none) and 1715 cm^{-1} (cyclohexanone); this characteristic cyclobutanone absorption was observed also in the infrared spectrum of the monoketone (ν_{max} 1783 cm^{-1}) from the alcohol **8**.

The mass spectra of **6** and **7** showed intense peaks at m/e 194 (M − 44, 84% of base peak) and 192 (M − 44, base peak), respectively. These were probably formed by cleavage of the cyclobutanol ring with loss of CH$_2$CHOH.[5]

The presence of an allylic secondary hydroxyl in the six-membered ring, a tetrasubstituted double bond carrying a hydroxymethyl (and no methyl group), and a cyclobutane ring fixed the carbon skeleton of illudol. The position of the hydroxyl in the cyclobutane ring was indicated by the splitting pattern of the proton α to it (in the nmr spectra of **6** and **7**), leading to the unique structure **5** for illudol.

In accordance with its terpenoid nature, illudol incorporated radioactivity from [2-C^{14}]mevalonic acid.

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The Isolation and Characterization of Two Diastereomeric Ammonium Salts Differing Only in Nitrogen Configurations

Sir:

The inversion of nitrogen of a tertiary amine is sufficiently rapid to prevent detection of the two diastereomeric forms in the proton magnetic resonance spectrum of a compound such as tropane.[1] Measurement of the spectrum in acidic medium permits observation of two signals for the nitrogen substituent due to a decrease in the rate of inversion on protonation of the nitrogen.[1,2] The reversibility of the protonation has prevented isolation of the two isomeric ammonium salts, however. We wish to report the isolation of two diastereomeric ammonium salts which differ only in the configuration of the ammonium nitrogen. This represents the first example of such isomers which are stable in solution at room temperature.

Dehydration of 3-phenyltropine (**1**) in 40% hydrobromic acid formed α-3-phenyltropidine hydrobromide (**2a**),[3] mp 179.5–181.0°, λ_{max}^{EtOH} (log ϵ) 216.2 (4.01), 247.9 (4.11), and 290.3 mμ (2.39). The base, 3-phenyltropidine (**3**), was prepared and converted to the known hydrochloride[4] and methiodide[5] whose properties were identical with those reported. Reaction of the base **3** with hydrogen bromide in anhydrous ether caused the precipitation of β-3-phenyltropidine (**2b**), mp 180–182°, λ_{max}^{EtOH} (log ϵ) 216.2 (4.07), 247.1 (4.17), and 290.0 mμ (2.40). The nonidentity of the α and β forms of 3-phenyltropidine hydrobromide (**2**) was clearly evident from the proton magnetic resonance (Figure 1) and infrared spectra and the X-ray powder pattern,[6] although the ultraviolet and mass spectra of **2a** and **2b** were nearly identical.

