356. *Proton Magnetic Resonance Studies of Cyclic Compounds. Part I.* 1,2,3,4-*Tetrahydroquinolines.*

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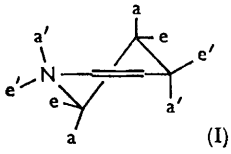
Proton magnetic resonance spectra are recorded for a number of 1,2,3,4-tetrahydroquinolines and are discussed in terms of the probable conformations adopted by the reduced heterocyclic ring.

Interest in the proton magnetic resonance spectra (p.m.r.) of 1,2,3,4-tetrahydroquinolines arose during a study [1] of the thermal decomposition of the quaternary hydroxides derived from these bases. The ease of β-elimination of quaternary hydroxides is related to the stereochemistry of the participating groups. Coplanarity of the four centres, $^{+}N{\cdot}C_{\alpha}{\cdot}C_{\beta}{\cdot}H$ appears to allow easy elimination, and in six-membered rings this condition is only achieved by a *trans*-relationship of the C_{β}–H and ^{+}N–C_{α} bonds about the C_{α}–C_{β} bond. It was hoped to use p.m.r. spectroscopy to determine the preferred conformation of tetrahydroquinolines and the derived quaternary salts.

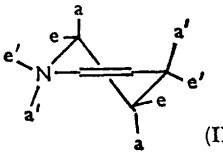
In the first place, it was assumed that a half-chair conformation would generally be adopted by the reduced ring, in preference to a half-boat conformation, owing to the lower repulsive non-bonded interactions involved in the former. Two half-chair conformations (I) and (II), are possible, and it was expected that the spectra would suggest whether a given tetrahydroquinoline existed as a rigid conformation, or as a mixture of rapidly inverting conformations, or as a mixture of noninverting or slowly inverting conformations.

[1] (*a*) Archer, Booth, Crisp, and Parrick, *J.*, **1963**, 330; (*b*) Archer, Booth, and (in part) Crisp, to be published.

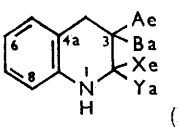
Musher [2] has drawn attention to the dangers inherent in drawing conclusions from p.m.r. spectra as to the flexibility of cyclic systems. As Musher had pointed out, firm conclusions as regards flexibility can only be drawn after spectra have been determined at



(I)



(II)



(III)

varying temperatures. Since the apparatus for studies at different temperatures was not available some of the conclusions given below are necessarily tentative.

The p.m.r. spectra of a number of 1,2,3,4-tetrahydroquinolines are recorded in the Table. Interest was centred on the conformation of the reduced heterocyclic ring, and

Chemical shift data (τ values) for 1,2,3,4-tetrahydroquinolines (splitting J in c./sec.).

