The rare earth complexes have been studied with various aims and objects. Most of the complexes were synthesized and characterized with a view to adding to our knowledge of these comparatively unfamiliar elements. Since the isolation of individual lanthanides was tedious, a number of attempts were made to prepare lanthanide complexes so as to use them for the separation of the individual members. Recently a number of complexes have been prepared and an attempt has been made to scan them for their use as pseudocontact n.m.r. shift reagents in the simplification of n.m.r. spectra of complex organic molecules.

Risentraut and Sievers synthesized and characterized volatile chelates of fifteen trivalent rare earths and separated mixtures of the complexes by gas chromatography. The ligand employed was 2,2,6,6-tetramethyl 3,5-heptanedione also called dipivaloyl methane and abbreviated as dpdm.

The chelates are thermally stable, anhydrous and unsolvated compounds. Molecular weight measurements on the La, Sm, Eu, Tb, Tm and Yb complexes indicate that the compounds are monomeric in benzene. Infrared measurements showing the absence of νOH stretching vibrations and the close agreement of elemental analyses have proved that the crystalline compounds are anhydrous.
The general method of preparation is illustrated by

the preparation of Th(dpm)₃. Sixty moles dpm was dissolved in 300 ml of 95% ethanol in a flask fitted with a stop-cock connected to a vacuum system. 1a(2.4g) dissolved in 30 ml of 50% ethanol was added. Immediately the flask was evacuated, sealed, and stirred for 2 hrs. The volume of the solution was reduced by 5%, employing reduced pressure distillation and 350 ml of distilled water was added. The Th(dpm)₃ which was separated, quickly vacuum filtered, dried and sublimed at 130°C in vacuo. The yield of the sublimed product was 92.2%. The sublimed crystals were recrystallized from n-hexane and vacuum dried.

One of the objectives of this study was to separate rare earth complexes by gas chromatography. Gas chromatographic experiments have shown that all of the dpm chelates can be chromatographed without decomposition. Benzene solutions of each of the complexes were injected into chromatographic column at 200°C, the chromatograph of each complex showed a single peak well separated from the effluent carrier gas stream and were shown to have been eluted without decomposition by comparison of melting points, u.v. and visible spectra with those of each complex before injection.
There appear to be appreciable and significant differences in the volatilities of the rare earth complexes as indicated by sublimation and gas chromatographic retention data. For example \( \text{Lu(dpm)}_3 \), \( \text{Yb(dpm)}_3 \) and \( \text{Tm(dpm)}_3 \) sublime at temperatures about \( 10^\circ \text{C} \) lower than that of those required for \( \text{La(dpm)}_3 \), \( \text{Er(dpm)}_3 \) and \( \text{Nd(dpm)}_3 \). The volatility differences have made it possible to separate rare earth complexes by fractional sublimation. A thermal gradient fractional sublimation apparatus (a modified version of the device described by Berg and Martlage\(^2\)) was constructed. The device was operated at atmospheric pressure with helium as a carrier. An equimolar mixture of \( \text{Tb(dpm)}_3 \) and \( \text{La(dpm)}_3 \) was introduced into the hottest zone of the tube. The thermal gradient along the tube ranged from \( 187^\circ \text{C} \) in the hottest zone to \( 60^\circ \text{C} \) at the cold end. The more volatile \( \text{Tb(dpm)}_3 \) moved much farther into the cooler zone than did the \( \text{La complex} \). The crystals that deposited in the temperature zone from \( 72^\circ \) to \( 141^\circ \text{C} \) melted at \( 173^\circ - 180^\circ \text{C} \) and emitted brilliant green fluorescence, characteristic of the \( \text{Tb complex} \), while the crystals found in the zone from \( 141^\circ \) to \( 187^\circ \text{C} \) exhibited no trace of fluorescence.

Examination of the gas chromatographic retention behaviour of the complexes reveals an interesting relationship. The retention behaviour shows clearly the effect of the
lanthanide contraction. The volatility of the complexes appears to decrease as the size of the metal ion increases. This can be examined if it is assumed that in going from the higher, larger, less volatile lanthanides to the smaller members local dipoles that act to decrease volatility either become smaller or else are more effectively shielded from near neighbours as the outer ligand shell becomes more compact. It should be noted that the retention times can not be corrected with mass. The yttrium complex has about the same retention time as that of erbium even though the atomic weight of yttrium is only about one half that of erbium.

