possibility of utilizing nitroimidazoles as precursors, at least in the 4-nitro case.

Experimental Section[7]

α-*N*-Acetyl-4-nitro-L-histidine Methyl Ester (1a).—α-*N*-Acetyl-4-nitro-L-histidine[4] (43 g, 0.18 mol) was added to 600 ml of methanol to which had previously been added 7 ml of thionyl chloride.[8] The solution was stirred at ambient temperature for 8 hr, after which time tlc showed almost complete esterification. The solvent was removed *in vacuo* (below 40°), 500 ml of cold water was added to the residue, and the aqueous solution was neutralized (pH 4) with solid sodium bicarbonate. The solution was chilled overnight and the colorless solid was collected by filtration. The product was recrystallized from water and then from ethanol to yield 29 g (63%) of **1a**, mp 202–205°.

Anal. Calcd for $C_9H_{12}N_4O_5$: C, 42.19; H, 4.72; N, 21.87. Found: C, 42.03; H, 4.92; N, 21.64.

The same compound was obtained in lower yield by introduction of hydrogen chloride gas into a cold, methanolic solution of the acid. Even at low temperature, N-deacylation occurred to a significant extent. Direct nitration of α-*N*-acetylhistidine methyl ester could not be effected without demethylation. Use of the free carboxylic acid in the irradiation step proved unsatisfactory.

α-*N*-Acetyl-4-nitrohistamine (1b).—This compound was prepared by nitration of α-*N*-acetylhistamine, following the published procedure for α-*N*-acetylhistidine.[4] The product was obtained in 44% yield following crystallization from water and ethanol–ethyl acetate, mp 225–229° dec (with gas evolution).

Anal. Calcd for $C_7H_{10}N_4O_3$: C, 42.42; H, 5.09; N, 28.27. Found: C, 41.90; H, 5.17; G, 28.42.

General Fluorination Procedure.—A solution of 20 mmol of the nitromidazole in 100 ml of 50% tetrafluoroboric acid was cooled to −10°. While the solution was stirred rapidly and was aerated with nitrogen, zinc dust was added in portions of *ca.* 25 mg, until a total of 4.25 g (65 mmol) had been added. Each addition was made only after the prior portion had dissolved and the temperature had fallen to at least −5°; the interval between additions ranged from 1 to 3 min, increasing toward the end of the reduction. Small aliquots were removed periodically and diluted with water, and the solutions were assayed at 298 nm. Total loss of the chromophore was taken to indicate complete reduction.[9] A solution of sodium nitrite (1.52 g, 22 mmol) in the minimum volume of water was then added dropwise over 15 min. The resulting solution was diluted to 185 ml with cold 50% tetrafluoroboric acid and was irradiated (Corex filter) as described previously.[10] Small aliquots were withdrawn periodically, diluted with water, and asayed at 270 nm; again, completion of the reaction was indicated by total loss of absorption at this wavelength. The solution was neutralized with cold, concentrated sodium hydroxide (the precipitate of zinc hydroxide was not removed), and the mixture was extracted continuously for 24 hr with ethyl acetate. The extract was dried (Na_2SO_4) and concentrated, and the residual solution was filtered through a short silica gel column to remove inorganic salts. The products were then purified by crystallization or sublimation, or both.

4-Fluoroimidazole was obtained in 17% yield, mp 101.5–104°; this material was identical with the product described previously.[1]

4-Fluoro-5-methylimidazole was obtained in 37% yield from 4-nitro-5-methylimidazole.[11] The product was purified by sublimation: mp 66–69°; nmr ($CDCl_3$) δ 2.20 (d, J = 1.5 Hz, 3 H, 5-CH_3)[12] and 7.11 ppm (d, J = 2 Hz, 1 H, 2-H).

Anal. Calcd for $C_4H_5N_2F$: C, 48.00; H, 5.03; N, 27.99. Found: C, 47.93; H, 5.03; N, 27.82.

α-*N*-Acetyl-4-fluoro-L-histidine Methyl Ester (4a).—The amino acid derivative was obtained in 10% yield from **1a**, mp 153.5–154.5° (ethanol–ethyl acetate).[13]

Anal. Calcd for $C_9H_{12}N_3O_3F$: C, 47.16; H, 5.28; N, 18.34. Found: C, 46.92; H, 5.42; N, 18.53.