Derivative	Solv.	*N*-Me	2-Proton(s)	3-Proton(s)	4-Proton(s)	2-Methyl	4-Methyl	Misc.
Unsubstituted...	1	—	7·16 [a] (J 5·7)	8·42 [b]	7·46 [a] (J 6·3)	—	—	*N*-H 6·75
1-Bz.....	2	—	6·09 [a] (J 6·3)	7·99 [b] (J 6·6)	7·17 [a] (J 6·8)	—	—	—
1-Me	1	7·41	7·12 [a] (J 5·8)	8·25 [b] (J 6·3)	7·41 [c] (J 6·3)	—	—	—
1-Me, MeI	2	6·04	5·68 [a] (J 5·5)	7·6 [b]	6·87 [a] (J 6·1)	—	—	—
2-Me	1	—	7·02 [d]	8·25—8·85 [e]	7·3, 7·38 7·47, 7·55 [f]	9·16 [g] (J 6·1)	—	*N*-H 6·86
1-Ac, 2-Me	2	—	5·13 [h] (J 6·8)	7·61,[i] 8·54 [i]	7·28, 7·36, 7·46 [f]	8·84 [g] (J 7·0)	—	Ac 7·82
1-Bz, 2-Me	1	—	5·13 [h] (J 6·4)	7·97,[j] 8·77 [j]	7·52, 7·61, 7·72 [f]	8·82 [g] (J 6·3)	—	—
,, ...	2	—	5·12 [h] (J 6·6)	7·58,[j] 8·40 [j]	7·12, 7·22, 7·33 [f]	8·76 [g] (J 6·9)	—	—
1,2-Me_2, MeI ...	3	6·28, 6·36	5·91 [j]	7·52	6·78 [a] (J 7·0)	8·29 [a] (J 6·8)	—	—
1-Bz, 4-Me	2	—	5·86, 5·91, 6·00, 6·12 [f]	7·75,[j] 8·35	6·96 [k]	—	8·58 [g] (J 7·2)	—
6-Me	1	—	7·12 [a] (J 5·5)	8·36 [b]	7·47 [a] (J 5·9)	—	—	*N*-H 6·28, Me 7·81
1-Bz, 6-Me	2	—	6·11 [a] (J 6·4)	8·00 [l] (J 6·4)	7·21 [a] (J 6·4)	—	—	Me 7·78
1,2,2-Me_3.....	1	7·47	—	8·48 [a] (J 6·6)	7·42 [c] (J 6·6)	9·05	—	—
2,2,4-Me_3.....	1	—	—	8·64 [g] (J 6·4)	7·21 [j]	9·06	8·81 [g] (J 6·8)	*N*-H 6·87
1-Ac,2,2,4-Me_3	2	—	—	8·0,[i] 8·65 [i]	7·21 [m]	8·26, 8·49	8·65 [g] (J 6·7)	Ac 7·9
1,2,2,4-Me_4	1	7·46	—	8·56 [g] (J 5·5)	7·35 [i]	8·97, 9·03	8·78 [g] (J 6·8)	—
1,2,2,4-Me_4, MeI	2	6·11, 6·28	—	[n]	[n]	8·11, 8·38	8·49 [g] (J 7·2)	—
1-Me, 2-Ph	1	7·39	5·86 [a] (J 4·8)	8·15 [j]	7·51 [c] (J 5·3)	—	—	—
1-Me, 2-Ph, MeI	3	6·23, 6·45	4·6, 4·64, 4·77, 4·81 [o]	[n]	[n]	—	—	—
3-Ph.....	1	—	7·06 [g, p]	[n]	7·24 [g, p]	—	—	*N*-H 6·85 [p]
1-Me, 3-Ph, MeI	3	6·13, 6·18	5·87	[n]	6·59 [g] (J 6·8)	—	—	—

Solvents: 1, benzene; 2, chloroform; 3, trifluoroacetic acid.

[a] Centre of 1 : 2 : 1 triplet. [b] Centre of quintet. [c] Centre of assumed 1 : 2 : 1 triplet (2 lines visible). [d] Centre of symmetrical multiplet (≥10 lines). [e] Unsymmetrical multiplet (≥10 lines). [f] Principal lines in unsymmetrical multiplet. [g] Centre of doublet. [h] Centre of 1 : 3 : 3 : 1 quartet. [i] Approximate centre of partly obscured multiplet. [j] Centre of symmetrical multiplet (≥6 lines). [k] Centre of symmetrical multiplet (≥4 lines). [l] Centre of assumed quintet (4 lines visible). [m] Centre of broad, partly resolved signal. [n] Not seen clearly. [o] 1 : 1 : 1 : 1 quartet. [p] Tentative assignment.

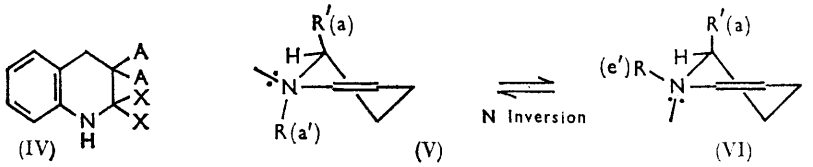
therefore the chemical shifts of the aromatic protons were not measured. Free bases were examined as solutions in benzene, since carbon tetrachloride or chloroform may have

[2] Musher, *J. Amer. Chem. Soc.*, 1961, **83**, 1146.

caused interaction. In most cases, the position of *NH* resonances was checked by deuteration.

