The Nuclear Magnetic Resonance Spectra of Cyclopentenones

C. H. DEPUY[1], C. E. LYONS, and L. B. RODEWALD

Department of Chemistry, Iowa State University, Ames, Iowa

The nuclear magnetic resonance chemical shifts and coupling constants are reported for eleven cyclopentenones, including cyclopentenone itself, 4-bromo and 4-acetoxycyclopentenone, 5-ethoxy and 3,5-diethoxy cyclopentenone, 3,5-cyclopentendione, 2-methyl-3, 4-cyclopentendione, 2-hydroxycyclopentenone, 5-diazo-2-methylcyclopentenone, and cyclopentenone ethylene ketal.

DURING the past several years, a study has been made of the chemistry of cyclopentenone and its substitution products (*1*). In the course of this study, accurate determinations and analyses were made of the NMR spectra of a variety of these enones. Several of these spectra were crucial for the determination of the structure of the compounds involved, and, taken as a whole, they proved to be both valuable for identification and useful as a means of examining the effect of structure on NMR in a relatively small molecule. These data are summarized in this paper from more extensive data by Lyons (*2*). The spectra were determined at 60 mc. using a Varian HR-60 spectrometer. With one exception, the solvent was CCl_4, and the chemical shifts were determined relative to internal tetramethylsilane by the sideband method.

The data are included in Table I, and are, for the most part, self-explanatory, but the following points are pertinent. The spectrum of cyclopentenone (I) is complex; the H_4–H_5 hydrogens make up an A_2B_2 pattern with the H_4 portion further split. The H_5 portion has been completely analyzed and matched to a calculated spectrum. As expected, the signs of the geminal coupling constants are opposite to those of the vicinyl ones, and are presumably negative. In other cases,

[1] Present address: Department of Chemistry, University of Colorado, Boulder, Colo.

Table I. Chemical Shifts (δ)[a] and Coupling Constants (J)[b] of Cyclopentenones

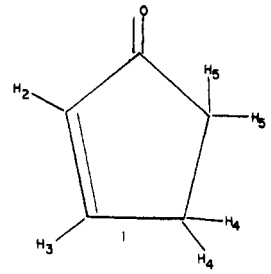
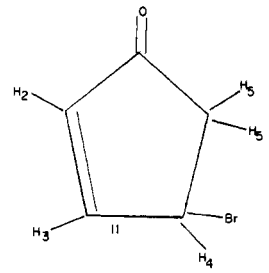
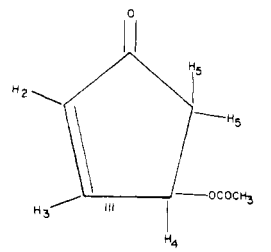
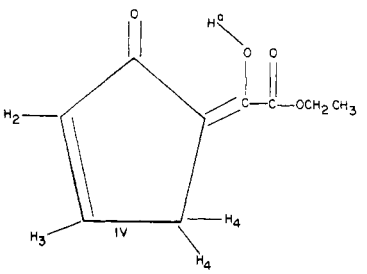
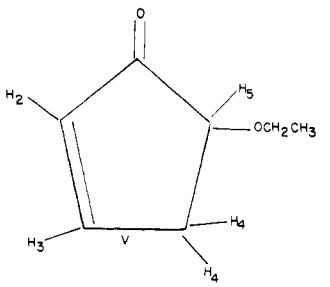
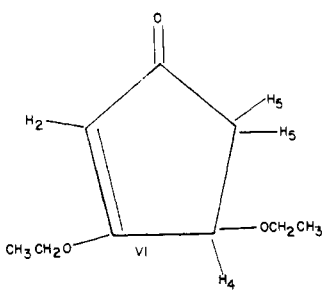
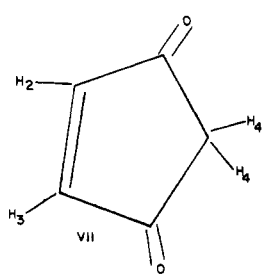
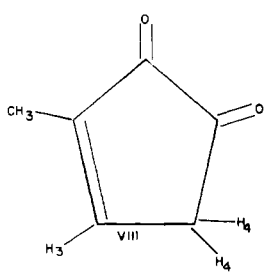
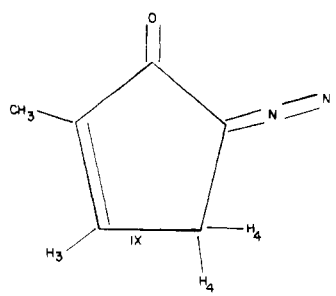
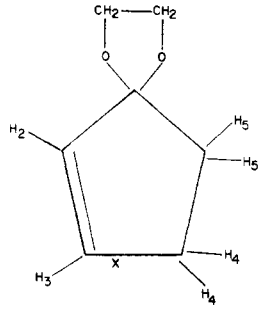
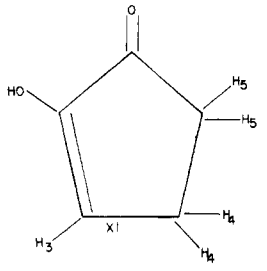
Compound	H_2	H_3	H_4	H_5	Other
	δ = 6.11 (6) $J_{2,3}$ = 5.8 $J_{2,4}$ = 2.2	7.63 (6) $J_{3,4}$ = 2.6	2.64 (X) $J_{4,4}$ = 19.0 $J_{4,5}$ = 7.3; 2.5	2.24 (8) $J_{5,5}$ = 19.5	
	δ = 6.21 (4) $J_{2,3}$ = 5.5 $J_{2,4}$ = 2.1	7.61 (4) $J_{3,4}$ = 2.6	5.13 (X) $J_{4,5}$ = 6.4; 1.8	2.95 (4); 2.63 (4) $J_{5,5}$ = 19.3	
	δ = 6.25 (4) $J_{2,3}$ = 5.6 $J_{2,4}$ = 1.3	7.51 (4) $J_{3,4}$ = 2.4	5.78 (X) $J_{4,5}$ = 2.4; 6.4	2.21 (4); 2.72 (4) $J_{5,5}$ = 18.6	CH_3 = 2.05 (1)