Acid hydrolysis of **4a** gave a quantitative recovery of 4-fluoro-L-histidine, identical with the earlier product[1] with respect to spectral, chromatographic, and optical rotatory properties.

α-*N*-Acetyl-4-fluorohistamine (4b).—This compound was obtained in 18% yield from **1b**, mp 172–173° (ethanol–ethyl acetate).

Anal. Calcd for $C_7H_{10}N_3OF$: C, 49.12; H, 5.89; N, 24.55. Found: C, 48.72; H, 5.94; N, 25.15.

Acid hydrolysis of **4b** gave 4-fluorohistamine, characterized as its picrate, mp 202–204° dec.[1]

Registry No.—**1a**, 41429-88-3; **1b**, 41366-97-6; **4a**, 41366-98-7; **4b**, 41366-99-8; α-*N*-acetyl-4-nitro-L-histidine, 41367-00-4; tetrafluoroboric acid, 16872-11-0; 4-fluorimidazole, 30086-17-0; 4-nitroimidazole, 3034-38-6; 4-fluoro-5-methylimidazole, 41367-01-5; 4-nitro-5-methylimidazole, 14003-66-8.

(7) Analytical and spectral data were supplied by the Analytical Services and Instrumentation section of this laboratory, under the direction of Dr. D. F. Johnson. Melting points are uncorrected. Identity and homogeneity were confirmed, wherever feasible, by tlc and mass spectrum.

(8) E. Taschner and C. Wasielewski, *Justus Liebigs Ann. Chem.*, **640**, 136 (1961).

(9) Since a stoichiometry could be demonstrated between the per cent loss of absorption and the amount of zinc added, it was evident that intermediate stages were undergoing reduction at least as fast as the nitro group. The calculation is based on three atoms of zinc per mole of nitro compound.

(10) K. L. Kirk, W. Nagai, and L. A. Cohen, *J. Amer. Chem. Soc.*, in press.

(11) W. E. Allsebrook, J. M. Gulland, and L. F. Strong, *J. Chem. Soc.*, 232 (1942).

(12) Both the C-4 methyl group and the C-2 hydrogen are coupled to the fluorine atom.

(13) Undoubtedly, the low yield reflects some ester hydrolysis in the 50% tetrafluoroboric acid solvent.

Detection of Protonated Aldimine Group by Proton Magnetic Resonance Spectroscopy

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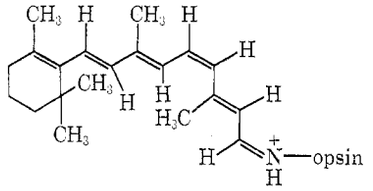
Rhodopsin, the visual pigment of the eye, is a Schiff base formed by the condensation of the aldehyde group of 11-*cis*-retinal with the ε-amino group of a lysine residue in the protein opsin.[1] Several models to explain the anomalous spectroscopic properties of rhodop-



rhodopsin

sin propose that the Schiff base linkage of this molecule is protonated.[2] However, except for the observation that the *N*-retinylidene moiety of rhodopsin shows λ_{max} in the same region where *N*-retinylidene-*n*-butylammonium ion (**8**) absorbs,[3] no direct experimental evidence for the presence of a protonated aldimine group (–HC=$^+$NH–) in the visual pigment has yet been obtained.

It occurred to us that the presence of a protonated aldimine group in rhodopsin may be directly observed by nmr spectroscopy. In principle, the resonance of the azomethine proton, H_a, of a protonated Schiff base

(1) D. Bownds, *Nature*, **216**, 1178 (1967).

(2) C. D. B. Bridges, "Comprehensive Biochemistry," Vol. 27, M. Florkin and E. H. Stolz, Ed., Elsevier, New York, N. Y., 1967, pp 31–78; J. Heller, *Biochemistry*, **7**, 2914 (1968); J. Toth and B. Rosenberg, *Vision Res.*, **8**, 1471 (1968).

(3) P. E. Blatz and J. H. Mohler, *Biochemistry*, **11**, 3240 (1972).