In the spectrum of 1,2,3,4-tetrahydroquinoline and 1-methyl base, the two hydrogen atoms at C-2 and the two hydrogen atoms at C-4 appear as clean, symmetrical 1 : 2 : 1 triplets. A clean, symmetrical 1 : 2 : 1 triplet is also observed for the two hydrogen atoms at C-3 in 1,2,3,4-tetrahydro-1,2,2-trimethylquinoline. Consider the situation if the reduced ring of tetrahydroquinoline has the conformation of a fixed half-chair. The hydrogen atoms at C-2 can be considered as the XY portion of an ABXY system [cf. (III); from the point of view of the XY protons, we may neglect the coupling of the AB protons with the protons at C-4]. Now the condition under which this system will give a simple triplet for the XY portion is given, according to Abraham and Bernstein,[3] by the expression $[\delta_{XY} + \frac{1}{2}(J_{AX} - J_{AY} + J_{BX} - J_{BY})]^2/2J_{XY} < 0{\cdot}3$ c./sec. Reasonable values for the tetrahydroquinoline case are as follows: $\delta_{XY} = 20$—50 c./sec. [cf. the tetrahydroquinolines (" dihydroquinoline dimers ") of fixed conformation examined by Dunathan, Elliot, and Yates,[4] in which the hydrogen atoms at C-3 differ in chemical shift by 40—50 c./sec.]; $J_{XY} = 16$ c./sec.; $J_{AX} = J_{ee} = 3{\cdot}5$ c./sec.; $J_{BX} = J_{ae} = 3{\cdot}5$ c./sec.; $J_{AY} = J_{ae} = 3{\cdot}5$ c./sec.; $J_{BY} = J_{aa} = 11{\cdot}5$ c./sec.

Whatever the value of δ_{XY} in the range 20—50 c./sec., the left-hand side of the above expression is $\geqslant 0{\cdot}3$ c./sec., *i.e.*, the condition for simple triplets does not hold. Since a triplet is observed, it is concluded that the reduced ring in tetrahydroquinoline is not a *rigid* half-chair, but a rapidly inverting half-chair [cf. (I) ⇌ (II)]. In this situation, the two hydrogen atoms at C-2 are equivalent and may therefore be considered as the X_2 portion of an A_2X_2 system [cf. (IV)].

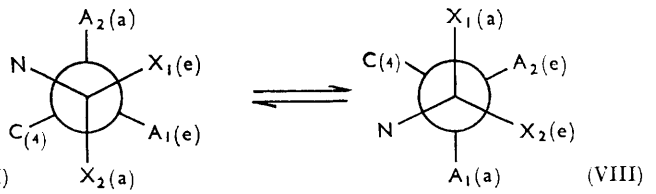


(IV) (V) (VI)

Now in tetrahydroquinoline itself, it is reasonable to assume that equal proportions of conformations (I) and (II) are present. A factor which apparently complicates the conformational equilibrium is the inversion of the nitrogen atom, which occurs in compounds containing a lone pair on this atom (cf. refs. 5 and 6). Since, for example, geometrical isomers of tetrahydroquinolines monosubstituted on carbon in the reduced ring, *e.g.*, (V) and (VI), have never been reported, it is likely that the rate of inversion of nitrogen in tetrahydroquinolines is high.

Next, it is assumed that this rate of inversion of nitrogen, *e.g.*, (V) ⇌ (VI), is high compared with the rate of inversion of half-chair conformations, *e.g.*, (I) ⇌ (II). The situation encountered when nitrogen inversion is prevented is discussed below.

For tetrahydroquinoline, conformations (I) and (II) are most easily appreciated from the projection formulæ (VII) and (VIII), the view as seen along the 2—3 bond being shown.



(VII) (VIII)

[3] Abraham and Bernstein, *Canad. J. Chem.*, 1961, **39**, 216.
[4] Dunathan, Elliot, and Yates, *Tetrahedron Letters*, 1961, 781.
[5] Roberts and Bottini, *J. Amer. Chem. Soc.*, 1958, **80**, 5203.
[6] Reeves and Strømme, *J. Chem. Phys.*, 1961, **34**, 1711.

