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ETHYLENIMINE KETONES XVI. PROTON MAGNETIC RESONANCE SPECTRA

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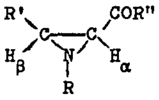
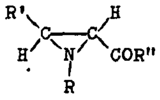
The preparation and characterization of *cis* (A) and *trans* (B) ethylenimine ketones has been the subject of continued investigation in this laboratory for quite some time.(1) These studies have shown that the *cis* (A) isomer normally absorbs at slightly shorter wavelengths in the ultraviolet and with slightly lower intensity than the *trans* (B) isomer. In addition the *cis* isomer in carbon tetrachloride usually exhibits two carbonyl absorption bands in the infrared, one in the 1685-95 cm.$^{-1}$ region and the other between 1660 and 1677 cm.$^{-1}$, presumably due to the *gauche* and *cisoid* forms respectively. The *trans* isomer absorbs about 1675 cm.$^{-1}$ and probably exists in a conjugated *cisoid* conformation.(1a) Chemical support for the assigned stereochemistry was found in the reactions of the *cis* and *trans* isomeric ethylenimine ketones with phenylhydrazine; the *trans* isomers were found to yield 4-amino pyrazolines, whereas the *cis* isomers yielded pyrazoles.(1b)



Cis (A)



Trans (B)

We now wish to report the salient features of the p.m.r. spectra of a large number of *cis* and *trans* ethylenimine ketones. These data allow one to assign the proper stereochemical configuration immediately to the cis or trans isomer on the basis of the relative position in the p.m.r. spectrum of the ethylenimine ring protons (H_α and H_β).

Examination of the spectral data listed in Table I reveals that in each cis-trans pair, the ring protons (H_α and H_β) of the cis isomers absorb at higher fields ($6.82 \pm 0.17\tau$) than do the ring protons of the trans isomers ($6.44 \pm 0.07\tau$). The difference in chemical shift between the cis and trans isomer ($\Delta\tau$) is normally ca. 0.38 p.p.m. (an average value from eight different cis-trans pairs). The cis and trans isomers are thus quite easily differentiated by inspection of their p.m.r. spectra.

An examination of Dreiding Models reveals that in the trans form, which presumably lies in the cisoid conformation,(1a) both H_α and H_β are strongly deshielded by the anisotropic effect of the β-phenyl substituent and by the carbonyl moiety. In compound XI, where a methyl group appears in the β-position, H_β is shifted to higher fields and appears in the complex multiplet due to the cyclohexyl ring protons. In the cis isomer, where the carbonyl assumes a gauche conformation with respect to the ethylenimine ring, H_α is shielded by the diamagnetic anisotropic effect of the carbonyl group and is thus shifted to higher fields. Recently it has been shown that cis-1,2-dibenzoyl ethylenimines absorb at 0.67-0.73 p.p.m. higher fields than do the corresponding trans isomers.(2) A similar result has been observed in the case of the cis and trans 1,2-dibenzoylcyclopropanes in which the α-protons of the cis isomers absorb at 0.17 p.p.m. higher fields than the trans.(3)

Since in both the cis and the trans isomers H_α and H_β are nonequivalent, one would expect to obtain two signals of equal intensity in both cases, which might be split further by spin-spin coupling with

TABLE I

p.m.r. Spectra of Ethylenimine Ketones[a]