TABLE I
THE NMR DATA FOR THE COMPOUNDS 1–4 IN $CDCl_3$, TFA, AND $CDCl_3$ + TFA AT −55°

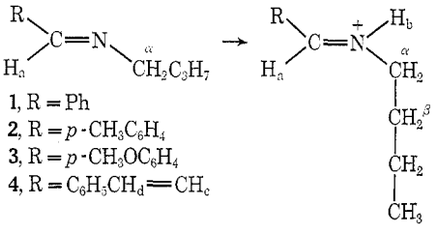
Schiff base	(Multiplicity, J in Hz) In $CDCl_3$ H_a	In $CDCl_3$ α-CH_2	In TFA H_a	In TFA α-CH_2	In $CDCl_3$ + TFA[a] H_a	In $CDCl_3$ + TFA[a] α-CH_2	Coalescence temp, °C
1	8.25 (t, $J_{a,\alpha}$ = 1.3)	3.6 (td, $J_{a,\alpha}$ = 1.3, $J_{\alpha,\beta}$ = 7.1)	8.81 (d, $J_{a,b}$ = 18)	4.06 (q, $J_{\alpha,b}$ = 7, $J_{\alpha,\beta}$ = 7)	8.72 (d, $J_{a,b}$ = 14)	3.96 (q, br)	−45
2	8.23 (s)	3.61 (t, $J_{\alpha,\beta}$ = 7.0)	8.68 (d, $J_{a,b}$ = 17.5)	4.00 (q, $J_{\alpha,b}$ = 7, $J_{\alpha,\beta}$ = 7)	8.63 (d, $J_{a,b}$ = 15.7)	3.9 (q, $J_{\alpha,b}$ = 5.5, $J_{\alpha,\beta}$ = 5.5)	−40
3	8.18 (t)	3.55 (td, $J_{a,\alpha}$ = 1.2, $J_{\alpha,\beta}$ = 6.6)	8.52 (d, $J_{a,b}$ = 17.6)	3.93 (q, $J_{\alpha,b}$ = 7, $J_{\alpha,\beta}$ = 7)	8.45 (d, $J_{a,b}$ = 16)	3.85 (q, $J_{\alpha,b}$ = 5, $J_{\alpha,\beta}$ = 5)	−33
4	8.02 (tt, $J_{a,\alpha}$ = 1.5, $J_{a,b}$ = 4.3, $J_{a,d}$ = 4)	3.51 (td, $J_{a,\alpha}$ = 1.5, $J_{\alpha,\beta}$ = 7)	8.45 (dd, $J_{a,b}$ = 16.7, $J_{a,c}$ = 10.5)	3.87 (q, $J_{\alpha,b}$ = 7, $J_{\alpha,\beta}$ = 7)	8.45 (m, $J_{a,b}$ = 14, $J_{a,c}$ = 4.5, $J_{a,d}$ = 4.5)	3.77 (q, $J_{\alpha,b}$ = 6.5, $J_{\alpha,\beta}$ = 6.5)	−40

[a] At −55°.

should exhibit additional splitting because of coupling to the proton, H_b, present on the imine nitrogen. The numerical value of the coupling constant $J_{a,b}$ should be 15–18 Hz if the protonated Schiff base has the trans configuration at the carbon–nitrogen double bond. On the other hand, if the stereochemistry at the carbon–nitrogen double bond is cis, then $J_{a,b}$ should be in the range of 8–12 Hz. Thus, the presence of a protonated aldimine group in a molecule may be inferred from the multiplicity of the azomethine proton resonance. However, it was realized at the outset that the above results would be obtained only if the proton exchange in protonated Schiff bases is slow on the nmr time scale. In addition, there should be no free rotation about the carbon–nitrogen bond of these positively charged species. The free rotation about the protonated Schiff base linkage of rhodopsin may be expected if there is a substantial delocalization of the positive charge over the polyene chain of the *N*-retinylidene moiety of this molecule. Furthermore, the nmr spectroscopy will be most effective in detecting the presence of a protonated aldimine group in rhodopsin if the resonance of the azomethine proton occurs in the region below 9 ppm. This region is normally free from absorption by other protons and the resonance due to an azomethine proton should be easily detectable. To gain information on these points we have studied the nmr spectra of *all-trans*-*N*-retinylidene-*n*-butylamine (**7**) and of the Schiff bases **1–4** in trifluoroacetic acid (TFA) and in $CDCl_3$ acidified with equimolar amounts of TFA. The results of these investigations are reported in this note.