Table I. Chemical Shifts (δ)[a] and Coupling Constants (J)[b] of Cyclopentenones (Continued)

Compound	H_2	H_3	H_4	H_5	Other
	δ = 6.36 (6) $J_{2,3}$ = 5.8 $J_{2,4}$ = 2.0	7.56 (6) $J_{3,4}$ = 2.3	3.50 (4)		H_a = 12.7 (1) CH_2 = 4.32 (4) CH_3 = 1.38 (3)
	δ = 7.05 (6)[c] $J_{2,3}$ = 6.3 $J_{2,4}$ = 2.1	8.73 (6) $J_{3,4}$ = 2.9	3.67 (X) $J_{4,4}$ = −19.5	5.02 (4) $J_{4,5} + J'_{4,5}$ = 8.4	CH_2 = 4.53 (4) CH_3 = 2.02 (3)
	δ = 5.2 (1)		4.37 (4) $J_{4,5}$ = 6.5; 2.3	2.55 (4); 2.21 (4) $J_{5,5}$ = −17.6	CH_2 = 4.06 (4); 3.61 (4) CH_3 = 1.45 (3); 1.19 (3)
	δ = 7.31 (1)	7.31(1)	2.90 (1) $J_{4,4}$ = −21.5		
		δ = 7.72 (X) $J_{3,4}$ = 2.2 J_3,CH_3 = 2.2	3.03 (3) J_4,CH_3 = 1.9		CH_3 = 1.80 (4)
		δ = 6.71 (X) $J_{3,4}$ = 2.2; J_3,CH_3 = 1.9	3.57 (5) J_4,CH_3 = 2.2	1.80 (4)	

(Continued on page 104)

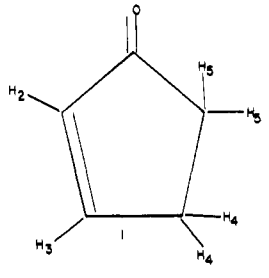
Table I. Chemical Shifts (δ)[a] and Coupling Constants (J)[b] of Cyclopentenones (Continued)

Compound	H_2	H_3	H_4	H_5	Other
	δ = 5.96 (6) $J_{2,3}$ = 5.4; $J_{2,4}$ = 2.0	5.58 (6) $J_{3,4}$ = 2.0	2.36 (X) $J_{4,4}$ = −19.0 $J_{4,5}$ = 8.6	1.96 (X) $J'_{4,5}$ = 4.2 $J_{5,5}$ = − 16.3	
		δ = 6.46 (3) $J_{3,4}$ = 2.5	2.40 (X)	2.40 (X)	

[a] In p.p.m. downfield from TMS, with the multiplicity of the peak given in parenthesis; (X) means highly complex. [b] In c.p.s. [c] In D_2O.

relative signs have not been determined. In the case of H_4–H_5 coupling, the larger of the two coupling constants undoubtably is due to *cis* coupling and the smaller to *trans* coupling. In 5-ethoxycyclopentenone (V) there is overlap between the absorption of the ethyl protons and those in the ring in CCl_4 solution, so that the peak positions and coupling constants were determined in D_2O solution. Because of the large size of $J_{4,4}$, in this compound, it was only possible to determine the sum, $(J_{4,5} + J'_{4,5})$, and not individual values.

The average coupling constants observed in the cyclopentenone system are summarized below.



J_{23} = 5.8 ± 0.2
J_{24} = 1.8 ± 0.4
J_{34} = 2.5 ± 0.2
J_{44} = J_{55} = −19.3 ± 0.7
J_{45} (*cis*) = 6.6 ± 0.3
J_{45} (*trans*) = 2.3 ± 0.2

H_5 is not coupled to either H_2 or H_3, and the attachment of an electron-withdrawing group in place of H_3 completely removes the H_2–H_4 coupling.

ACKNOWLEDGMENT

This work was supported by a grant from Public Health Service, National Institute of General Medical Services. A Shell fellowship to C. E. L. and an NIH fellowship to L. B. R. are also gratefully acknowledged.

LITERATURE CITED

(1) DePuy, C.H., Isaks, M., Eilers, K.L., Morris, G.F., *J. Org. Chem.* **29**, 3503 (1964).
(2) Lyons, C.E., Ph.D. dissertation, Iowa State University, Ames, Iowa, 1961.

RECEIVED for review October 29, 1964. Accepted October 22, 1965