In view of the success of the above mentioned studies, Berg and Costa reinvestigated the volatile character of the $\beta$-diketone chelates of the lanthanides and a few closely related elements. The ligands chosen for study were $\beta$-acetylacetone, trifluoroacetylaceton, hexafluoroacetylaceton and dipivaloylmethane. The plan of study was to prepare and characterize the various $\beta$-diketone chelates of the lanthanides and related elements and ascertain if they were sufficiently stable and volatile to be sublimed at low temperatures. In as much as previous studies had suggested that the chelate stability and volatility increased with an
increase in the degree of fluorination of the ligand and an increase in the spherical nature of the chelate, it was anticipated that most volatile and stable chelates would be formed with hexafluoroacetylacetonate and dipivaloylmethane. The studies reported here have extended the knowledge of the lanthanides and related elements and suggested possible new approaches for separating the mixtures of the elements.

1. Acetylacetonates: The lanthanide acetylacetonates were prepared by the method of Titie et al. The lanthanide chloride was dissolved in water and the solution pH was adjusted to a value of approximately 5.0. An aqueous solution of ammoniumacetylacetonate was added to the lanthanide solution with constant stirring, while the pH of the reacting mixture was maintained at a value just below that of the pH of precipitation of the corresponding rare earth hydroxide. The mixture was stirred for 12 hrs to ensure the conversion of any basic acetylacetonate to the normal compound.

2. Trifluoroacetylacetonates: All these chelates were prepared by the method suggested by Young. An aqueous solution of the ammonium salt of the trifluoroacetylacetonate was added to the aqueous solution of lanthanide chloride. The mixture of the two solutions should be neutral to the litmus. The trifluoroacetylacetonate was precipitated and filtered.
precipitate was washed with water, air dried and finally recrystallized from benzene as a dihydrate.

3) *Hexafluorooacetylacetonates:* An aqueous solution of the lanthanides or related chloride was shaken with a diethyl ether solution of ammonium-hexafluoroacetylacetonate. The metal ion reacted with the ligand, and the chelate was extracted in ether phase. The ether solution of the chelate was dried with sodium sulphate, and then ether was evaporated.

4) *Dipivaloylmethanates:* These were prepared as suggested by Lisenbraut and Sievers. The solution of the lanthanide chloride in 1:1 ethanol water was thoroughly mixed with an alcoholic solution of the sodium salt of dipivaloylmethane. The chelate precipitated immediately in the form of a well formed solid. The solid was filtered, washed and recrystallized from hexane.

The β-diketone chelates of Ce(III), Y(III), Th(IV), U(VI), Pu(IV) and the lanthanides were sublimed in a fractional vacuum sublimator and the recrystallization temperature zones were recorded for individual chelates. None of the acetylacetonates is volatile but Ce(III), Th(IV), U(VI) and dioxo-uranium(VI) acetylacetonates are thermally stable and quite volatile below 150°C at 1 mm mercury pressure. The lanthanides
Sc(III), Y(III) and dioxouranium(VI) trifluoroacetylacetonates are volatile and can be vacuum sublimed below 150°C, but are thermally unstable. Only the Th(IV) chelate is sufficiently stable to be quantitatively recovered by sublimation. The Sc(III), Y(III), Th(IV), and lanthanide hexafluoroacetylacetonates are thermally stable and easily sublimed below 125°C in vacuo or at atmospheric pressure. All the dpm chelates studied are thermally stable and volatile and could be quantitatively recovered by vacuum sublimation below 140°C.

The volatility of the hexafluoroacetylacetonates and dpm lanthanide chelates increases with an increase in atomic weight (a decrease in ionic radii) of the lanthanides. The lack of volatility observed for the lanthanide acetylacetonates and trifluoroacetylacetonates is attributed to the fact that only hydrates of the chelates are formed, which decompose at elevated temperatures in vacuo to form basic polymeric compounds.