The imines **1–4** and **7** were prepared according to the procedures reported in the literature.[4,5] All spectra were recorded on a Varian HR-220 MHz nmr spectrometer. The discussion is restricted in the main to the nmr parameters of azomethine protons (H_a) and α-methylene protons (α-CH_2). The other spectral features were much as expected and showed no abnormalities.

In the nmr spectra of the trifluoroacetic acid (TFA) solutions of **1**, **2**, and **3**, the resonances of H_a and α-CH_2 appear as doublets and quartets, respectively. When deuteriotrifluoroacetic acid is used as the solvent, the azomethine protons give singlets and the α-methylenes appear as triplets. These results show that the Schiff bases **1–3** are protonated in trifluoroacetic acid. The splitting of H_a resonances into doublets ($J_{a,b}$ = 16–18 Hz) and of α-CH_2 resonances into quartets ($J_{\alpha,b}$ = $J_{\alpha,\beta}$ = 7 Hz) is due to coupling with the proton H_b present on the imine nitrogen. The resonance of the azomethine proton of the protonated species **5** (R = $C_6H_5CH_d{=}CH_c$) (produced by dissolving **4** in TFA) was a doublet of doublets ($J_{a,b}$ = 16.7 and $J_{a,c}$ = 10.5 Hz) because of coupling to H_b and H_c.



5

The nmr data collated in Table I suggest that the resonances of H_a and α-CH_2 shift downfield when the Schiff bases **1–4** are protonated. The numerical values of the coupling constants $J_{a,b}$ = 16–18 Hz indicate that the protonated Schiff bases have trans configuration **5** at the carbon–nitrogen double bond. These coupling constants further suggest that there is no rotation about the CN bond of protonated Schiff bases.

The Schiff bases **1–3** dissolve readily in $CDCl_3$ acidified with equimolar amounts of TFA. In the nmr spectra of these solutions determined at −55°, the azomethine protons and the α-methylenes exhibit the same multiplicities as observed in trifluoroacetic acid (Table I). As the temperature is raised, the doublets due to H_a and the quartets due to α-CH_2 broaden and finally coalesce to give singlets and triplets, respectively. The coalescence temperatures are given in Table I. These spectral data suggest that the Schiff bases **1–3** are protonated in $CDCl_3$ by equimolar amounts of TFA, and at −55° the protonated species exhibit extremely slow exchange rates allowing the observation of well-resolved nmr spectra.

The Schiff base **4** is also protonated in $CDCl_3$ acidified with equimolar amounts of TFA. The azomethine

(4) C. S. Irving and P. A. Leermakers, *Photochem. Photobiol.*, **7**, 665 (1968).

(5) K. A. W. Perry, P. J. Robinson, P. J. Sainsbury, and M. J. Waller, *J. Chem. Soc. B*, 700 (1970).