In (VII), $J_{X_1A_1} = J_{ee} = 3{\cdot}5$ c./sec.; in (VIII), $J_{X_1X_1} = J_{aa} = 11{\cdot}5$ c./sec.
Therefore mean $J_{X_1A_1} = 7{\cdot}5$ c./sec. $= J$
By similar calculations,

$$\text{mean } J_{X_1A_2} = 3{\cdot}5 \text{ c./sec.} = J^1,$$
$$\text{mean } J_{X_2A_2} = 7{\cdot}5 \text{ c./sec.} = J,$$
and $$\text{mean } J_{X_2A_1} = 3{\cdot}5 \text{ c./sec.} = J^1.$$

Thus, when conformations (I) and (II) are equally populated, the situation is reduced to an A_2X_2 type in which only two different coupling constants, J and J^1, are involved. The condition under which an A_2X_2 system of this type gives simple triplets has been given by Abraham and Bernstein [3] as

$$(J - J^1)^2/2(J_{A_1A_2} - J_{X_1X_2}) < 0{\cdot}3 \text{ c./sec.} \quad (2)$$

For tetrahydroquinoline, $J_{A_1A_2}$ and $J_{X_1X_2}$ are likely to be in the range 10—16 c./sec. Thus $J_{A_1A_2} - J_{X_1X_2}$ is unlikely to be >6 c./sec., so that the L.H.S. of equation (2) is $>0{\cdot}3$ c./sec. Nevertheless, a simple triplet is observed for the C-2 hydrogens, suggesting that the treatment outlined above is not adequate for the A_2X_2 system under discussion. However, it may be noted that the observed separation in the triplet (5·7 c./sec.) is in good agreement with the calculated mean coupling constant of 5·5 c./sec. $[\frac{1}{2}(J + J^1)]$.

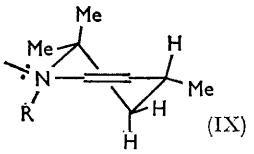
Further evidence, supporting a mixture of rapidly inverting conformations for tetrahydroquinoline, comes from the p.m.r. spectra of the related cyclic bases piperidine and *trans*-decahydroquinoline. The piperidine molecule is expected to consist of two rapidly inverting chair conformations, in each of which the nitrogen atom is undergoing very rapid inversion. The hydrogen atoms at C-2 are thus equivalent. The p.m.r. spectrum of piperidine has been examined at 40 Mc./sec. by Roberts and Bottini,[5] who report that the resonance signal of the protons at C-2 and C-6 is a broad envelope showing no fine structure. In our experiments at 60 Mc./sec. the spectra of neat piperidine and of a solution of piperidine in benzene show at low field (τ 7·38) a triplet, $J \sim 4{\cdot}7$ c./sec., due to the protons at C-2 and C-6. The resolution on the low-field side of the triplet is good, the low-field component of the triplet being seen clearly, but on the high-field side only a shoulder is visible. The low-field triplet in 1-deuteropiperidine shows no more fine structure than that in piperidine. The protons at C-2 and C-6 of 1,1-dimethylpiperidinium iodide appear in the n.m.r. spectrum as a well-resolved triplet, $\tau = 6{\cdot}68$, J 5·7 c./sec. *trans*-Decahydroquinoline almost certainly possesses a rigid conformation, and the protons at C-2 constitute the XY part of an ABXY system. The spectrum [7] of the 1-deutero-derivative shows two distinct regions. The low-field region is complex ($\geqslant$12 lines) and has an area proportional to two protons: one of these is the proton at C-8a and the other is *one* of the two protons at C-2. Whilst the spectrum is difficult to interpret because of the probable overlapping of resonance signals, it is clear that the two protons at C-2 are not giving a simple triplet. As the closely related tetrahydroquinoline gives a simple triplet for the C-2 protons, a fixed conformation for this molecule is unlikely.

