Investigations of Keto–Enol Tautomerism by Carbon-13 Nuclear Magnetic Resonance Spectroscopy

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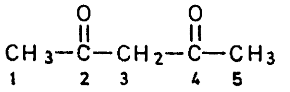
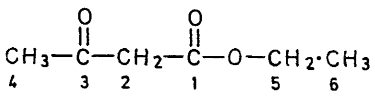
Keto–enol ratios determined by Fourier transform ^{13}C n.m.r. spectroscopy compare favourably with ratios found by other analytical methods.

WE have explored the use of natural abundance ^{13}C spectroscopy for observing keto–enol tautomerism in compounds (1)—(6). All the compounds except isopropylidene malonate (4) were commercially available in relatively pure state, as established by i.r. spectra.



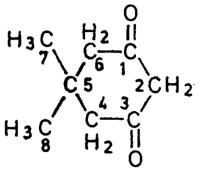
$\underset{1}{CH_3}-\underset{2}{\overset{\overset{O}{\|}}{C}}-\underset{3}{CH_2}-\underset{4}{\overset{\overset{O}{\|}}{C}}-\underset{5}{CH_3}$

(1)

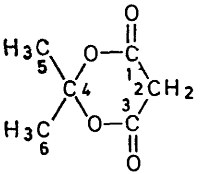


$\underset{4}{CH_3}-\underset{3}{\overset{\overset{O}{\|}}{C}}-\underset{2}{CH_2}-\underset{1}{\overset{\overset{O}{\|}}{C}}-O-\underset{5}{CH_2}\cdot\underset{6}{CH_3}$

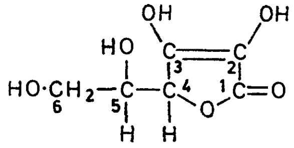
(2)



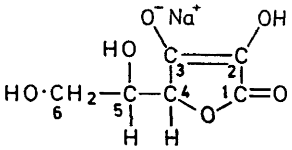
(3)



(4)



(5)



(6)

Compound (4) was prepared according to the procedure of Davidson and Bernhard,[1] and its identity was verified by m.p. and i.r. spectrum. The n.m.r. spectra were examined by use of equipment described previously.[2] Table 1 gives the ^{13}C chemical shifts relative to carbon disulphide.

TABLE 1 [a]

Compound		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
(1)	Keto	164·3(q)	−8·3 (−8·9) [b]	136·2(t)	−8·3 (−8·9)	164·3(q)			
	Enol	170·3(q)	2·3 (1·9)	93·8(d)	2·3 (1·9)	170·3(q)			
(2)	Keto	26·2 (26·0)	144·3(t)	−7·0 (−7·2)	164·6(q)	133·1(t)	180·3(q)		
	Enol	20·6	104·2(d)	17·3	173·5(q)	134·0(t)	180·3(q)		
(3)	Keto	−10·6	135·8(t)	−10·6	139·1(t)	160·4	139·1(t)	164·9(q)	164·9(q)
	Enol	2·6	90·3(d)	2·6	146·8(t)	162·4	146·8(t)	164·9(q)	164·9(q)
(4)	Keto	29·8	157·4(t)	29·8	86·8	166·4(q)	166·4(q)		
	Enol								
(5)		19·7	75·0	37·4	116·8(d)	123·9(d)	130·7(t)		
(6)		15·7	79·7	17·6	114·6(d)	123·3(d)	130·2(t)		

[a] Chemical shifts in p.p.m. relative to carbon disulphide. Multiplicities are those observed in non-decoupled spectra. [b] Values in parentheses reported by J. B. Stothers and P. C. Lauterbur (*Canad. J. Chem.*, 1964, **42**, 1563).

Peak assignments were based on examination of splitting patterns in non-decoupled spectra,† on peak intensities, and on comparisons with existing ^{13}C spectral data for analogous compounds. In some cases where ^{13}C resonance positions are nearly degenerate, the assignments may be reversed.

TABLE 2 [a]

Compound	C atom [b]	% Enol (^{13}C n.m.r.) [c]	% Enol (i.r.) [d]	% Enol (^{1}H n.m.r.) [e]
(1)	C-1	78	81 (20°)	81 (33 ± 2°)
	C-3	78		
(2)	C-2	11		8 (33 ± 2°)
	C-4	9		
	C-5	14		
(3)	C-2	60	15·5 (20°)	
	C-6	53		

[a] Spin-lattice relaxation times (T_2) were measured using the method of Allerhand [4] for all carbon atoms in compound (1). The greatest T_1 value measured was 8·0 s for the quaternary carbon atom C-2. Thus a pulse interval of 25 s was chosen as adequate for complete relaxation of all carbon atoms in the series of similar compounds. [b] Integrated peak intensities due to these carbon atoms were measured for both the enol and keto forms in completely proton-decoupled spectra.[2] The ratio of these peak intensities × 100 gives the number in the next column. [c] Temperature of the probe was 42 ± 2°. [d] Values from H. Sterk, *Z. Naturforsch.*, 1968, **236**, 112. [e] Values from J. Burdett and M. Rogers, *J. Amer. Chem. Soc.*, 1964, **86**, 2105.

The percentage of enol form was calculated for compounds (1)—(3) by comparing the integrated peak intensities of the carbon atoms indicated in Table 2. Only protonated carbon atoms were used in these

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† By ' non-decoupled ' spectra we mean spectra obtained by using a single frequency off-resonance decoupling technique.[3]

[1] S. Davidson and S. Bernhard, *J. Amer. Chem. Soc.*, 1948, **70**, 3426.

[2] A. Allerhand, D. W. Cochran, and D. Doddrell, *Proc. Nat. Acad Sci. U.S.A.*, 1970, **67** (3), 1093.

[3] H. J. Reich, M. Jautelat, M. T. Messe, F. J. Weigert, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1969, **91**, 7445, and references therein.

calculations since the spin-lattice relaxation time is expected to be much shorter for these than for non-protonated carbon atoms.[4] Table 2 also compares the observed percentages of enol with literature values obtained by other instrumental techniques.

The higher value for the enol content of 5,5-dimethylcyclohexane-1,3-dione (**3**) measured here is due to the concentration dependence of the keto–enol ratio for this compound.[5]

The enol tautomer of ester (**4**) and the keto-tautomers of the furan derivatives (**5**) and (**6**) were not detected by this method. Indeed, these compounds are known to exist essentially completely in the forms shown.[6,7]

Thus, ^{13}C n.m.r. spectroscopy is demonstrated to be a potentially useful tool in the study of keto–enol tautomeric mixtures. The structures of isopropylidene malonate (**4**), ascorbic acid (**5**), and sodium ascorbate (**6**) have been confirmed by this technique.

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[4] A. Allerhand, D. Doddrell, and R. Komoroski, *J. Chem. Phys.*, 1971, **55**, 189.

[5] L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Wiley, New York, 1964, p. 142.

[6] M. Eigen, G. Ilgenfritz, and W. Druze, *Chem. Ber.*, 1965, **98**, 1623.

[7] C. Hurd, *J. Chem. Educ.*, 1970, **47**, 181.