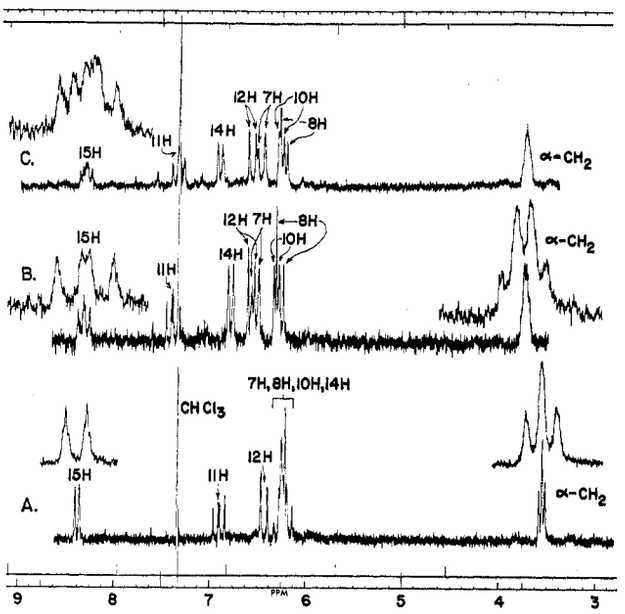
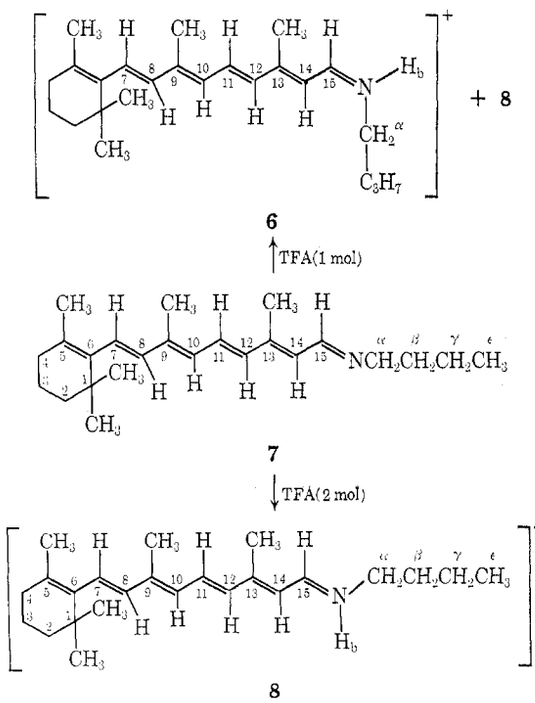


Figure 1.—The 3-9-ppm regions of the nmr spectra of *N*-retinylidene-*n*-butylamine (**7**) in $CDCl_3$ at −5° (trace A), in $CDCl_3$ + 2 mol equiv of TFA at −5° (trace B), and in $CDCl_3$ + equimolar amounts of TFA at −50° (trace C).

proton of the protonated species gives a sextet ($J_{a,b}$ = 14 and $J_{a,c} = J_{a,d}$ = 4.5 Hz) in the nmr spectrum determined at −55°.

The *N*-retinylidene-*n*-butylammonium ion (**8**) was obtained by treating the deuteriochloroform solution of **7** at −60° with 2 mol equiv of TFA (Scheme I).

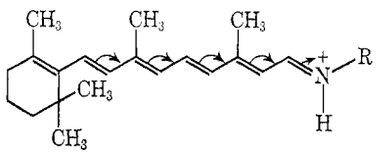
SCHEME I



The formation of **8** was recognized by the presence of a doublet of doublets at δ 8.3 (1 H, $J_{15,b}$ = 15.5, $J_{14,15}$ = 11.5 Hz, 15-H) and a quartet at 3.7 (2 H, $J_{\alpha,b} = J_{\alpha,\beta}$ = 7 Hz, α-CH_2) in the nmr spectrum of the acidified solution, determined at −5°. The other protons of **8** showed bands at δ 7.38 (dd, 1 H, $J_{11,12}$ = 15 and $J_{10,11}$ = 12 Hz, 11-H), 6.73 (d, 1 H, $J_{14,15}$ = 11.5 Hz, 14-H), 6.52 (d, 1 H, $J_{11,12}$ = 15 Hz, 12-H), 6.47 (d, 1 H, $J_{7,8}$ = 16 Hz, 7-H), 6.27 (d, 1 H, $J_{10,11}$ = 12 Hz, 10-H), 6.22 (d, 1 H, $J_{8,7}$ = 16 Hz, 8-H), 2.3 (s, 3 H, 13-CH_3), 2.07 (s over m, 5 H, 4-CH_2 and 9-CH_3), 1.72 (s over m, 5 H, 3-CH_2 and 5-CH_3), 1.62 (m, 2 H, β-CH_2), 1.48 (m, 2 H, 2-CH_2), 1.34 (m, 2 H, γ-CH_2), 1.04 (s, 6 H, 1-CH_3), and 0.95 (t, 3 H, ε-CH_3). The signals of 15-H and α-CH_2 did not coalesce as the temperature was raised to 17°. The coupling constant $J_{15,b}$ = 15.5 Hz again suggests that the ion **8** has trans configuration at the aldimine linkage.