Springer, Meek and Sievers, also prepared the lanthanide chelate of β-diketones. They used 1,1,1,2,2,3,3 heptafluoro 7,7 dimethyl 4,6-octanedione i.e H(fod) as a chelating agent. The hydrated rare earth nitrates (C.C11 mole) were dissolved in the minimum amount of absolute methanol and the pH of the resulting solution was adjusted between 4 and 6 as indicated by pH paper, by adding required amount of solution of 4.12.
aqueous caustic soda. A solution of $\text{H}(\text{fod})$ (0.033 mole) in approximately 20 ml of absolute methanol was neutralized with 8.01 ml of 4.12 M caustic soda solution. Addition of an excess of caustic soda was avoided in order to preclude hydrolysis of the ligand. Upon addition of the first portion of the aqueous caustic soda solution the formerly homogeneous solution separated into two phases, because the unneutralized $\text{H}(\text{fod})$ is insoluble in the resulting mixture. Then an equivalent amount of base is added, the solution becomes homogeneous. The two solutions were then mixed with a magnetic stirrer, and a small amount of white sodium nitrate precipitated immediately. The resulting mixture was then added dropwise over a period of approximately 2 hrs. to a 400 ml of distilled water which was stirred vigorously. The complex precipitated, the mixture was stirred until the precipitate was in the form of fine granules. A stirring rod was used during precipitation to crush the granules and prevent coagulation into a tar. The final concentration of methanol was kept very low to minimize the possibility of oiling. The suspended precipitate was isolated by suction filtration and air dried. The crude product was recrystallized twice by dissolving it in the minimum amount of methylene chloride at room temperature and cooling the solution to $\angle 0^\circ\text{C}$. The compound was dried in vacuo for 12 hrs. The complexes were characterised
by i.r., n.m.r. gas chromatography, and t.g.a. The chelates of trivalent rare earth ions with d(sod) were isolated as monohydrates. The presence of water is also confirmed by i.r. spectra. The broad band at 3400 cm\(^{-1}\) undoubtedly arises from an (OH) stretch due to water present. The anhydrous tris-chelate, \(\text{Ln(sod)\textsubscript{3}}\) can be produced by dehydration of the monoaquo complexes in two ways. 1. vacuum pumping of the monohydrates over \(\text{P}_2\text{O}_5\) for several days yields anhydrous tris-chelate. 2. Likewise heating the anhydrated species above 100°C in an anhydrous atmosphere causes loss of water.

Thermograms obtained for hydrated (sod) complexes revealed a 1-2% weight loss at temperatures in the vicinity of 100°C, suggesting the volatilization of water present. The anhydrous dysprosium complex was characterized by Karl Fischer titrations and elemental analysis. Triplicate Karl Fischer titrations of the monohydrate revealed the presence of \(2.0 \pm 0.3, \text{H}_2\). The agreement between Karl Fisher and t.g.a method is excellent.

The weight loss corresponding to 0.4% for the anhydrous compounds is attributed to water picked up during transfer from the desiccator to t.g.a apparatus. The anhydrous complexes are hygroscopic in nature. The anhydrous europium complex is bright yellow in contrast to the white monoaquo complex, but the latter emits a more intense red fluorescence upon irradiation with u.v. light at 366 nm. In the same way the
green fluorescence of the terbium complex is visibly enhanced by the presence of water. All of monoaquo complexes and anhydrous complexes are soluble in many organic solvents but are not soluble in water. Hydration of the anhydrous complexes lowers the melting point in most cases, in some rather markedly, a phenomenon which has been noted for other rare earth-β-diketonates in previous investigations. The association of one mole of water with anhydrous (fod) complex is evidently a totally reversible process which can be effected by drying a sample or exposing it to atmosphere. The melting point changes in the appropriate direction. The rather wide melting range exhibited by a particular (fod) sample in either state is indicative of the sensitivity of this property to moisture. When the monoaquo europium melts at 60°C, a colourless liquid is obtained, however, at 150°C water is given off in the form of steam bubbles producing a yellow liquid. The n.m.r. spectra for anhydrous diamagnetic complexes in CDCl₃ at 40°C are all very similar. Chromatographically, the trend of lower retention time with decreasing ionic radius first reported by Linentraut and Sievers is reaffirmed with the (fod) complexes. The retention data cannot be correlated with the mass of complex. By tga analysis it was reported that the anhydrous (fod) complexes of the smaller metal ions are volatilized at lower temperature than
their larger analogues. The only exception to this trend is the tga of Sc(fod)₃ which is almost coincidental with the curve for Tm(fod)₃. In these complexes having three bulky fluorinated ligands, the water molecule may be hydrogen bonded to an electronegative site on the ligand shell rather than coordinated to the metal ion. Davis and Sutherland have reported i.r. evidence suggesting such interactions.

