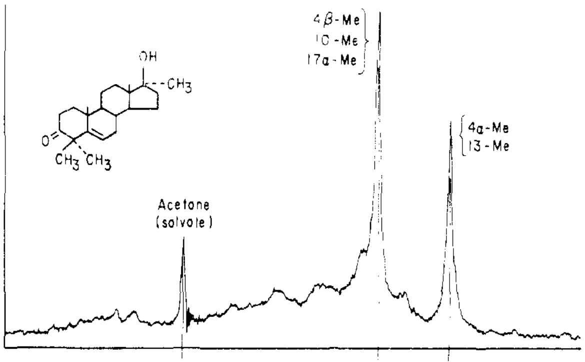
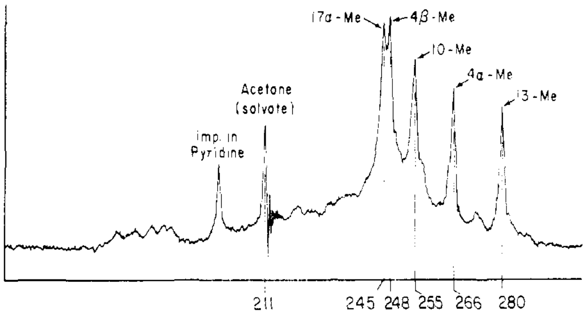


Cps. at 60 mc., relative to water.



Cps. at 60 mc., relative to water.

Fig. 1.—Portions of the spectra of 4,4,17α-trimethyl-17β-hydroxy-5-androsten-3-one in deuteriochloroform (upper) and in pyridine (lower).

Pyridine was suggested[2] as a useful solvent for n.m.r. studies on polar steroids. Its n.m.r. spectrum has been studied in detail[3] and it consists of only two groups of lines at rather low frequencies. It was expected that resonance frequencies from samples dissolved in pyridine would be uniformly shifted from those ordinarily observed in chloroform due to the different magnetic susceptibilities of the two solvents.[4]

When steroid spectra obtained in deuteriochloroform and pyridine solvents were compared, marked differences appeared. Some of the lines were shifted much more than others. It appeared that the pyridine preferred certain sites for coördination and that the large shifts were due to the anisotropy associated with its ring current effects.[5] Absorptions from similar types of hydrogens were shifted by different amounts because of small differences in environment. We have consistently found that lines which were superimposed in deuteriochloroform solution spectra were rearranged in pyridine solution spectra.

This information is valuable in characterizing unknowns. It permits confirmation of uncertain assignments for superimposed lines and spin multiplets. An interesting example of the former case was 4,4,17α-trimethyl-17β-hydroxy-5-androsten-3-one. The n.m.r. spectrum (see Fig. 1) in deuteriochloroform solvent showed only two lines ascribable to methyl hydrogens but in pyridine solvent all five methyl absorptions were resolved.

Spin multiplets usually retained the same spacing in both solvents and therefore were easily distinguished from chemically shifted groupings of lines. This method of differentiation usually was more convenient than obtaining a spectrum at a different frequency.

Solvent shifts have been compiled for the unique protons of about thirty steroids. They ranged from +20 cps. for the 21-CH_2 of the dihydroxyacetone side chain to +60 for the 19-methyl of 3-keto-Δ^4-steroids with no other substituents in the A, B or C rings. Nearby F, $C{=}O$ and OH increased the solvent shift in that order. Axial methyls were shifted more than those which were equatorial.

N.m.r. spectra were observed with a Varian 4300–2 spectrometer operating at 60 mc. on solutions (*ca.* 0.3 ml., *ca.* 0.15 molar) of the steroids in deuteriochloroform and in pyridine. The spectra were calibrated against internal tetramethylsilane[6] using the audiofrequency side-band technique.[7] Frequencies are reported relative to water.

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STRUCTURE AND EXCHANGE IN METHYL ALUMINUM CHLORIDES

Sir:

Trimethylaluminum and the methylaluminum halides are dimeric in the liquid state. In the partially halogenated methyl compounds the methyl groups are bridging between the two aluminum atoms in the dimer.[1] Therefore in trimethylaluminum dimer and in dimethylaluminum chloride dimer there should be two different types of methyl groups. The two kinds of methyl groups recently have been observed by proton resonance spectroscopy at −75°.[2] At higher temperatures the two peaks coalesce to a single one due to rapid chemical exchange of the methyl groups, and allow an activation energy for the process to be calculated.[3]

We had previously obtained the proton resonance spectra of trimethylaluminum, dimethylaluminum chloride and methylaluminum dichloride in cyclohexane solution. In each case a single line was observed for the aluminum alkyl. The chemical

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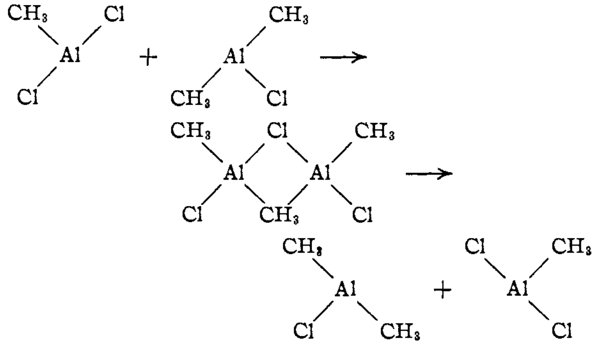
shifts were 1.75, 1.75 and 1.45 p.p.m., respectively, to higher fields than the resonance due to the solvent protons. Cooling the solutions to their freezing point, approximately 0°, produced no line splitting. Therefore in dimethylaluminum chloride also, exchange between bridging and nonbridging groups probably occurs readily.