Compound[b]				Chemical Shift (τ) (J, c.p.s.)			
	R	R'	R"	$H_a + H_\beta$ [i]	C-C$\underline{H}_3$ O-C$\underline{H}_3$	-C$\underline{H}_2$Ar	-N-C$\underline{H}_3$
IA	C_6H_{11}	C_6H_5	C_6H_5	6.78^e(7.0)[2.0]			
IB	C_6H_{11}	C_6H_5	C_6H_5	6.43^f(3.0)[1.9]			
IIA	C_6H_{11}	C_6H_5	p-C_6H_5-C_6H_4	6.83^e(7.0)[2.0]			
IIB	C_6H_{11}	C_6H_5	p-C_6H_5-C_6H_4	6.44^f(3.0)[1.8]			
IIIA	C_6H_{11}	C_6H_5	pBr-C_6H_4	6.99^c [2.0]			
IIIB	C_6H_{11}	C_6H_5	p-BrC_6H_4	6.48^c [1.8]			
IVA	C_6H_{11}	C_6H_5	p-CH_3-C_6H_4	6.85^f(7.5)[1.9]	7.72^c		
IVB	C_6H_{11}	C_6H_5	p-CH_3-C_6H_4	6.48^c [1.9]	7.70^c		
VA	C_6H_{11}	p-CH_3O-C_6H_4	C_6H_5	6.85^e(7.5)[2.0]	6.45^c		
VB	C_6H_{11}	p-CH_3O-C_6H_4	C_6H_5	6.43^e(2.5)[1.4]	6.30^c		
VIA	C_6H_{11}	p-NO_2-C_6H_4	C_6H_5	6.63^f(7.0)			
VIB	C_6H_{11}	p-NO_2-C_6H_4	C_6H_5	6.37^c			
VIIA	$CH_2C_6H_5$	C_6H_5	C_6H_5	6.75^e(7.0)[2.0]		6.22^f(9.0)	
VIIB	$CH_2C_6H_5$	C_6H_5	C_6H_5	6.38^c [2.0]		5.96^g	
VIIIA	$CH_2C_6H_5$	C_6H_5	p-$CH_3C_6H_4$	6.77^e(8.5)[2.0]	7.70^c	6.22^f(9.0)	
VIIIB	$CH_2C_6H_5$	C_6H_5	p-$CH_3C_6H_4$	6.40^c [2.0]	7.67^c	5.96^c	
IXA	CH_3	C_6H_5	C_6H_5	6.94^f(6.5)[1.9]			7.47^c
XB	CH_3	C_6H_5	p-C_6H_5-C_6H_4	6.49^g(2.5)[1.7]			7.32^c
XIA	C_6H_{11}	CH_3	p-C_6H_5-C_6H_4	7.07^d(5)(?)^h	8.83^d(6)		
XIB	C_6H_{11}	CH_3	p-C_6H_5-C_6H_4	6.68^c(5)(?)^h	8.71^d(6)		
XIIA	CH_3	CH_3	p-C_6H_5-C_6H_4	7.13^d(6)7.67-8.33^g	8.85^d(6)		7.50^c
XIII	C_6H_{11}	H	C_6H_5	7.17^g[0.9]7.74^g[1.3]			
XIV	C_6H_{11}	H	p-C_6H_5-C_6H_4	7.10^2[0.8]7.72^g[0.9]			

TABLE I FOOTNOTES

(a) All spectra were determined at 37° in deuterochloroform solutions (ca.20%) at 60M c.p.s. on a Varian A-60 spectrometer with tetramethylsilane[3] as internal standard. (b) For compound preparation, see for I, ref. 1b; II, ref. 1c; III, this paper; IV, ref. 1b; V, ref. 1a; VI, ref. 1d; VII, ref. 1b; VIII, ref. 1e; IX, ref. 1g; X, ref. 1c; XI, ref. 1f; XII, ref. 1h; XIII, ref. 1b; XIV, ref. 1b. (c) Singlet. (d) Center of doublet. (e) Center of triplet. (f) Center of quartet. (g) Center of complex multiplet. (h) Masked by the C_6H_{11} multiplet. (i) The total number of hydrogens $H_\alpha+H_\beta$ obtained through integration appears in brackets following the splitting constants.

one another thus leading to a total of four peaks. However for the compounds in Table I the differences in chemical shift for H_α and H_β are small in comparison with J, so that one observes normally either a single peak, a triplet, or a quartet.

One must also consider the relative position of the substituent on the nitrogen atom (R) with respect to H_α and H_β. No additional multiplicity was observed however in any of the spectra, presumably because the spectra were obtained at temperatures at which rapid inversion occurred. Such rapid inversion has been reported previously for the 1,2-dibenzoylaziridines.(2)

When either isomer of three pairs of cis and trans ethylenimine ketones (I, VIII, XI) was allowed to stand 4-6 days at room temperature in deuteromethanol solution containing 0.5 molar equivalents of sodium methoxide, only the cis-α-deuterated isomers were recovered (40-72% yields). The p.m.r. spectra of the resulting cis-α-deuterated compound show through integration the presence of only one ethylenimine ring proton which now appears as a singlet. In the case of compound XI, the β-hydrogen atom is found (by integration) to be masked by the C_6H_{11} multiplet, and so deuteration causes complete loss of the H_α absorption at 7.07τ. The epimerization of trans ethylenimine ketones to the corresponding cis isomers has been observed by us previously under the influence of both ultraviolet(1e) light and by dry hydrogen chloride.(4) The epimerization using sodium methoxide of several *trans*-1-substituted-2,3-dibenzoylaziridines and *trans*-1-substituted-2-phenyl-3-aroylaziridines has also been reported recently.(2)