Cunningham et al. have shown by X-ray that one of the water molecules in $\left[ Y (\text{acac})_3 \right]_2 \cdot H_2O$ is not coordinated to the metal ion but is instead hydrogen bonded between two adjacent eight coordinate complex molecules. The (fod) rare-earth complexes are the most volatile complexes. The fluorocarbon substitution in the ligand shell markedly increases the volatilities of the complexes over those of compounds containing a similar nonfluorinated ligands. With Cr(III) and Al(III) the tris(fod) complexes have been shown to have volatilities greater than those of the analogous tris(acac), tris(dpm) compounds and only slightly less than those of the analogous tris(tfa) compounds. The increased volatility of compounds containing the highly electronegative fluorocarbon ligands implies that these groups produced a more repulsive shell around the complex molecule than that in similar hydrocarbon chelates. Another interesting effect is demonstrated
by the correlation between lanthanide contraction and the volatilities of the tris(fod) chelates as evidenced by the retention data. Several possible explanations can be advanced to account for the correlation. One may assume that the position of the possible monomer polymer equilibrium would vary with ionic radius and cause the observed trend in volatility. The acetylacetonates of the rare earths tend to polymerize in solution. Other examples of possible monomer-dimer equilibrium have recently been reported. One can imagine that monomer-polymer transformation could take place in the condensed phase (solid liquid, or solution, as in chromatographic experiments) in equilibrium with monomeric gaseous species. If the large complexes were to polymerize more extensively than the more compact members they would be expected to exhibit a lower apparent vapour pressure. However, the molecular weight data which are in excellent agreement with that required for monomeric species in solution, render this hypothesis improbable. More tenable explanations relate to the ways in which a change in ionic radii can affect the Vander Waals forces of attraction for tris complexes containing unsymmetrical ligands as in the case of (fod)molecules which have permanent molecular dipoles. If it is assumed that the size of the molecule decreases with the radius of central metal
ion, then it is likely that the size of the molecular dipole also decreases. In addition all β-diketonates have smaller permanent local dipoles, irrespective of the symmetry of the ligand. These could be expected either to decrease in the magnitude or to become more effectively shielded as the size of the central metal ion decreases. Finally, as the size of these pseudo-spherical molecules decreases, one would expect the polarizability to be reduced. All of these factors would be expected to decrease the dipole-dipole (molecular or local) interactions, the dipole induced dipole interactions and induced dipole induced dipole interactions and consequently to increase the volatility as the ionic radius becomes smaller.

Recently, it was found that tris β-diketone complexes of lanthanides are the best shift reagents as they are air stable, soluble in organic solvents and are known to expand their coordination number by acquiring ligands with lone pairs.

C.C. Hinckley observed the pmr spectra of cholesterol and the Eu(dpm)₃-2py-cholesterol in carbon tetrachloride as a solvent. In these spectra he observed that there is very little broadening and there are substantial shifts of resonance peaks. Narrow pmr lines may be expected for solutions containing complexes of all the rare earths with the exception of gadolinium having a high electron relaxation time, which causes broadening
at normal temperatures. The observed paramagnetic shifts are the direct consequence of bonding between the metal complex and cholesterol. There are no pmr absorptions due to the metal complex or free pyridine in the cholesterol region of spectrum.

Paramagnetic shift arises from the two sources, contact or pseudocontact interactions. When the metal ion is a rare earth then pseudocontact contribution is expected to be a substantial contribution particularly in the absence of extensive conjugation. For ions of $C_{2v}$ or $C_{2}$ symmetry, pseudocontact shift experienced by the $j$th proton in a complex is given by:

$$\frac{\Delta H_{(H)}}{(H)_{j}} = - \varepsilon \frac{(g_{1} + g_{2} + g_{3})}{R_{j}^{3}} \left( g_{1} - g_{2/2} - g_{3/3} \right)$$

$$(3 \cos^{2} X_{j} - 1) - \frac{3}{2} (g_{2} - g_{3})$$

$$\sin^{2} X_{j} \cos \lambda \lambda_{j}$$

where the distance from metal ion to $j$th proton is $R_{j}$, angles $X_{j}$ & $\lambda \lambda_{j}$ define the position of the proton in the symmetry coordinates of the metal ion, $g_{1}, g_{2}, g_{3}$ are the components of the $g$ tensor, $\varepsilon = |\beta| S(S+1)/27KT$. 
For shifts produced by either the contact interaction in the absence of extensive conjugation or pseudocontact interactions, the general expectation is that the shift produced will decrease with increasing distance between the metal ion and the affected protons.\textsuperscript{16} Apparently, the pseudocontact interaction is the major contributor to the observed paramagnetic shift, with the possible exception of the proton nearest the metal complex, for this system.