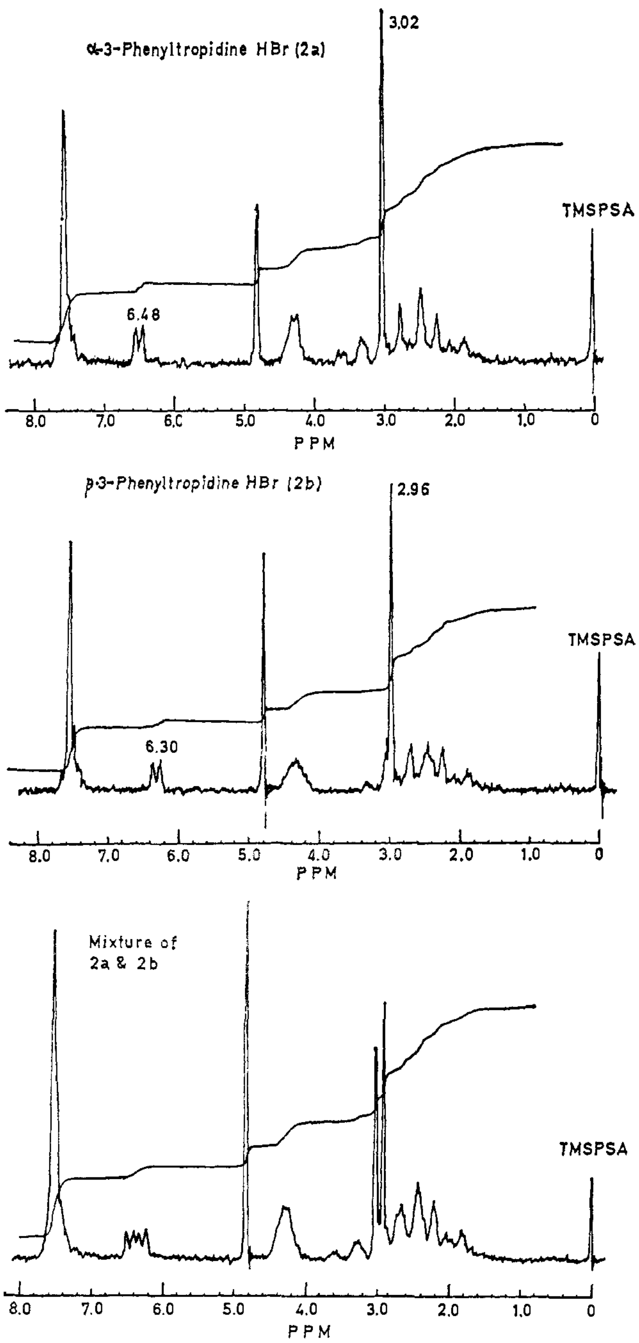

Figure 1. The proton magnetic resonance spectra of α-3-phenyltropidine hydrobromide (**2a**), β-3-phenyltropidine hydrobromide (**2b**), and a mixture of the two isomers formed on heating a solution of either. The spectra were determined in deuterium oxide using the sodium salt of trimethylsilylpropanesulfonic acid (TMSPSA) as the internal standard.

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(1) (a) J. C. N. Ma and E. W. Warnoff, *Can. J. Chem.*, 43, 1849 (1965); (b) G. L. Closs, *J. Am. Chem. Soc.*, 81, 5465 (1959); (c) D. L. Griffith and J. D. Roberts, *ibid.*, 87, 4089 (1965).

(2) R. W. Horobin, J. McKenna, and J. M. McKenna, *Tetrahedron Suppl.*, 7, 35 (1966).

(3) All new compounds gave correct elemental analyses and infrared, ultraviolet, and nmr spectral data consistent with the assigned structures.

(4) M. R. Bell and S. Archer, *J. Am. Chem. Soc.*, 82, 4638 (1960).

(5) A. C. Cope and D. A. D'Addieco, *ibid.*, 73, 3419 (1951).

(6) The authors wish to thank Professor Helmut M. Haendler for assistance in obtaining and interpreting these data.

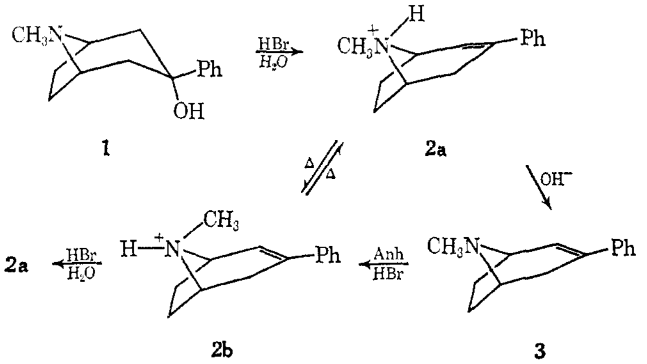
Warming solutions of either isomer **2a** or **2b** in deuterium oxide or various alcohols caused equilibration to a mixture of the two isomers. The pmr spectra of the α and β isomers (**2a** and **2b**) and the equilibrium mixture are shown in Figure 1 and indicate that the chemical shifts of the N–CH_3 and vinyl protons are different for the two isomers while the remainder of the spectra are very similar. The mass spectra of the α and β isomers (**2a** and **2b**) or the equilibrium mixture were identical and showed the loss of hydrogen bromide in the inlet system; the molecular ion peak was at *m/e* 199. The strongest peak in each spectrum was at *m/e* 170 and probably corresponded to 1-methyl-4-phenylpyridinium ion.

Either of the isomeric hydrobromides (**2a** and **2b**) or the equilibrium mixture was converted to the same amine **3** as evidenced by identical infrared and pmr spectra. The purified amine was recovered in 75–85% yield. The fragmentation pattern in the mass spectrum of the amine **3** was identical with that obtained from the hydrobromides.