With 1,2,3,4-tetrahydro-2-methylquinoline, it is doubtful whether the rapidly inverting conformations (I) and (II) are equally populated, since the methyl substituent will prefer an equatorial orientation. It follows that the protons at C-4 will not be equivalent, and the fact that the spectrum of the base does not show a triplet for these protons is intelligible. The effect of substitution in the aromatic ring is also of interest. The spectrum of 1,2,3,4-tetrahydro-6-methylquinoline resembles very closely that of 1,2,3,4-tetrahydro-6-methoxyquinoline,[8] as far as the protons of the reduced ring are concerned. A clean triplet is observed for the protons at C-4 but the middle line of the " triplet " due to the C-2 protons shows fine structure.

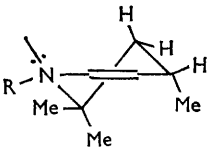
[7] Booth and Franklin, unpublished work.
[8] High Resolution N.M.R. Spectra Catalog, Varian Associates, Palo Alto, California, 1962.

The spectrum of 1,2,3,4-tetrahydro-1-methylquinoline shows that whilst the replacement of *N*-H by *N*-Me affects only slightly the chemical shifts of the protons of the reduced ring, the largest effect is on the protons at C-3; this is due possibly to the well-known repulsive interaction between 1,3-substituents which are axial in a reduced six-membered ring. The spectrum of 1,2,3,4-tetrahydro-1,1-dimethylquinolinium iodide is interesting for two reasons. In the first place, clean 1 : 2 : 1 triplets are again observed for the protons at C-2 and C-4, indicating that quaternisation of the nitrogen atom, whilst preventing nitrogen inversion, has not prevented ring inversion. By contrast, the conversion of 1,2,3,4-tetrahydro-1-methyl-2-phenylquinoline into the methiodide produces a molecule of fixed conformation, for the proton at C-2 is in the case of the base a clean 1 : 2 : 1 triplet (X part of an A_2X system with both As exactly equivalent), but in the case of the salt a 1 : 1 : 1 : 1 quartet (X part of an ABX system). Secondly, comparison of the quaternary iodide with the tetrahydro-1-methyl-base shows that the deshielding effect of the positively charged nitrogen atom extends to protons at all three proton-carrying positions of the reduced ring. The magnitude of the effects are: 1·44, 0·67, and 0·55 p.p.m. for protons at C-2, C-3, and C-4, respectively.

It seemed likely, *a priori*, that the reduced ring of 1,2,3,4-tetrahydro-2,2,4-trimethylquinoline and derivatives would be fixed in conformation (IX) to avoid the repulsive interactions between the axial methyl groups at C-2 and C-4 in the alternative conform-



(IX)



(X)

ation (X). However, the protons at C-3, which are expected to form the AB part of an ABX system, appear in the spectrum as a doublet, suggesting instead an A_2X system. It is possible that the heavy substitution produces half-chair conformations which are extensively deformed, to minimise 1,3-interactions, and which are so easily interconvertible as to cause equivalence of the protons at C-3 (cf. ref. 9).

The spectrum of 1-benzoyl-1,2,3,4-tetrahydro-2-methylquinoline is interesting, as the protons at C-3 appear as two groups of multiplets with at least 5 lines in each group, the separation of the groups being about 48—50 c./sec. The pattern is symmetrical about a point midway between the groups, and each group is itself symmetrical. Presumably one of the groups, centred on $\tau = 7{\cdot}58$ (solvent : chloroform), is due to the equatorial proton at C-3 and the other, centred on $\tau = 8{\cdot}4$, is due to the axial proton at C-3. Now the relatively compact resonance signal of the C-3 protons in 1-benzoyl-1,2,3,4-tetrahydroquinoline is at $\tau = 7{\cdot}99$, a position exactly half-way between the two groups of signals due to the corresponding protons in 1-benzoyl-1,2,3,4-tetrahydro-2-methylquinoline. It is probable, therefore, that 1-benzoyl-1,2,3,4-tetrahydro-2-methylquinoline has a rigid half-chair conformation. The same conclusion holds for 1-benzoyl-1,2,3,4-tetrahydro-4-methylquinoline, the spectrum of which shows, for the protons at C-3, two groups of multiplets separated by about 36 c./sec. In the case of 1-benzoyl-1,2,3,4-tetrahydro-2-methylquinoline, a change in solvent from chloroform to benzene causes the protons at C-3 and C-4 to move to higher field by about 0·4 p.p.m., the proton at C-2 being unaffected.

