo-2-pyrone	6.2	7.3	—	7.5	9.7	—	1.16	—	2.7	—
6-Chloro-2-pyrone	6.08	7.32	6.21	—	9.0	0.8	—	6.8	—	—
5-Nitro-2-pyrone	6.45	8.10	—	8.80	10.5	—	1.0	—	3.0	—
4-Methyl-2-pyrone	6.10	—	6.03	7.29	—	1.6	1.15	—	—	5.20
2-Pyrone-5-R (f)	6.25	7.80	—	7.24	9.5	—	1.0	—	2.0	—
3,5-Dichloro-2-pyrone (c)	—	7.55	—	7.65	—	—	—	—	2.25	—
3,5-Dibromo-2-pyrone	—	7.63	—	7.80	—	—	—	—	2.5	—
4-Methyl-6-chloro-2-pyrone	5.95	—	6.15	—	—	1.1	—	—	—	—
5,6-Dihydro-2-pyrone (4) (g)	6.23	7.09	5.33	4.14	10.0	~0	~0	5.5	~0	3.0
5,6-Dibromo-5,6-dihydro-2-pyrone	6.20	7.10	5.04	6.82	9.7	~0	~0	5.7	2.0	1.0
5-Bromo-6-fluoro-5,6-dihydro-2-pyrone	6.2	7.0	4.7	6.3	10.0	~0	~0	6.0	2.0	1.3
5-Bromo-6-acetoxy-5,6-dihydro-2-pyrone	6.17	7.10	4.70	6.72	10.0	~0	~0	5.5	2.0	1.5
3,5,6-Tribromo-5,6-dihydro-2-pyrone	—	7.45	5.0	6.8	—	—	—	6.2	2.0	1.0
3,5-Dibromo-6-fluoro-5,6-dihydro-2-pyrone	—	7.37	4.73	6.25	—	—	—	6.0	2.0	1.0
Coumaly Chloride (2)	6.51	7.87	—	9.68	10.0	—	1.0	—	2.8	—
5,6,7,8-Tetrahydrocoumarin (3)	6.10	7.15	—	—	10.0	—	—	—	—	—
3-Nitro-5,6,7,8-tetrahydrocoumarin (e)	—	8.25	—	—	—	—	—	—	—	—

(a) Samples run as 10-20% solutions in deuteriochloroform unless otherwise indicated. (b) Parameters used for spectral computation (see Figure I). (c) Carbon tetrachloride solution. (d) Value could not be measured from the spectrum. (e) N. P. Shusherina, N. D. Dmitrieva, T. F. Kozlova and R. Y. Levina, *Zh. Obshch. Khim.*, 30, 2829 (1960) (Engl. Ed., p. 2808). (f) R represents the steroidal moiety of hellebrigenin (see S. M. Kupchan, R. J. Hemingway and J. C. Hemingway, *Tetrahedron Letters*, 149 (1968)). (g) Ref. 9.



IV

## EXPERIMENTAL

The compounds used in this study will shortly be described elsewhere (1). All NMR spectra were determined on Varian A-60, A-60-A or A-56/60-A spectrometers using ca. 15% solutions in deuteriochloroform with TMS as an internal standard.