Examination of the spectrum of cholesterol-\textsubscript{2}Eu(dpm)\textsubscript{3}-2py reveals a number of significant changes in comparison to that of cholesterol alone.

Sizeable shifts are observed for the vinyl proton and proton nearest the hydroxyl group, which indicate association through the hydroxyl group. The methyl resonances are shifted and new resonances appear downfield from the unresolved bands characteristic of cholesterol and other steroids. A change in shifts was observed as the metal complex concentration was increased ie shifts are concentration dependent which indicates rapid metal complex-cholesterol exchange. Shifts for protons close to the point of association are larger than those for protons further removed.

Coordination of the metal to hydroxyl group above the ring and second, below the ring where steric interference with
vicinal protons is expected. In the first case the methyl protons should be closer to europium ion than vinyl protons and should experience greatest shift.

In the second case the reverse shift relationship should be obtained. Shift magnitude corresponding to the first case are experimental findings, which suggests that the metal complex bonds in a trans configuration to the hydroxyl vicinal protons and that steric interference with that proton is sufficient to affect the configuration of the complex.

C.C. Hinckley\textsuperscript{17} suggested a mechanism for the shift reagent and the organic substrate for which pmr is observed. When the pyridine adducts of (dpm) rare earth chelates are dissolved in carbon tetrachloride, the molecule dissociates according to the equations.

\begin{align*}
M(\text{dpm})_3\cdot 2\text{py} & \rightleftharpoons M(\text{dpm})_3\cdot \text{py} + \text{py} \\
M(\text{dpm})_3\cdot \text{py} & \rightleftharpoons M(\text{dpm})_3 + \text{py}
\end{align*}

If an organic compound B, having a basic coordinating group is added to the above solution, associations with the metal complexes may occur

\[ M(\text{dpm})_3\cdot \text{py} + B \rightleftharpoons M(\text{dpm})_3\cdot \text{pyB} \]
Contact shifts in the pmr spectrum of B are a consequence of this association if M is paramagnetic when M is a rare earth ion, pseudocontact contribution is observed.

Sanders and Williams\textsuperscript{18} reported that Cu(dpm)$_3$ is also a good shift reagent. They suggested the new compound pyridine added to Cu(dpm)$_3$ might be a superior shift reagent in coordinating more effectively with lone-pair bearing functionalities in organic substrates. They reported that selective shifts observed in cholesterol are increased by a factor of 4 at comparable concentrations. In normal n.m.r. spectrum of benzyl alcohol (CCl$_4$ solution) the aromatic protons resonate as a sharp singlet. In addition of Cu(dpm)$_3$ to the solution, the spectrum becomes amenable to a first order analysis. The substrate associates with the complex at the hydroxyl group, and the induced shifts decrease rapidly with increasing distance of the protons from the hydroxyl group.

Briggs et al.\textsuperscript{19} have reported that praseodymium complex of dpm shows shifts, which compared with corresponding europium compounds are usually reversed in direction and about triple in magnitude. Hence they found that Pr(dpm)$_3$ added to a carbon tetrachloride solution of n-pentanol
induces the potential spectrum to become first order but with all other peaks greatly shifted to high field. The capacity of producing shifts in either direction at will, by the use of Pr<sup>3+</sup> or Lu<sup>3+</sup> complex, must greatly increase the utility of the method.

The relative sign and magnitude of shifts produced by different lanthanides (which depend on the appropriate g-factor) are illustrated by the proton resonance shifts of acetonitrile solutions of the new series of complexes. \( \text{Pr} \) (C<sub>10</sub>H<sub>12</sub>)<sub>3</sub>[iPr(NH<sub>2</sub>)<sub>3</sub>]<sup>+</sup> = 1.5; \( \text{Nd} \) = 1.15; \( \text{Sm} \) = 0.27; \( \text{Lu} \) = 1.33; \( \text{Tb} \) = 19.2, \( \text{Dy} \) not observed; \( \text{Ho} \) = 17.00; \( \text{Er} \), 4.4; \( \text{Tm} \), 6.9; \( \text{Yb} \), 6.66; \( \text{Lu} \), 0.0. The resonances of the \( \text{Pr}^{3+} \) complex in this and other series are the sharpest to those of like sign. It is suggested that lanthanide complexes other than \( \text{Lu(dpm)}_3 \) will probably act as a shift reagent.