As already mentioned, the spectrum of 1,2,3,4-tetrahydro-1,1-dimethyl-2-phenylquinolinium iodide suggests a rigid conformation, on account of the quartet due to the proton at C-2. This proton is coupled only to the two protons at C-3 and thus forms the X part of an ABX system. The relatively bulky phenyl group is likely to be equatorial, leaving the hydrogen at C-2 axial, so that $J_{AX} = J_{aa}$ and $J_{BX} = J_{ea}$. The measured

[9] Friebolin, Kabuss, Maier, and Luttringhaus, *Tetrahedron Letters*, 1962, 683.

separations in the observed spectrum give $J_{AX} = 10{\cdot}2$ c./sec. and $J_{BX} = 2{\cdot}3$ c./sec., in reasonable agreement with accepted values for J_{aa} and J_{ea}.

Finally, it is notable that the *gem*-methyl groups at C-2 are equivalent in 1,2,3,4-tetrahydro-2,2,4-trimethylquinoline but are nonequivalent in the derived 1-methyl base and 1-methyl methiodide. Similar effects have been observed [7] in the decahydro-2,2,4-trimethylquinoline series. On the other hand, the *gem*-methyl groups in the tetrahydro-1,2,2-trimethyl-base are equivalent. It is difficult to account satisfactorily for these observations.

Experimental

P.m.r. spectra were obtained on an A.E.I. spectrometer R.S.II operating at 60 Mc./sec., with tetramethylsilane as internal reference. Deuteration of secondary amines was carried out by the method of Fales and Robertson.[10]

The preparation of most of the compounds examined has been described previously.[1]

1,2,3,4-*Tetrahydro*-1,2,2-*trimethylquinoline* (with P. W. Barker).—2-Methylquinoline methiodide (18 g.) was treated with methylmagnesium iodide [from magnesium (3·8 g.) and methyl iodide (22 g.)] by the method of Bradley and Jeffrey.[11] The product, 1,2-dihydro-1,2,2-trimethylquinoline was a yellow oil, b. p. 140—141°/19 mm.; $\nu_{max.}$ (liquid) 2800, 1648, 775, and 745 cm.$^{-1}$ (Infracord). Formulation of this base as a 1,2- rather than a 1,4-dihydroquinoline was supported by the p.m.r. spectrum (cf. spectrum of 1,2-dihydro-2,2,4-trimethylquinoline, given below). A solution in benzene showed the following: (i) singlet (area 6) at $\tau = 8{\cdot}88$ (protons of *gem*-dimethyl groups); (ii) AB quartet (area 2), with $\tau_A = 4{\cdot}82$ and $\tau_B = 3{\cdot}85$, and J_{AB} 9·4 c./sec. (olefinic protons at C-3 and C-4); (iii) singlet (area 3) at $\tau = 7{\cdot}55$ (protons of *N*-methyl group).

When exposed to air, the oil quickly turned green and soon deposited a blue solid. The picrate had m. p. 136—138° (lit.,[12] 138°).

The foregoing base was hydrogenated, as its hydrochloride, in ethanol over 10% palladised charcoal at room temperature and pressure (1·05 mols. of hydrogen were absorbed). The solution was filtered and the filtrate was evaporated to remove ethanol. The residue was basified and extracted with ether, giving 1,2,3,4-tetrahydro-1,2,2-trimethylquinoline as a pale yellow oil, b. p. 136—138°/15 mm.; $\nu_{max.}$ (liquid) 2815, 745, and 715 cm.$^{-1}$ (1648 and 775 cm.$^{-1}$ absent) (Infracord). The derived picrate had m. p. 178—179° (lit.,[12] 178°).