The 3–9-ppm regions of the nmr spectra of **7** and **8** are compared in Figure 1 (trace A and trace B). The comparison reveals that the resonances of 7-H, 11-H, and 14-H suffer a large downfield shift (0.3, 0.52, and 0.6 ppm, respectively) when the imine nitrogen of **7** is protonated. The protonation, however, does not affect the chemical shift of the azomethine proton, 15-H.

The deshielding of 7-H and 11-H upon protonation of *N*-retinylidene-*n*-butylamine indicates that there is a delocalization of the positive charge over the polyene chain of *N*-retinylidene-*n*-butylammonium ion owing to the resonance interaction of the type[6-8] shown in **8a**.



8a

The resonance of 15-H is not affected by protonation because the deshielding induced by the residual positive charge on the imine nitrogen is balanced by the decrease in the double-bond character and hence by the decrease in the anisotropy of the C–N bond. The large deshielding of the resonance of 14-H upon protonation of **7** is anomalous and cannot be explained on the basis of charge delocalization.

Addition of equimolar amounts of TFA to the deuteriochloroform solution of **7** at −60° appears to produce two products. Thus, in the nmr spectrum of the acidified solution at −50°, the azomethine proton, 15-H, gave seven lines and α-CH_2 appeared as a broad band (Figure 1, trace C). Above −16° (coalescence temperature) the resonances of 15-H and α-CH_2 were doublets ($J_{14,15}$ = 10.5 Hz) and triplets, respectively. These results indicate the formation of isomeric (cis and trans) monoprotonated species **8** and **6**. The doublet of doublets due to 15-H of **8** ($J_{15,b}$ = 15.5 and $J_{14,15}$ = 11.5 Hz) and the doublet of doublets due to 15-H of **6** ($J_{15,b} \simeq 11$ and $J_{14,15} \simeq 9$ Hz) would partially overlap to give seven lines in the nmr spectrum.

In conclusion it may be remarked that, in the low temperature nmr spectra of the protonated Schiff bases, the azomethine protons and the α-methylenes exhibit additional fine structure because of coupling to the proton present on the imine nitrogen. This observation is of diagnostic value and may be used to detect the presence of a protonated aldimine group in simple organic molecules. It may be noticed that the azo-

(6) D. J. Patel, *Nature*, **221**, 825 (1969).
(7) D. J. Patel, *Nature*, **224**, 700 (1969).
(8) D. J. Patel and R. G. Schulman, *Proc. Nat. Acad. Sci.*, **65**, 31 (1970).

methine proton of *N*-retinylidene-*n*-butylammonium ion (**8**) resonates at 8.3 ppm. If in the nmr spectrum of rhodopsin the region around 8.3 ppm is not masked by bands from the aromatic protons of the protein moiety (opsin) and the resonance due to the azomethine proton is easily detectable, then this technique (nmr spectroscopy) may reveal whether the Schiff base linkage of the visual pigment is protonated or not. We would have been more confident if the resonance of the azomethine proton had occurred in the region below 9 ppm.

Acknowledgments.—This work was supported in part by NSF Grant No. GB-29946 and Grants from the Research Corporation and Sloan Foundation to a consortium at the Rockefeller University for 220-MHz nmr facilities. We wish to thank Peter Ziegler for assistance in obtaining the nmr spectra.

Registry No.—**1**, 1077-18-5; **2**, 7020-93-1; **3**, 3910-55-2; **4**, 15286-55-2; **7**, 36076-04-7; **8**, 32798-55-3.

The Methyl Signals in the Proton Magnetic Resonance Spectra of Some 2-Methylnorbornanes. A Cautionary Tale

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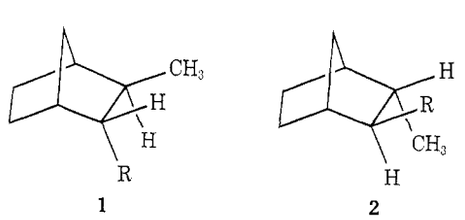
Proton magnetic resonance spectroscopy is frequently used for distinguishing between a methyl group bonded to a quaternary carbon atom and a methyl group bonded to an sp^3 carbon atom bearing a hydrogen atom. Although in the latter case the signal may deviate from a simple AX_3 doublet owing to strong or virtual coupling, it is usually readily distinguishable from the singlet signal in the former case, because the chemical shift differences between the methyl and methine protons is normally appreciable. If, however, there were accidental chemical equivalence between the methyl and methine protons because of special structural features in the molecule, the methyl signal could appear as a singlet, superimposed on the methine signal. We have observed examples of this circumstance in the spectra of the norbornanes **1a–c**.