The individual ethylenimine ketones also show the following resonances. The cyclohexyl derivatives show broad, complex absorption bands in the 8.0-9.17τ region due to coupling between the axial and equatorial protons of the cyclohexyl ring. The N-benzyl derivatives VIIA and VIIIA exhibit poorly resolved quartets resulting from splitting of the benzylic hydrogens by one another into a pair of doublets. The *trans*-N-benzyl derivative VIIB exhibits a complex multiplet in this region; the benzyl protons of VIIIB appear as a broad singlet. In every case the two aromatic protons adjacent (ortho) to the carbonyl moiety absorb at lowest field strength (ca.1.75-2.25τ) as a result of diamagnetic deshielding of these protons by the carbonyl group. In the case of the nitro compound VI the protons ortho to the nitro group are also found (by integration) in this same region (1.75-2.25τ). Compound V exhibits a doublet centered at 3.37τ due to the two protons ortho to the methoxy group, whereas in III the two protons ortho to the bromine atom appear as a single peak at 2.42τ. These results correlate well with the known electron-releasing and withdrawing power of the methoxy and bromo groups respectively. The remainder of the aromatic protons are found as a complex multiplet in the 2.25-3.17τ region.

The preparation of *cis*- and *trans*-1-cyclohexyl-2-phenyl-3-p-bromobenzoyl ethylenimine (III) was performed as follows: To 44.70 g. (0.10 mole) of 4'-bromo chalcone dibromide in 125 ml. of dry benzene was added 29.75 g. (0.30 mole) cyclohexylamine with cooling. The mixture was allowed to stand overnight at room temperature. The precipitated cyclohexylamine hydrobromide was removed by filtration, and the filtrate was evaporated to dryness. After addition of 200 ml. of petroleum ether (b.p. 60-70°), the light yellow precipitate was filtered to yield 34.37 g. (89.4%) III, m.p. 98-102°. Successive extraction of this solid with petroleum ether yielded the white, cis isomer (IIIA), m.p. 116-117° after recrystallization from methanol, $\nu_{max}^{CCl_4}$ 1695, 1673 cm.$^{-1}$ (C=O), $\lambda_{max}^{CH_3OH}$ 264 mμ (ε 22800). The petroleum ether extracts yielded the yellow trans isomer (IIIB), m.p. 102-103° after recrystallization from methanol, $\nu_{max}^{CCl_4}$ 1667 cm.$^{-1}$ (C=O), $\lambda_{max}^{CH_3OH}$ 265 mμ (ε 33400). Anal. Calc'd for $C_{21}H_{22}BrNO$: %C, 65.63; %H, 5.77, %N, 3.65, %Br, 20.79. Found for IIIA: %C, 65.81; %H, 5.95; %N, 3.83; %Br, 20.50. Found for IIIB: %C, 65.64; %H, 5.49; %N, 3.72; %Br, 20.51.

The isomerization of trans-1-cyclohexyl-2-methyl-3-(p-phenylbenzoyl) ethylenimine (XIB) was carried out in deuterated methanol as follows: To a 0.4 g. (0.0013 mole) sample of XIB in 5 ml. of deuterated methanol was added 0.07 g. (0.0006 mole) of sodium methoxide. The reaction mixture was refluxed for two days, diluted with 5 ml. of deuterium oxide, and the precipitate removed by filtration. The solid was treated with charcoal and recrystallized from petroleum ether to give 0.20 g. (50%) of a colorless solid, m.p. 125-127°. The infrared spectrum of this solid was identical to that of an authentic sample of XIA. The p.m.r. spectrum showed complete loss of the α-proton.

In a similar manner IB yielded 57% IA (α-deuterated) and VIIIB yielded 41% VIIIA (α-deuterated). The cis isomers (XIA, IA, and VIIIA) under the same conditions yielded the cis-α-deuterated isomers in 50, 72, and 45% yields respectively.

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