Journal of Heterocyclic Chemistry

Volume 5, Number 6 December 1968

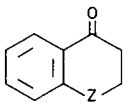
Proton Resonance Spectra of Heterocycles. VI. Chromanones, Thiochromanones, and 2,3-Dihydro-4-quinolones (1)

A. R. Katritzky and B. Ternai

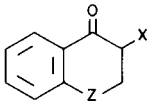
School of Chemical Sciences, University of East Anglia

The nmr spectra of the title compounds and some substituted derivatives are recorded and discussed. It is concluded that 3-halogeno substituents probably occupy largely pseudo axial positions whereas a 3-methyl group is predominantly pseudo equatorial.

4-Chromanone (I) and 2,3-dihydro-1-methanesulphonyl-4-quinolone (II) disclosed A_2X_2 patterns for the protons of the heterocyclic ring (Fig. 1). Chemical shifts are given in Table I: the only coupling constant parameter which can be obtained is $|J + J'|$ where $J = \frac{1}{2}(J_{aa} + J_{ee})$ and $J' = \frac{1}{2}(J_{ae} + J_{ea})$, assuming that the rings are rapidly inverting half-chair forms. 1-Thio-4-chromanone (III) disclosed an A_2B_2 pattern (Fig. 2), which was analysed by a computer method (2). The best fit gave the parameters in Table I and further: J_{gem} (CH_2CO), -17.7; J_{gem} (CH_2S), -15.3; J, 8.2; J', 3.6 c./sec.).



I, Z = O
II, Z = NSO_2Me
III, Z = S



IV

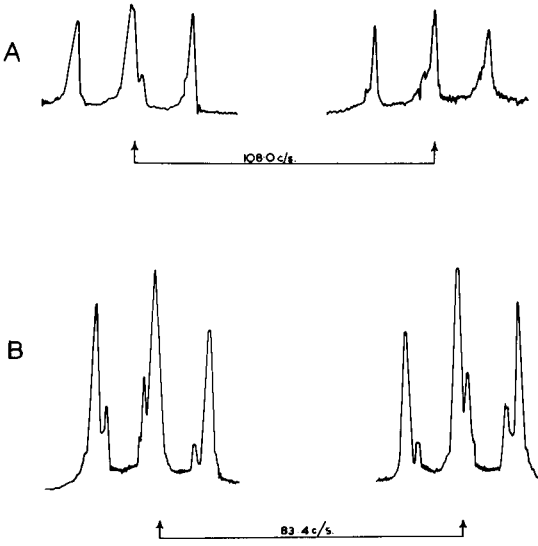
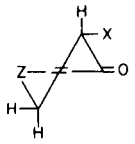
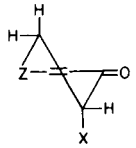


Figure 1. Nmr spectrum of (A) 4-chromanone and (B) 2,3-dihydro-1-methanesulphonyl-4-quinolone.



V



VI

The 3-substituted compounds were of type IV. They all disclosed ABX or AMX spectra for the heterocyclic ring protons which afforded the parameters given in Table II (3-chloro-2,3-dihydro-1-methanesulphonyl-4-quinolone had a deceptively simple spectrum which precluded

TABLE I

Nmr Spectra of Parent Compounds in Acetone

Compound	Chemical Shifts τ		$\lvert J + J' \rvert$ (c./sec.)	M.P.	Lit. M.P.	Lit. Ref.
	$CO\text{-}CH_2$	$CH_2\text{-}Z$				
I	8.87	5.41	13.0	39°	39°	5
II	7.15	5.76	13.0	117-118	–	–
III			11.8	27-29	29-30	6

TABLE II

Nmr Spectra of 3-Substituted Chromanones, Thiochromanones and Dihydroquinolones

Structure IV		Chemical Shifts			Coupling Constants (c./sec.)			
Z	X	2-(*cis*) (a)	2-(*trans*) (a)	3-	2 (gem)	2/3 (*cis*)	2/3 (*trans*)	Solvent
O	Br	5.24	5.40	5.26	-13.8	2.7	4.4	acetone
O	I	5.60	5.64	5.18	-13.5	2.6	4.6	CCl_3CN
O	Me				-11.4	5.4	10.8	CCl_4
S	Br	5.93	6.07	5.10	-14.1	3.0	8.6	CCl_4
S	I	6.38	6.71	4.62	-14.9	2.7	5.9	acetone
NSO_2Me	Br	5.25	5.47	4.90	-15.1	3.1	5.1	acetone
NSO_2Me	Cl	5.52	5.52	4.90	(b)	(c)	(c)	acetone
NSO_2Me	I	5.28	6.12	4.68	-15.1	2.8	3.5	CF_3COOH

(a) With respect to the hydrogen atom at the 3-position. (b) Not available. (c) The average of the two coupling constants, $\frac{1}{2}(J_{AX} + J_{BX}) = 5.2$ c./sec.