Isbrandt and Rogers<sup>20</sup> reported the use of \( \text{Lu(fod)}_3 \) as a paramagnetic shift reagent, in assigning the proton resonance spectra in substituted amides. The paramagnetic shift arises from the association of lanthanide complex with the polar organic substrate and is dominated by dipolar (pseudo-contact) interactions. The magnitude of the shift is distance dependent. The anisotropy of the magnetic
susceptibility of the amide group in tertiary amides, leads to a chemical shift between the cis and trans substituents on nitrogen and this shift is normally observable when rotation about the central C-N bond is slow on the n.m.r. time scale. Amides are known to protonate preferentially on the carbonyl oxygen, since the nitrogen lone pair is extensively delocalized, one would, therefore, expect that the chemical shift reagent would be complexed through the lone pair of electrons on oxygen and that the induced shift in cis and trans N-alkyl substituents would differ. The concentration of reagent was increased up to a 0.4 molar ratio of shift reagent to amide. When chemical shifts were plotted versus mole ratio a linear correlation was found for each group of the protons. Extrapolation of these lines to an equimolar ratio of Cu(fod)₃ to amide gave values of \( \Delta \) for each group of protons. Extrapolation of the lines to a mole ratio of zero allows assignments to be made for the resonances in the uncomplexed amide. To establish the validity of the method, 1-Methyl-pyrrolidin-2-one was chosen as a model system since the N-methyl group is fixed in the cis-position. The cis-methyl group protons were shifted to a greater extent than the trans methylene protons in the solution containing the complexed amide. For the
remaining amides, e.g., N,N-dimethylformamide, N,N-dimethylacetamide, and others, resonances of the cis-trans pair shifted the greater amount are assigned to cis-group.

W. Rahman et al.\textsuperscript{21} also reported the use of Lu(fod)\textsubscript{3} for elucidation of the structure of naturally occurring biflavones, to determine the position of linkage between two flavone nuclei.

Ahmad, Bhacca, Selbin and Vander\textsuperscript{22} have also studied n.m.r. spectra of tris(dpm) lanthanides to show temperature dependence of shift reagents. During investigation of this phenomenon, it was noted that these signals displayed substantial shifts of field position (of the order of several ppm, reversible on cooling) as the probe temperature was increased gradually to about 75°C. They prepared a sample of 2-heptanone in carbon tetra chloride, added maximum amount of Lu(dpm)\textsubscript{3}, and recorded the n.m.r. spectrum of the sample at temperatures throughout the liquid range of carbon-tetrachloride.

Proportional enhancement of all signals in the substrate is observed as the sample temperature is lowered and suggested possible utility of reduced temperature determinations in cases where the limited solubility of the lanthanide complexes is inadequate, or of variable temperature
studies in lieu of measurements at a number of different relative concentrations. It was found that the use of untreated COCl₂ as a solvent for such studies promoted decomposition of at least several of the complexes the tert-butyl resonance of solutions of Pr(dpm)₃, Nd(dpm)₃ and Sm(dpm)₃ in untreated COCl₂ were shown to diminish upon standing and/or dilution with concurrent appearance of a second signal.

Witanowski et al. reported the properties of rare earth and actinide dpm chelates in order to find the most suitable shift reagent for nitrogen-14 n.m.r. resonance i.e. one which causes maximum chemical shift with minimum signal broadening. They made comparative studies of lanthanide and actinide dpm chelates on ¹⁴N n.m.r. spectrum of pyridine to show that Dy(dpm)₃ is by far the best high field shift reagent whilst Yb(dpm)₃ is the best low field shift reagent. Pyridine was chosen for the comparison of the effect of the lanthanide and actinide dpm chelates on ¹⁴N n.m.r. spectra because of its high sensitivity to chemical shifts. The selection of a deshielding reagent must be based on the broadening effects since all the chelates in this group (i.e., Ce, Pr, Nd, Sm, Yb) are equally active. Yb(dpm)₃ is the best shift reagent. They also reported that nitromethane is a suitable internal standard in the presence of ¹⁴N shift reagents.
T. H. Siddall\textsuperscript{24} reported tris dpm chelate of europium as an upfield \( ^{1}H \) n.m.r. shift reagent. The n.m.r. observed for \( 0.4M \) \( 2-6\text{-di-2} \) propylacetanilide plus \( 0.4M \) \( Eu(dpm)_{3} \) at 35\( ^{\circ} \)C in CDCl\(_{3}\). This amide exhibits isomerism due to slow rotation around the carbon-nitrogen bond.Rotation around the nitrogen-benzene ring bond is also slow on the n.m.r. time scale in both isomers. Rotation around this bond becomes rapid above -60\( ^{\circ} \)C in the endo isomers (benzene ring cis to the carbonyl oxygen) but remains slow in exo isomers (benzene trans to oxygen) to above 75\( ^{\circ} \)C at room temperature this leads to two complete sets of signals, one for each isomer, with a further doubling of \( \beta \)-methyl signals of the 2-propyl groups of the exo-isomer. The upfield shift of one of the \( \beta \)-methyl doublets in exo-isomer persists under all conditions examined. These included lowering the temperature to -30\( ^{\circ} \)C. Signal becomes very broad below -50\( ^{\circ} \)C. A possible explanation for upfield shifts would be a substantial alternation of geometry in the interactions of the compound with shift reagent as compared to the interaction of planar steroids with shift reagent. With such an alternation the dependence of shift on angle could become important enough to change the sign of the shift.