In addition to methyl exchange within the dimer, halogens and methyl groups may exchange between molecules in the mixed methylaluminum halides. Trimethylaluminum, aluminum iodide and the intermediate iodomethyl compounds were shown to be in rapid equilibrium.[4,5] A solution of methylaluminum chloride (25%) in dimethylaluminum chloride (75%) shows only a single sharp proton resonance signal both at room temperature and at −60°. Since the chemical shift between the two compounds is 12 cycles at a frequency of 40 Mc. one can estimate[3] that the maximum energy for intermolecular methyl exchange is 12 kcal. mole^{-1}. This is similar to that reported, 6–14 kcal. mole^{-1}, for the methyl groups in trimethylaluminum.[2] In this case, however, it is difficult to envision a mechanism for intermolecular methyl group exchange which does not involve dissociation to monomers. One possible mechanism for the exchange is shown.



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LINKAGE ISOMERISM: SYNTHESIS AND ISOMERIZATION OF NITRITOPENTAMMINE COMPLEXES OF RHODIUM(III) AND IRIDIUM(III)[1]

Sir:

The only reported example of linkage isomerism for metal complexes is that of nitro ($Co-NO_2$) and nitrito (Co-ONO) ammines of cobalt(III).[2] We wish to report the successful synthesis of $Rh(NH_3)_5ONO^{2+}$ and $Ir(NH_3)_5ONO^{2+}$ salts and their isomerization to the corresponding stable nitropentammine complexes. Some question had been raised as to the existence of nitritoammine cobalt(III) complexes[3] so that the isolation of such rhodium(III) and iridium(III) compounds is further proof of this type of isomerism, if additional proof is needed. The preparation of these compounds serves as a good example of the usefulness of reaction mechanism studies in the carrying out of preparative work.

On the basis of kinetic studies[4] it had been proposed that the formation of $Co(NH_3)_5ONO^{2+}$ takes place by an attack of N_2O_3 or NO^+ on the oxygen of $Co(NH_3)_5OH^{2+}$. That there is no Co–O bond cleavage in this reaction was substantiated by oxygen-18 experiments.[5] It would therefore appear that a similar low energy reaction path should be available to analogous metal complexes. Then if rearrangement to the stable nitro compound is sufficiently slow, reaction at mild conditions may yield the kinetic nitrito product. This communication reports just such an observation.

At elevated temperatures the reactions of $Rh(NH_3)_5OH^{2+}$ and $Ir(NH_3)_5OH^{2+}$ with NO_2^- are reported[6] to produce salts of $Rh(NH_3)_5NO_2^{2+}$ and $Ir(NH_3)_5NO_2^{2+}$. However, at ice-bath temperatures similar reaction mixtures yield instead salts of $Rh(NH_3)_5ONO^{2+}$ and $Ir(NH_3)_5ONO^{2+}$. For example, to an ice cold solution containing 0.67 g. of $[Ir(NH_3)_5H_2O]Cl_3$ in 20 cc. of water was added 0.96 g. of solid $NaNO_2$. Once the solid had dissolved 1 cc. of 6*M* HCl was added and a crystalline material separated immediately. This salt was collected and washed with dilute ice cold HCl and acetone, then air dried (yield 0.54 g. or 83%.)

Anal. Calcd. for $[Ir(NH_3)_5ONO]Cl_2$: N, 21.3; H, 3.8; Cl, 18.0. Found: N, 21.2; H, 3.7; Cl, 17.6.

Under similar conditions a good yield of $[Rh(NH_3)_5ONO]Cl_2$ was obtained.

Anal. Calcd. for $[Rh(NH_3)_5ONO]Cl_2$: N, 27.3; H, 4.9; Cl, 23.3. Found: N, 27.9; H, 4.7; Cl, 22.7.

The presence of M–ONO linkage was verified and its rate of isomerization to $M-NO_2$ followed by an examination of the infrared spectra of the solid compounds. Using KBr disks of the solids, absorption peaks at 1460 and 1060 cm.$^{-1}$ are found which decrease in intensity and simultaneously two new bands appear at 1420 and 830 cm.$^{-1}$. These bands have been shown to be due to M-ONO and $M-NO_2$, respectively, for cobalt(III) complexes.[7]

The isomerizations of solid $[M[NH_3]_5ONO]Cl_2$ in KBr disks have half-lives of 6 hr. at 48°, 3.5 hr. at 22° and 2.5 hr. at 57° for M = Co(III), Rh(III) and Ir(III), respectively. Work is now in progress on the kinetics and mechanism of forma-

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)-315. Reproduction in whole or in part is permitted for any purpose of the United States Government.

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