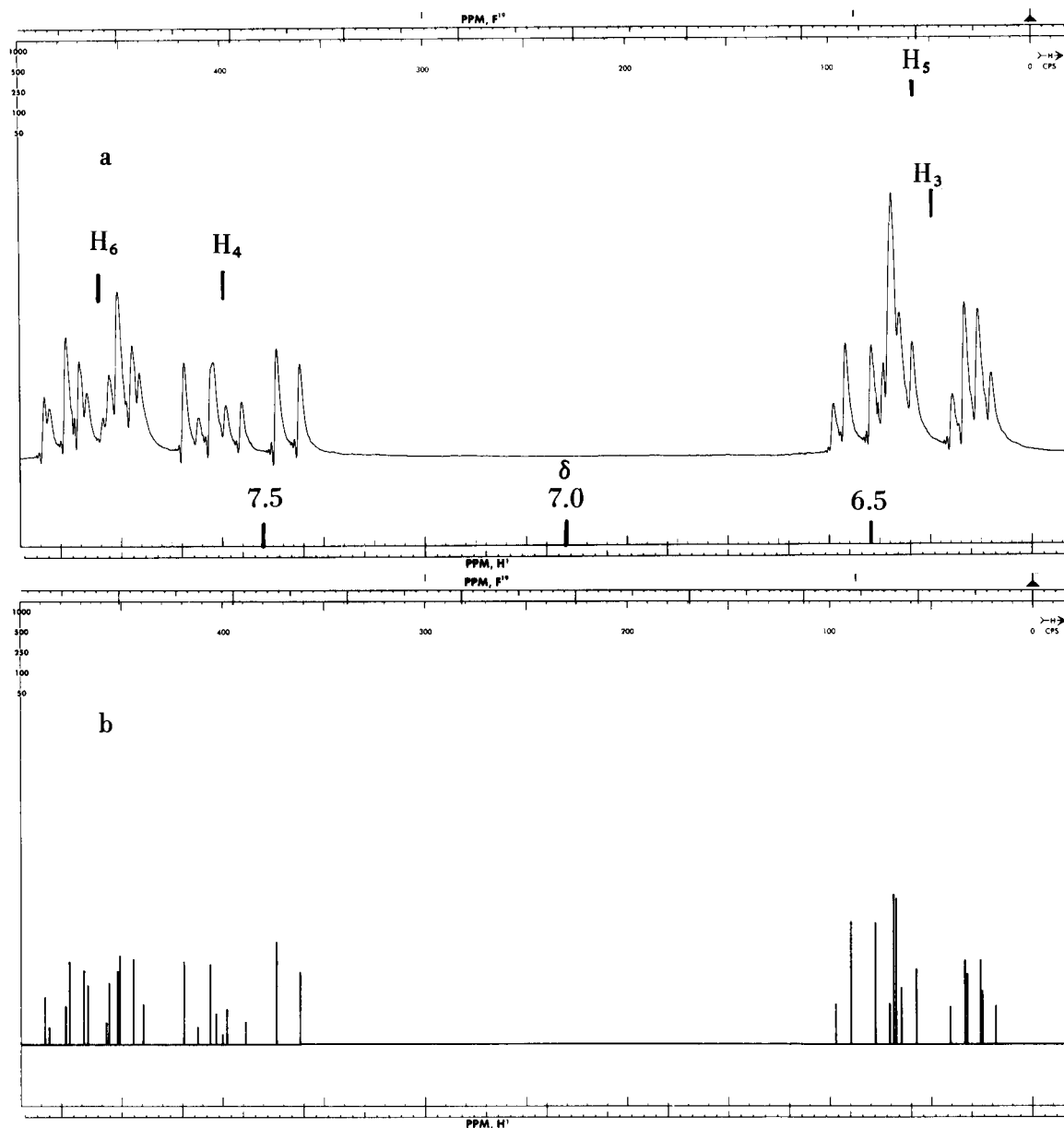


Figure I. Observed (a) and calculated (b) 60 MHz NMR spectra of neat 2-pyrone. Sweep width is 100 Hz.

#### REFERENCES

- (1) Data in this paper is abstracted in part from the doctoral dissertation of M. D., University of Illinois, 1968.
- (2) The authors gratefully acknowledge the assistance of Dr. Jiri Jonas of these laboratories, who provided the program used for the calculation.
- (3) See, for instance, R. Mayer, W. Broy and R. Zabradinte in "Advances in Heterocyclic Chemistry," Vol. 8, A. R. Katritzky and A. J. Boulton, Ed., Academic Press, New York, N. Y., 1967, p. 260.
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- (5) N. Bland and J. F. Thorpe, *J. Chem. Soc.*, 101, 857 (1912).
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- (8) For an example see K. B. Wiberg, B. R. Lowry and B. J. Nist, *J. Am. Chem. Soc.*, **84**, 1594 (1962).
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