Preliminary studies showed that the interconversion of **2a** and **2b** occurred very slowly at room temperature in solution in deuterium oxide but within minutes at 50°. At about 100° the two N–CH_3 resonance signals for the two isomers began to coalesce, showing that the rate of interconversion was comparable with the pmr time scale. The equilibration is hindered by addition of acid.

The isomers **2a** and **2b** must contain the same type of π-electron system because of the similarity in ultraviolet spectra. The skeletal arrangements of the two isomers must be the same or undergo rearrangement of a very unusual nature since the same base was formed from either isomer by thermal decomposition (identical mass spectra) or basic conditions (isolation experiments). The rearrangement of an unsaturated cyclic system such as **2** or **3** during salt formation or heating of a salt would logically occur by a carbonium ion mechanism. Thus, the decrease in ease of interconversion of **2a** and **2b** in an acidic medium also argues against **2a** and **2b** being skeletal isomers.

The experimental data seem to preclude an explanation of the isomerism of **2a** and **2b** based on structural differences and require a rationale based on stereoisomeric differences. The data are consistent with the hypothesis that the α- and β-hydrobromides differ only in the configuration of the ammonium nitrogen. The resonance of the methyl hydrogens of the β isomer at higher field suggests the assignment of structure **2b** in which the methyl is shielded by the π electrons of the double bond. This situation can be compared with the relative chemical shifts of the two methyl signals of the pinenes, the high-field signal being assigned to the methyl group nearest to the unsaturation.[7]



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[8] UNH Research Fellow, University of New Hampshire, 1964–1967.

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Nitrogen Hyperfine Splittings in the Electron Spin Resonance Spectrum of the $Cr(NH_3)_5NO^{2+}$ Ion[1]

Sir:

The electron spin resonance spectrum of the $Cr(NH_3)_5NO^{2+}$ ion in aqueous solution has been reported recently by several groups,[2-4] but neither Danon, *et al.*,[3] nor Meriwether, *et al.*,[4] observed ^{14}N hyperfine lines; Bernal, *et al.*,[2] reported the presence of hyperfine structure but were not able to resolve the spectrum. Trapp and Shyr[5] have also noted the presence of hyperfine ^{14}N structure in $Cu(NH_3)_6Cl_2$ in solid solution in diamagnetic lattices, but the spectra have not yet been analyzed.[6] We now report a well-resolved esr spectrum of $Cr(NH_3)_5NO^{2+}$ in DMF solution which appears to be the first reported example of an NH_3 ligand (^{14}N) hyperfine splitting. The esr data, combined with MO calculations, provide considerable information concerning the electronic structure of the ion.

The spectrum was obtained using the compound $[Cr(NH_3)_5NO][B(C_6H_5)_4]_2$ which was prepared by directly interacting equivalent amounts of $[Cr(NH_3)_5NO]Cl_2$ and sodium tetraphenylborate, $NaB(C_6H_5)_4$, in aqueous solution; $[Cr(NH_3)_5NO]Cl_2$ was prepared by the method of Griffith.[7] The precipitate obtained was washed with cold water and then with ether, and analysis showed that it had the formula $[Cr(NH_3)_5NO][B(C_6H_5)_4]_2$. A magnetic susceptibility measurement proved the presence of one unpaired electron. The esr spectrum was obtained using a freshly prepared solution of this compound in DMF which was deaerated before use by passing through a stream of nitrogen gas. An experimental esr spectrum of $Cr(NH_3)_5NO^{2+}$ ion is shown in Figure 1 (solid line). It consists of an intense central line due to ^{52}Cr which is further split by hyperfine interactions with ^{14}N of both NO and all five NH_3 groups. There is a considerable amount of overlapping of lines in the spectrum. Some of the lines due to the interactions with the ^{53}Cr nucleus (10% abundance) and the ^{14}N nuclei are seen in the lower field region of the spectrum. The high-field lines due to ^{53}Cr and ^{14}N interactions are not seen because the line widths have become greater; instead only one broad line due to the ^{53}Cr

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[1] This work was supported through a contract with the U. S. Army Research Office, Durham.

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