Ekong et al\textsuperscript{25} reported the tris(dpm)europium as induced upfield and downfield shift reagents in the n.m.r. spectra of the meliacins. Both the upfield and downfield shifts were
observed for 3-deacetyl-khivorin. The chemical shift at a molar ratio (reagent to substrate) of 1 show certain regular features which may be useful in structural determination. For 3 \( \beta \)-hydroxy compounds the \( \omega \)-4 methyl signal appears in the range 45-55 Hz. But in 3 \( \alpha \)-hydroxy compounds, while the 4 \( \alpha \)-methyl groups give signals in the same range, the 4 \( \beta \)-methyl signals appear further upfield at 230-280 Hz. All the 3-hydroxy compounds examined gave the other methyl signals in the ranges 150-170 (\( \omega \)-3), 210-265 (\( \omega \)-17) and 150-140 Hz (\( \omega \)-13). Although a hydroxy-group when present in the molecule takes up most of the reagent and therefore dominates the induced shifts, a significant proportion of the reagent is simultaneously coordinated at other lone pair centres. This may explain the relatively low shifts obtained for 3-deacetyl-khivorin, on account of its three ester/lactone carbonyl groups. The low shifts may be partially accounted for by steric factors which affect the concentration of the bulky reagent around the coordinated site. Surprisingly, however, in 3-deacetylkhivorin, while all the other protons showed downfield shifts one of the acetoxy methyl signals suffered an upfield shift. To relieve steric interaction between the bulky reagent (coordinated at 3\( \alpha \)-\( \omega \)-H) and the 1\( \alpha \)-\( \omega \)-ac, the acetoxy group might have adopted a conformation
for which the angle term was sufficiently important to change the sign of the induced shift.

Recently, Selbin, Ahmad and Bhacca\textsuperscript{2b} have reported 47 compounds of rare earth dipivaloylmethane with pyridine, 1,10-phenanthroline, and 2,2'-dipyridyl of the type \( M(dpm)_3 \), where \( M = Yr, \text{Nd}, Sm, Lu, Gd, \text{Tb}, Dy, Ho, Er, \text{Yb} \) and \( Lu \). \( M(dpm)_3 \cdot py \) (\( M=\text{same 12 metals} \) \( M(dpm)_3 \cdot dipy \) (\( M=\text{same first 11 metals except Lu} \) \( M(dpm)_3 \cdot ophen \) (\( M=\text{same first 11 metals except Lu} \) and \( Ce(dpm)_4 \). They have described the preparation and characterization of the lanthanide chelates and reported the results of n.m.r. study of their magnetic moments and Weiss constants and of a low temperature (77\(^\circ\)K) study of their optical spectra. All 34 adducts of mixed ligand compounds, i.e. those with pyridine, bipyridyl and o-phenanthroline are new. These mixed ligand compounds are the first to contain the latter bidentate nitrogen donors complexed to tris(dipivaloylmethanates).

In view of rather bulky nature of the \( \beta \)-diketo-enolate ligands, it is somewhat surprising to find that an additional bidentate ligand can still attach to tris(dpm) lanthanide chelates, raising the coordination number of the lanthanide ions to eight. Thermal data also show that these compounds are roughly as stable as analogous complexes with less bulky \( \beta \)-diketo-enolates.