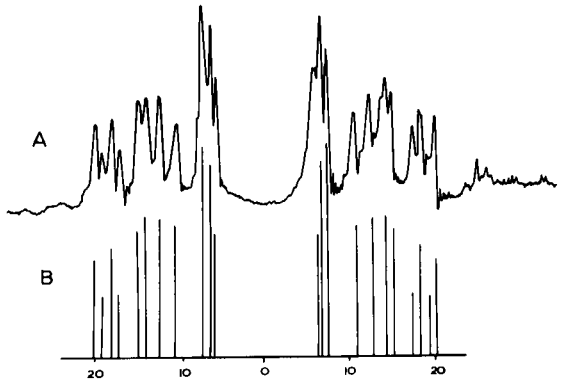


Figure 2. Nmr spectrum of 1-thio-4-chromanone (III), (A) observed, (B) calculated.

determination of the coupling constants). The value of the 2/3 *trans* coupling constant can be used as an indication of the *axial/equatorial* substituent ratio: $J_{trans} = x J_{aa} + (1 - x)J_{ee}$ where x is the mole fraction of the conformer with the substituent equatorial (V) and (1 - x) that of the axial conformer (VI). The relatively low values for the halogeno compounds indicate that (with the possible exception of 3-bromo-1-thio-4-chromanone) they probably all exist with the halogen atom predominantly axial. The larger value of J_{trans} for 3-methyl-4-chromanone indicates that this compound probably has the methyl group largely equatorial.

Infrared spectroscopy supports the conclusion that the 3-halogen atoms largely occupy axial positions. For VI the carbonyl frequency of 1670 cm^{-1} observed is in good agreement with the calculated (3) frequency (1675 cm^{-1}) for an axial halogen. However, it should be noted that nmr studies indicate (4) that while for the α-bromocyclohexanone the axial-bromo conformer predominates, the proportion (52-91%) varies with concentration.

EXPERIMENTAL

Preparation of Compounds.

4-Chromanone (5), 1-thio-4-chromanone (6), 3-bromo-4-chromanone (7), 3-methyl-4-chromanone (7) and 3-bromo-1-thio-4-chromanone (8) were prepared by literature methods. 2,3-Dihydro-1-methanesulphonyl-4-quinolone, m.p. 117-118° was prepared by following the method (9) for the preparation of the 1-toluene sulphonyl derivative. 3-Bromo-2,3-dihydro-1-methanesulphonyl-4-quinolone was obtained by direct bromination, white needles from absolute ethanol, m.p. 155° dec.

Anal. Calcd. for $C_{10}H_{10}BrNO_3S$: N, 4.60. Found: N, 4.44.

The 3-iodo compounds were obtained by refluxing (for 1-3 hours) the parent compound (1 g.) with iodine monochloride (0.9-1.7 g.) in carbon disulphide. 3-Iodo-4-chromanone, yellow prisms from absolute ethanol, m.p. 73-73.5°, 3-iodo-1-thio-4-chromanone, yellow prisms from carbon tetrachloride, m.p. 93-94°, were too unstable for analysis. 2,3-Dihydro-3-iodo-1-methanesulphonyl-4-quinolone, white needles from methanol and acetone, had m.p. 160° dec.

Anal. Calcd. for $C_{10}H_{10}INO_3S$: N, 3.96. Found: N, 3.98.

3-Chloro-2,3-dihydro-1-methanesulphonyl-4-quinolone was prepared by the reaction of the parent compound (1 g.) with chlorine (0.35 g.) in carbon tetrachloride (5 g.) at room temperature, as white needles from carbon tetrachloride and acetone, m.p. 129-130°.

Anal. Calcd. for $C_{10}H_{10}ClNO_3S$: N, 5.39. Found: N, 5.25.

Spectra.

Nmr spectra were obtained using a Perkin-Elmer R10 spectrometer operating at 60 Mc./sec. TMS was used as internal reference standard. Nmr spectral parameters were calculated using the ATLAS computer, NIRNS, Didcot, Berkshire.

Infrared spectra were measured on a Perkin-Elmer 125 spectrometer in carbon tetrachloride solution.

REFERENCES

(1) Part V. A. R. Katritzky, E. Lunt, B. Ternai, and G. J. T. Tiddy, *J. Chem. Soc.*, (B), 1243 (1967).

(2) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, 41, 3863 (1964).

(3) B. Waegell and G. Ourisson, *Bull. Soc. Chim. France*, 496 (1963).

(4) E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, 86, 1780 (1964).

(5) J. D. Loudon and R. K. Razdan, *J. Chem. Soc.*, 4299 (1954).

(6) F. Krollpfeiffer and H. Schultze, *Chem. Ber.*, 56, 1819 (1923).

(7) J. Colonge and A. Guyot, *Bull. Soc. Chim. France*, 329 (1958).

(8) F. Krollpfeiffer and H. Schultze, *Chem. Ber.*, 58, 1654 (1925).

(9) W. S. Johnson, E. L. Woroch, and B. G. Buell, *J. Am. Chem. Soc.*, 71, 1901 (1949).

(10)

Received August 25, 1968 Norwich, England