Compounds **1a–c** were prepared from the acid **1d**.[1] Although the methyl group of **1d** gives rise to a conventional CH_3CH doublet (Table I), the methyl groups of **1a–c** give rise to singlets. By contrast, the methyl groups of **2a–c** give rise to doublets; these compounds were prepared from the acid **2d**,[1] whose spectrum also showed a methyl doublet. It is known that the endo proton signal in norbornane occurs at unusually high field,[2,3] and we conclude that this effect, combined with a further upfield shift resulting from shielding by the endo C–CH_2X bond in **1a–c**,[4] results in accidental chemical equivalence of the methyl protons and the endo methine proton.[5] As expected for this interpretation, the methyl singlets are superimposed on multiplets, the total peak area corresponding to four protons. The absence of this effect in the spectrum of **1d** is attributable to deshielding of the endo methine proton by the carboxylic acid group and in the spectra of **2a–d** to the fact that exo protons are not shielded by the norbornane system.[2,3]



1 2

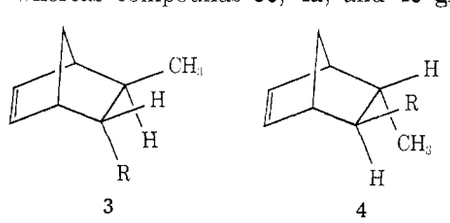
a, R = CH_2OH
b, R = CH_2Cl
c, R = CH_2OAc
d, R = CO_2H

TABLE I
METHYL PROTON SIGNALS[a]

Compd	δ	Compd	δ
1a	0.93 (s)	**2a**	0.97 (d)
1b	0.98 (s)	**2b**	1.01 (d)
1c	0.95 (s)	**2c**	0.97 (d)
1d	0.97 (d)	**2d**	1.06 (d)
3a	1.10 (d)	**4a**	0.84 (d)
3b	0.79 (d), 1.03 (d)	**4c**	0.93 (d)
3c	1.18 (d)		

[a] For all doublets, J = 6–7 Hz.

Related observations have been made in the norbornene series. Compounds **3a** and **3b** give rise to methyl doublets in which the higher field component is considerably more intense than the lower field component,[6] whereas compounds **3c**, **4a**, and **4c** give rise to conventional CH_3CH doublets.[7] It is known that signals arising from endo protons in norbornene occur at yet higher field than those in norbornane.[2] Thus, the spectra of **3a** and **3b** can be interpreted in terms of a shift of the endo methine signals to higher field than those of the exo methyl protons; indeed, such signals are observed as multiplets as $\delta \sim 0.90$ and 0.80, respectively.



3 4

a, R = CH_2OH
b, R = CH_3
c, R = CO_2H

(1) S. Beckmann, A. Dürkop, R. Bamberger, and R. Mezger, *Justus Liebigs Ann. Chem.*, **594**, 199 (1955).

(2) A. P. Marchand and N. W. Marchand, *Tetrahedron Lett.*, 1365 (1971).

(3) J. I. Musher, *Mol. Phys.*, **6**, 93 (1963); T. J. Flautt and W. F. Erman, *J. Amer. Chem. Soc.*, **85**, 3212 (1963); P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965).

(4) R. G. Foster and M. C. McIvor, *Chem. Commun.*, 280 (1967).

(5) Broadening of the methyl singlets indicates that the chemical equivalence is not exact.

(6) In the case of **3b**, this refers to the lower field doublet, assigned to the exo methyl group; the endo methyl group gives rise to a conventional CH_3CH doublet.

(7) The pmr spectra of **3a** and **4a** have been discussed earlier,[8] but no reference was made to the methyl signal of **3a**.

(8) H. Christol, J. Coste, and F. Plénat, *Ann. Chim. (Paris)*, **4**, 93, 105 (1969).