1-*Benzoyl*-1,2,3,4-*tetrahydro*-4-*methylquinoline*.—A solution of 4-methylquinoline (7·1 g.) in boiling butanol (800 ml.) was treated during 1 hr. with sodium (19 g.) added gradually in small pieces. The crude base, isolated by the usual procedure, was at once converted into the benzoyl derivative (Schotten–Baumann), which crystallised from ethanol in plates (14 g.), m. p. 137—138° (lit.,[13,14] 138°).

1-Acetyl-1,2,3,4-tetrahydro-2-methylquinoline, prepared in the normal way from the pure secondary base,[14a] crystallised from light petroleum (b. p. 40—60°) in colourless prisms, m. p. 56—58° (ref. 15 mentions yellow crystals, m. p. 57°). 1-Benzoyl-1,2,3,4-tetrahydro-6-methylquinoline, prepared in the usual way (Schotten–Baumann) from a commercial sample of the secondary base (L. Light & Co.), crystallised from light petroleum (b. p. 60—80°) in prisms, m. p. 81—83° (lit.,[16] 78°). 1-Acetyl-1,2,3,4-tetrahydro-2,2,4-trimethylquinoline, prepared from the secondary base (Monsanto Chemicals Ltd.), crystallised from light petroleum (b. p. 60—80°) in prisms, m. p. 84—85° (lit.,[17] 83°).

The p.m.r. spectrum of piperidine (free from pyridine and 1,2,5,6-tetrahydropyridine) in benzene showed the following: (i) unsharp singlet at $\tau = 8{\cdot}61$ (protons on C-3, C-4, and C-5); (ii) triplet at $\tau = 7{\cdot}38$, $J = 4{\cdot}7$ c./sec. (protons on C-2 and C-6). The N–H resonance was sharp but its position ($\tau = 8{\cdot}3$—$8{\cdot}7$) varied with the concentration of the solution, being at higher

[10] Fales and Robertson, *Tetrahedron Letters*, 1962, 111.
[11] Bradley and Jeffrey, *J.*, 1954, 2770.
[12] Freund and Richard, *Ber.*, 1909, **42**, 1110.
[13] Sauer and Adkins, *J. Amer. Chem. Soc.*, 1938, **60**, 402.
[14] Bringi and Deshmukh, *J. Org. Chem.*, 1962, **27**, 4117.
[15] Diesbach, Pugin, Morard, Nowaczinski, and Dessibourg, *Helv. Chim. Acta*, 1952, **35**, 2322.
[16] von Braun, Grabowski, and Kirschbaum, *Ber.*, 1913, **46**, 1271.
[17] Knoevenagel, *Ber.*, 1922, **55**, 2314.

field in more concentrated solution. The spectrum of 1,1-dimethylpiperidinium iodide, measured in deuterium oxide, with t-butyl alcohol as internal standard at $\tau = 8{\cdot}8$, showed the following: (i) broad resonance at $\tau = 7{\cdot}94$—$8{\cdot}38$ (protons on C-3, C-4, and C-5); (ii) singlet at $\tau = 6{\cdot}93$ (*N*-methyl protons); (iii) symmetrical triplet at $\tau = 6{\cdot}68$, J 5·7 c./sec. (protons on C-2 and C-6).

The spectrum of 1,2-dihydro-2,2,4-trimethylquinoline (Monsanto Chemicals Ltd.), in benzene showed the following:[18] (i) singlet (area 6) at $\tau = 8{\cdot}96$ (protons of *gem*-dimethyl groups); (ii) doublet (area 3) at $\tau = 8{\cdot}14$, J 1·4 c./sec. (protons of methyl groups at C-4, showing allylic coupling with C-3 proton); (iii) broad singlet (area 1) at $\tau = 6{\cdot}69$ (*N*-H); (iv) unsharp singlet (area 1) at $\tau = 4{\cdot}88$ (olefinic proton at C-3).

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[18] Cf. Elliot and Yates, *J. Org. Chem.*, 1961, **26**, 1287.